LITERATURE ESSAY:

MODELLING SUPERCRITICAL ENTRAINMENT DISTILLATION: THERMODYNAMICS AND SEPARATION TECHNOLOGY.

A.A. van Ekelenburg

Graduate Student from
Delft University of Technology

Supervision : Prof.dr.ir. J. de Swaan Arons.

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Location : AKZO Salt and Basic Chemicals Nederland b.v.,
The Netherlands.

Supervision : Prof.dr.ir. J.M.L. Penninger.
ir. F.J. Budde.

Summary

In this literature essay a review has been given how phase equilibria are modelled where a supercritical fluidum is involved. Two types of equations of state have been analysed: cubic equations of state and the virial equation of state. An analysis of degrees of freedom has been made.

Applying phase equilibria in process technological devices has also been reviewed. Phase equilibria where a supercritical fluidum is involved are applied in supercritical extraction columns. A model has been given for packed columns, both operating with reflux and without reflux. The number of degrees of freedom has been evaluated.

Unless its restriction of application limitations, the virial equation of state gives a first feeling about these types of phase equilibria. Above densities, however, larger than three fourths the critical density of the supercritical fluidum, the virial equation of state begins to deviate too much from reality. Cubic equations of state can be applied at higher densities of the supercritical fluidum.

The virial equation of state makes it possible to regard chemical interactions separately from the volatility of the compounds that need to be dissolved by the supercritical fluidum. These effects are completely strangled with each other when cubic equations of state are used.

In order to model phase equilibria where a supercritical fluidum is involved it can bestly be started with the virial equation of state.

When the system is studied and it appears that the system also has to be modelled at densities of the supercritical fluidum larger than three fourths the critical density, cubic equations of state may be used in order to be able to describe a larger range of pressure.

Contents

1. Introduction

In this literature essay it will be pointed out how phase equilibria can bestly be modelled at supercritical conditions, thus at high pressure. Technological aspects of supercritical entrainment distillation will also be reviewed.

An comprehensive analysis of degrees of freedom has been taken into account. In this way it can be seen how many parameters are relevant to know.

The scope of this essay is to get a first insight in how the process is supposed to occur. Mass transfer takes place from both phases to each other. Therefore both phase equilibria modelling and column technology become of interest.

Supercritical fluida are neither gases nor liquids. A consideration will be given what the effect will be in modelling these types of separation processes.

Supercritical entrainment distillation is applied to separate mixtures of high boiling and/or heat sensitive compounds. The great advantage of this process-type is the relatively low temperature at which the process is operated. The volatility of the high boiling / heat sensitive compounds is not enhanced by enlarging the temperature, but by enlarging the help substance's density. The help substance is a supercritical compound. The density is enlarged by enlarging pressure. Reminding this scope, supercritical extraction is operated at relatively low temperatures and relatively high pressures.

2. Qualitative Consideration of Supercritical Fluida and Supercritical Entrainment Distillation

In order to model the supercritical entrainment distillation process it is necessary to understand a supercritical fluidum (SCF) physically. A SCF is a compressed, dense gas. It is neither a gas nor a liquid but it is best understood to be some fluidum in between. Temperature and pressure of the considered fluidum are both above the critical temperature and pressure respectively.

Supercritical entrainment distillation is similar to the term supercritical extraction. In literature the latter term is more often used, but because the process cannot be regarded as a real extraction the first term is also used.

Considering the process, supercritical extraction will neither be a process of Liquid-Liquid Extraction nor a process of Vapour-Liquid Stripping.

Normal Liquid-Liquid Extraction modelling will take into account mutual solubilities of both phases, but because of the fact that no vapour phase is present, heat effects are ignored. Heat effects can indeed be ignored because heats of vaporization are never taken into account in heat balances. In case heat effects will be very small, the temperature can be assumed constant in the column.

Normal Vapour-Liquid Stripping modelling will not take into account the solubility of vapour in the liquid phase because this normally will be very small. Solubility of liquid phase components in the vapour phase are taken into account of course (because else no separation will occur) but it is assumed to be small. In that case flows in the column can be assumed to be constant.

Because the presence of a vapour phase, heats of vaporization should be considered, so the temperature would not be constant in the column. However, because flows were assumed to be constant, because of small mutual solublities, heat contents of both phases will remain constant so temperature can also be taken constant.

In supercritical extraction flows cannot be assumed to be constant because mutual solubilities cannot be neglected: the solubility of the SCF in the liquid phase can be rather significant (solubility of 40 mass % could be possible!). Because of the fact that the SCF can partly be considered as a gas, heat effects must be taken into account. Thus, neither temperature nor flows in the column can be assumed constant, involving a lot more variables in the column.

It is clear now that both mass and heat balances must be taken into consideration. The next problem will be the determination of the latent heat in the heat balance. In normal Vapour-Liquid contacting devices the latent heat equals the heat of vaporization. In Liquid -SCF contacting devices this is not the case. The latent heat of a component can be defined to be the heat necessary to put into the system in order to establish a change from the liquid phase to the "vapour" phase of one component. Change of phases in the opposite direction ("vapour" to liquid) will cause the latent heat to be liberated.

It has now become clear that supercritical extraction is neither extraction nor stripping. It can, however, be regarded as either a bad extraction or a good stripping. The term supercritical entrainment distillation is also used: the volatility of the compound to be extracted is enhanced. The supercritical nature of the help phase will cause entrainment-like occurences to take place.

This was a general consideration about technological design of SCE columns. The specific application to the column will be given in section 4.

3. Modelling Phase Equilibria

Thermodynamic models describe phase equilibria for a certain system to occur. Phase equilibria, where a supercritical component is involved, have to be modelled at high pressure. Equilibrium will occur between phases; in the scope of supercritical entrainment distillation this means equilibrium between the supercritical phase, consisting mostly of the supercritical gas that is used and the liquid phase in which a considerable amount of supercritical compound can be dissolved. The purpose, thus, is to model the phase equilibrium between the supercritical ("vapour") and liquid phase.

In this chapter two equations of state will be considered. First a review is given regarding cubic equations of state, applied in both the liquid and supercritical phase, and the virial equation of state.

Prausnitz [2], De Loos [3] and McHugh [4] state that high pressure phase equilibria cannot be described with sufficient accuracy by means of models involving activity coefficients. Activity coefficients can be calculated with models like Margulus, Van Laar, UNIFAC, UNIQUAC and others. The dependence on pressure is not taken into account in these models. The authors mentioned above state that the best way to describe phase equilibria at high pressure is to assume that an appropriate equation of state (EOS) stands for both liquid and "vapour" phase. This indicates that instead of an activity coefficient for the liquid phase a fugacity coefficient is calculated. The equilibrium can be expressed in the following relationship:

$$\phi_i^L * x_i = \phi_i^V * y_i \qquad (1)$$

In equation (1) x and y symbolize mole fractions in respectively the liquid and "vapour" phase. ϕ stands for the fugacity coefficient. The superscripts L and V are respectively Liquid and Vapour. The subscript i symbolizes component i.

The fugacity coefficients in equation (1) are functions of pressure, temperature, the compressibility factor and the composition of the considered phase. The compressiblity factor can be calculated from an EOS which must be specified. This scope is widely used in cubic equations of state, for example the Peng Robinson EOS.

When the supercritical ("vapour") phase is considered only, the virial EOS becomes very useful. The supercritical phase's non-ideality can be accounted for, while the liquid phase is in a normal way modelled:

$$\gamma_i * x_i * P_i^{sat} * POY_i = \phi_i * y_i * P \qquad (2)$$

In (2) γ symbolizes the activity coefficient, P^{sat} is the vapour pressure, while POY stands for the Poynting factor which is included for correcting the liquid phase's fugacity for high pressures.

Equation (2) is applied in modelling solubilities of heavy compounds in the supercritical phase. In order to know the solubility of the supercritical compounds in the liquid phase, another model must be chosen, because the virial EOS cannot be applied for the liquid phase. First knowledge about the solubility of the supercritical compounds in the liquid phase can be obtained from Henry's law:

$$f^{L}_{SCF} = x_{SCF}{*}H_{SCF,i}{*}POY_{SCF} = f^{V}_{SCF} = \phi_{SCF}{*}y_{SCF}{*}\ P \qquad (2a)$$

In (2a) H symbolizes the Henry constant for the supercritical fluidum in the liquid compound i. Henry's law provides a good result at infinite dilution cases. When pressure becomes too large and, thus the SCF's solubility increases, activity coefficients must be incorporated.

In section 3.1 equations of state are considered for a pure substance. Then the equation of state will be made applicable to mixture by means of mixing rules, followed by a section that deals with fugacity coefficients. This latter section will relate an equation of state for some mixture in some phase to the fugacity coefficient of each components in the mixture in the considered phase. Finally an overall view is given concerning phase equilibria calculations at high pressure with the equations summarized in the first part of this section.

3.1 Equation of State for Pure Substances

An EOS is an equation that relates the quantities pressure, temperature and molar volume of one pure substance. Cubic equations of state are widely used in modelling phase equilibria at supercritical conditions. All basic properties causing the phase equilibrium to install, like vapour pressure and chemical interactions, are strangled with each other in these types of equations of state. The virial EOS, however, provides insight in the properties that cause the equilibrium to install. The great disadvantage of applying the virial EOS is the limited range of densities of the supercritical compound that is used. Truncated after the second coefficient, the virial EOS can be applied up to half the supercritical compound's critical density, while the virial EOS truncated after the third coefficient can be used up to three fourths the critical density of the considered supercritical compound [22].

3.1.1 Cubic Equations of State

Cubic equations of state are widely used in modelling phase equilibria at supercritical conditions. An example of such a cubic EOS is the Peng Robinson EOS. The Peng Robinson EOS which was first introduced in 1976 will now be considered here. The Peng Robinson EOS is now chosen because it is widely applied to supercritical mixtures. The equation is:

$$p = \frac{R*T}{V-b} - \frac{a(T)}{V*(V+b) + b*(V-b)} \qquad (3)$$

In (3) p, T and V symbolize pressure, temperature and molar volume. a(T) is a certain function of temperature and b is a constant. R stands for the ideal gas constant.

a(T) and b can be determined by different methods. The most general and a relative new method proposed by Brunner [5] will be evaluated here.

a(T) and b are determined generally by analysis of the critical point. At the critical point the first and second derivative of pressure with respect to molar volume equal zero. These calculations (with a(T) considered constant) result finally in:

$$b = 0.07780*R*T_c/p_c \qquad (4)$$

$$a = 0.45724*R^2*T_c^2/p_c \qquad (5)$$

In (4) and (5) p_c and T_c symbolize respectively the critical pressure and critical temperature.

In order to reproduce vapour pressures Peng and Robinson made a(T) a function of temperature and acentric factor ω:

$$a(T) = \{ 0.45724*R^2*T_c^2/p_c \}* \\ [1 + (0.37464 + 1.54226*\omega - 0.26992*\omega^2)*\{1-(T/T_c)^{0.5}\}]^2 \qquad (6)$$

The acentric factor is a pure component constant defined as:

$$\omega = -\log\{p_i^{sat} \text{ at } (T/T_c=0.7) \} - 1 \qquad (7)$$

In (7) p_i^{sat} stands for the vapour pressure of component i.

When the acentric factor has not been given in literature it thus can be calculated from vapour pressure data.

With known critical properties and acentric factor, a and b can be calculated by equations (4) through (7). In that case the EOS is purely a function of pressure, temperature and molar volume. In other words: with given pressure and temperature, the molar volume can be calculated.

The compressibilty factor, Z, can now be calculated by the definition of this quantity:

$$Z = p*V/(R*T) \tag{8}$$

Substituting equation (8) in (3) results in another form of the Peng Robinson equation of state:

$$Z^3 - (1-B^*)*Z^2 + (A^* - 3B^{*2} - 2B^*)*Z - A^* * B^* + B^{*3} + B^{*2} = 0 \tag{9}$$

In (9) the new variables A^* and B^* are defined by:

$$A^* = a(T) * \{p/(R^2*T^2)\} \tag{10}$$

$$B^* = b * p / (R*T) \tag{11}$$

The rewritten form of the Peng Robinson EOS (9) can directly be used in order to calculate the compressibility factor at given pressure and temperature.

As indicated above, the variables a(T) and b can also be evaluated by means of other methods. Brunner [5] proposes a relatively new method for determing a(T) and b. In this method a(T) and b are no longer a function of the critical properties. Because of this reason the method could be very useful.

Critical properties of many high boiling substances have not been determined experimentally, because they are often heat sensitive with relatively low decomposition temperatures. This indicates that critical properties should be estimated by methods like Joback's estimation procedure, which for example can be found in [2]. Brunner states that these estimation procedures would not be sufficiently accurate.

In case of supercritical extraction this problem occurs. Critical properties have not been determined experimentally. Supercritical extraction is applied in systems involving high boiling and/or heat sensitive compounds. Thus, for these substances it would be worth while to examine the possibility to calculate a(T) and b by Brunner's method.

The method proposed by Brunner can be expressed by the following equations:

$$b = k_1 * V(20) + k_2 \tag{12}$$

$$a(T) = a_c * \{1 + x_0 * (1 - 2.4243 * [R * T * b / a_c]^{0.5})\}^2 \tag{13}$$

$$a_c = k_3 * V(20) + k_4 \tag{14}$$

$$x_0 = k_5 * \{V(20)\}^{k_6} \tag{15}$$

In equations (12) through (15) k_1, k_2, k_3, k_4, k_5 and k_6 are constants, which were experimentally determined by Brunner for many substances. The only parameter in these equations is V(20). This is the molar volume of the considered substance at 20 °C. As can be seen this method of determing a(T) and b is independent of the critical properties of the considered substance.

It could, however, be possible the considered compound has a melting point above 20 °C. The molar volume at liquid state should be substituted to result in the correct a(T) and b by Brunner's method. wo methods of determing a(T) and b have been presented. Brunner [6] also presented a derivated procedure to determine a_c, b and x_0. This determination has been done by calculation from p-V-T data. The method is not presented here because of its analogy with the first method proposed by Brunner [5].

After choosing the method for determing a(T) and b, the compressibility factor can be calculated for a pure substance, when pressure and temperature are fixed.

3.1.2 Virial Equation of State and Henry's Law

As indicated above the virial EOS is very illustrative when it is desired to examine the effects of properties causing the equilibrium to install separately. The solubility of heavy compounds in the supercritical fluidum can be described using this EOS, while the solubility of the supercritical compound in the liquid phase can be estimated from Henry's Law.

The virial EOS is a polynomal series in inverse molar volume which is explicit in pressure:

$$p = \frac{R*T}{V} * \{ 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots\ldots \} \quad (16)$$

In (16) B, C, D, ... symbolize the second, third, fourth, ... virial coefficient. The virial coefficients are only functions of temperature. In literature estimation methods are available for the second and third coefficient.

No method has been found in order to estimate the fourth coefficient, so the EOS can be applied with best accuracy truncated after the third coefficient. The virial coefficients are the only variables that are needed to be known. Because of their function of temperature it easily can be seen that the equation of state is a relation between p, V and T, just as the above discussed cubic equations of state.

A compilation of second virial coefficients is given by Dymond and Smith (1969). For estimating the B-coefficient a number of techniques are available. Most are based on intergration of some theoretical expression relating intermolecular energy to the distance of separation between molecules. Little is known about these energies and it is more common to estimate the virial coefficient by means of corresponding states correlations.

Corresponding states correlations (CSC) are available for B and C. The concept of corresponding states correlations provides general relations for certain properties, depending on parameters that are readily known. These parameters determine the state of the considered compound. They are the critical properties. Depending on critical properties, the correlations provide in "overall" behaviour, correlating the desired property to a standard state: the critical point in which the critical properties are valid.

For the second virial coefficient two CSC have been found in literature for both polar and nonpolar systems. The general form of the CSC for the second virial coefficient (B) is:

$$\frac{B * P_c}{R * T_c} = f0\ (T_r) + \omega * f1\ (T_r) + f2\ (T_r) \qquad (17)$$

The temperature dependence is expressed in the reduced temperature, T_r (= T / T_c). Tsonopoulos [23] has developed the following functions for nonpolar gases. For nonpolar gases f2 (T_r) equals zero.

$$f0\ (T_r) = 0.1445 - 0.330/T_r - 0.1385/T_r^2 - 0.0121/T_r^3 - 0.000607/T_r^8 \qquad (18)$$

and

$$f1\ (T_r) = 0.0637 + 0.331/T_r^2 - 0.423/T_r^3 - 0.008/T_r^8 \qquad (19)$$

For polar systems the last term of equation (17) has to be taken into account. Tsonopoulos developed:

$$f2\ (T_r) = a/T_r^{\ 6} - b/T_r^8 \qquad (20)$$

a and b are in (20) parameters determined by the geometry of the nonpolar compound. Parameter a is a function of the reduced dipole moment μ_r, which is defined as:

$$\mu_r = 10^5 * \mu^2 * P_c \ / \ T_c^2 \qquad (21)$$

In (21) is μ the dipole moment, which is a characteristic quantity for compounds. It is not, however, a good quantity for correlating all compounds, since the dipole moment is a vector and its direction and location are also important.

Therefore it is impossible to correlate one function for all types of compounds and only global correlations can be made for some type of compound, for example ketones, aldehydes, alcohols etcetera.

Tsonopoulos correlated functions for parameter a as function of reduced dipole moment for ketones, ethers and alcohols.

Parameter b equals zero for non-hydrogen bonded gases. For alcohols Tsonopoulos reported values for b, and fitted for 1-chain alcoholes parameter b as a linear function of the reduced dipole moment. It goes beyond the scope of this essay to summarize all functions for a and b for every type of compounds. For these functions it is refered to [23].

Prausnitz [2] refers to Van Ness and Abbott (1982). They found more comprehensive function for f0 (T_r) and f1 (T_r):

$$f0\ (T_r) = 0.083 - 0.422/T_r^{1.6} \tag{22}$$

and

$$f1\ (T_r) = 0.139 - 0.172/T_r^{4.2} \tag{23}$$

Van Ness and Abbott's technique in estimating f0 (T_r) and f1 (T_r) is prefered, because it is more recent and it is more often refered to.

Less is known about estimating the third virial coefficient (C). De Santis and Grande [24] reported a technique. The great disadvantage of their technique is the use of uncommon parameters for corresponding states correlations, like dipole polarizability and molecular volume, even for nonpolar compounds. More common is the use of critical properties and acentric factor in corresponding states correlations, like equations (17) - (23), except for (17). Orbey and Vera [22], however, correlated such a CSC for nonpolar compounds. The general form (in agreement with (17)) is:

$$\frac{C * P_c^2}{(R * T_c)^2} = f3\ (T_r) + \omega * f4\ (T_r) \qquad (24)$$

Orbey and Vera found for f3 (T_r) and f4 (T_r) :

$$f3\ (T_r) = 0.01407 + 0.02432/T_r^{2.8} - 0.00313/T_r^{10.5} \qquad (25)$$

and

$$f4\ (T_r) = -0.02676 + 0.01770/T_r^{2.8} + 0.040/T_r^{3.0} - 0.003/T_r^{6.0} - 0.00228/T_r^{10.5} \qquad (26)$$

Like the second coefficient, B, the third coefficient, C, can readily be evaluated as function of temperature by knowledge of the critical pressure and temperature of the considered compound and its acentric factor.

The virial EOS is used for modelling the vapour phase's fugacity of the heavy compounds, that need to be dissolved by the supercritical fluidum. For cubic equations of state it was mentioned that it was assumed that these EOS also would hold for the liquid phase's fugacity. The virial EOS has the restriction of being valid at densities of the supercritical fluidum smaller than three fourths of the critical density. The supercritical fluidum's density in the liquid phase is larger than in the supercritical phase. Therefore another model for estimating the liquid phase's fugacity of the supercritical fluidum must be chosen. The concept of vapour pressure is for the supercritical fluidum irrelevant, because temperature exceeds the critical temperature. The most logical approach in estimating the supercritical fluidum's liquid phase's fugacity would be Henry's Law:

$$f^L_{SCF} = x_{SCF} * \gamma_{SCF} * H_{SCF,i} * POY_{SCF} \qquad (27)$$

In equation (27) x symbolizes the mole fraction in the liquid phase, while subscript SCF stands for supercritical fluidum. H is the Henry coefficient, which is a function of temperature, of the supercritical fluidum in some liquid compound i refered to the vapour pressure of the liquid compound, while γ stands for the activity coefficient. Because the model must stand for high pressures the Poynting factor is again invoked. When equilibrium is reached, the liquid phase's fugacity equals the vapour phase's fugacity, so

$$y_{SCF} * \phi_{SCF} * P = \gamma_{SCF} * x_{SCF} * H_{SCF,i} * POY_{SCF} \qquad (28)$$

Because the mole fraction of dissolved heavy compound in the vapour phase is very small and less then 1 percent, the Lewis rule is applied:

$$\lim_{y \to 1} \phi_{SCF}(\text{mixture}) = \phi_{SCF} \text{ (pure SCF)} \qquad (29)$$

As will be shown later, the fugacity coefficient is determined by the chosen EOS.

No estimation method has been found in literature in order to estimate Henry coefficients. Henry coefficients must be determined experimentally, either in literature available or necessary to measure yourself. All other input variables in the model in order to calculate the output variables, x and y, can be estimated by corresponding states correlations.

The Poynting factor in equation (27) is defined by the following expression:

$$POY_{SCF} = \exp\ \left(\int_{P_i^{sat}}^{P} \{ v^{\infty}_{SCF} / (R*T) \}\ dP \right) \qquad (30)$$

In (30) v^{∞}_{SCF} symbolizes the molar volume of the supercritical fluidum at infinite dilution in the liquid compound i. It is assumed that this molar volume is independent of pressure, so it follows that

$$POY_{SCF} = \exp\ (\{ v^{\infty}_{SCF} / (R*T) \} * \{P-P_i^{sat}\}) \qquad (31)$$

However, if pressure becomes very large, the solubility of the supercritical fluidum increases and the assumption of infinite solution is no longer valid. At infinite dilution the activity coefficient is unity. The activity coefficient is a expermentally determined parameter depending on composition and temperature. In the model the molar volume at infinite dilution is used at high pressure. This is rather discrepant, but it is assumed that the invoked activity coefficient will adjust all deviations from reality including the mistake caused by the molar volume assumption at infinite dilution.

The molar volume at infinite dilution can also be estimated from corresponding states correlations. Brelvi and O'Connell [10] reported a CSC depending on characteristic volumes of the considered compounds (both supercritical fluidum and heavy compound) as well as the compressibility of the liquid, heavy compound. If the characteristic volumes are not known, critical volumes can be used.

The molar volume at infinite dilution of the supercritical compound can be evaluated by the following expressions:

$$v^{\infty}_{SCF} = K^{\infty}_{i} * R * T * (1 - C^{\infty}_{SCF,i}) \qquad (32)$$

$$\ln \left(1 + \frac{1}{\rho * K^{\infty}_{i} * R * T} \right) = -0.42704 * (\rho_r -1) + 2.089 * (\rho_r -1)^2 - 0.42367 * (\rho_r -1)^3 \qquad (33)$$

$$\ln (-C^{\infty}_{SCF,i} * \{v_{c,i} / v_{c,SCF}\}^{0.62}) =$$

$$\text{if } 2.0 < \rho_r < 2.785 : -2.4467 + 2.12074 * \rho_r \; .....$$

$$\text{if } 2.785 < \rho_r < 3.2 : 3.02214 - 1.87085 * \rho_r + 0.71955 * \rho_r^2 \qquad (34)$$

In equations (32) through (34) ρ_r symbolizes the reduced density of the heavy, liquid compound, while v_c stands for the characteristic molar volume, which could be set equal to critical molar volume. K symbolizes the compressibility of the liquid compound while C is some reduced volume integral, which is evaluated by (34) by means of corresponding states.

The molar volume at infinite dilution can now be evaluated.

3.2 Equation of State for Mixtures

In problems of separation of substances always mixtures are present because else there will not be anything to separate.

The EOS still remains very important in this case. To extend the EOS to mixtures, the EOS must be modified to include the additional variable of composition of the mixture. This inclusion is accomplished by averaging the constants of the pure substances to result in constants which are assumed to be valid for the mixture. Equations that perform this averaging of constants are called mixing rules.

Mixtures consist of substances which have seldom the same chemical structure. If this is the case, interaction parameters must be included in the mixing rules. As many interaction parameters as desired can be used, but normally one or two binary interaction parameters pro two components are believed to be sufficient to describe p-V-T behaviour of the mixture. It is of course possible to set the binary interaction parameters dependent on temperature and or pressure, but the disadvantage of doing this would be that more parameters have to be included. Setting the binary interaction parameters not constant will cause the EOS to describe p-V-T behaviour more accurately.

It is not only very important to choose an appropriate EOS but also to know what mixing rule have to be used to give the best results.

In this section several mixing rules will be discussed.

3.2.1 Cubic Equations of State

Mixing rules are comprehensively evaluated in literature. Several types have been reported for especially cubic equations of state, for example the Peng Robinson EOS. The first mixing rules that will be discussed are the classical ones. These can be expressed in the following equations:

$$a_m(T) = \sum_{i}^{n}\sum_{j}^{n} (y_i * y_j * [a_i(T)*a_j(T)]^{0.5}*\{1-k_{ij}\}) \tag{35}$$

$$b_m = \sum_{i}^{n} (y_i * b_i) \tag{36}$$

In equations (35) and (36) the subscripts i and j refer to the component that is considered. The subscript m refers to the mixture. n stands for the total number of components in the mixture. $a_i(T)$, $a_j(T)$ and b_i symbolize the a(T) and b of pure component i or j. These values can thus be calculated by the methods decribed in the previous section 3.1. k_{ij} is a binary interaction parameter. When only chemical similar substances are present in the mixture, k_{ij} equals zero.

In the same way interaction parameters between two molecules of the same substance also equal zero: all k_{ij} equal zero if i=j. The chemical interactions between molecule i and j are assumed to be the same as the interactions between molecule j and i, so $k_{ij}=k_{ji}$. The more difference in chemical structure is present, the closer k_{ij} becomes to unity.

Normally k_{ij} is assumed to be constant, but it is also possible to set k_{ij} to be a function of pressure for example, involving more parameters:

$$k_{ij} = k_{1,ij} + k_{2,ij} * p \tag{37}$$

Equation (37) was proposed by Mohamed. This equation was refered to by Johnston et.al.[7].

The above mixing rules are known as the classical quadratic mixing rules. There are a lot of other mixing rules. Some of them will be pointed out here.

Zou et.al.[21] uses the following mixing rule of the Peng-Robinson EOS parameter a(T):

$$a_m(T) = \sum_i^n \sum_j^n (y_i * y_j * \{a_i(T) * a_j(T)\}^{0.5} * [1 - k_{ij} - (k_{ij} - k_{ji}) * y_i] \tag{38}$$

This mixing rule will predict the p-V-T relation of the mixture with more accuracy than the classical mixing rule, but more interaction parameters occur. This equation is the same as the classical quadratic mixing rule with the binary interaction parameter varying with composition:

$$k_{ij} = k_{1,ij} - (k_{1,ij} - k_{2,ij}) * y_i \tag{39}$$

This mixing rule was proposed by Panagiotopoulos and Reid whom were refered to by Johnston et.al.[7]. They did not assume that all $k_{ij}=k_{ji}$. Substituting this in equation (38) also result in the classical mixing rules.

Gangadhara Rao et.al. [8] uses the covolume dependent (CVD) mixing rules:

$$a_m(T) = b^q * \sum_i^n \sum_j^n (y_i * y_j * a_{ij} / b_{ij}^q) \qquad (q=1.667) \qquad (40)$$

Equation (40) will not be elucidated here. For elucidation see [8].

Now p-V-T behaviour of the mixture is determined as function of composition and several parameters. The compressiblity factor can now be calculated for the mixture using an EOS.

3.2.2 Virial Equation of State and Henry's Law

In section 3.1 the approach has been elucidated for using the virial equation of state to estimate solubility of the heavy compounds in the vapour phase and Henry's Law to estimate solubility of the supercritical fluidum in the liquid phase.

For the virial EOS the generally accepted mixing rules are [2] :

$$T_{c,ij} = (1-k_{ij}) * \sqrt{(T_{c,i} * T_{c,j})} \qquad (41)$$

$$V_{c,ij} = [\ \{ V_{c,i}^{1/3} + V_{c,j}^{1/3} \} * 0.5\ ]^3 \qquad (42)$$

$$Z_{c,ij} = 0.5 * (Z_{c,i} + Z_{c,j}) \qquad (43)$$

$$\omega_{ij} = 0.5 * (\omega_i + \omega_j) \qquad (44)$$

$$p_{c,ij} = Z_{c,ij} * R * T_{c,ij} \ / \ V_{c,ij} \qquad (45)$$

In this set of equations the critical properties are averaged. The resulting properties are called pseudo-critical properties. k_{ij} is a binary interaction parameter.

Prausnitz [2] refers to an estimation for this parameter. If the studied system is not known, i.e. if no equilibrium data are available, a first estimate can be made by:

$$k_{ij} = 1 - [\sqrt{} (V_{c,i} * V_{c,j})] / V_{c,ij} \qquad (46)$$

When for the (binary) mixture the pseudo-critical properties are calculated, these properties can be used in the corresponding states correlations, described in section 3.1, in order to calculate cross virial coefficients: B_{ij} and C_{ij}. The virial coefficients of the mixture can be calculated from:

$$B_m = \sum_i^n \sum_j^n y_i * y_j * B_{ij} \qquad (47)$$

In a mixture containing n components, the mixture virial coefficient B_m can be calculated.

The mixture third coefficient is calculated by [22]:

$$C_m = \sum_i^n \sum_j^n \sum_k^n y_i * y_j * y_k * C_{ijk} \qquad (48)$$

Concluding from (48) the C_{ijk} coefficients are needed, while the mixing rules result in pseudo-critical properties, which result in C_{ij} coefficients. The coefficient C_{ijk} is calculated from binary contributions C_{ij} by:

$$C_{ijk} = (C_{ij} * C_{ik} * C_{jk})^{1/3} \qquad (49)$$

Now, all needed cross and mixture virial coefficients can be calculated.

Properties that occur in Henry's Law have been reviewed in section 3.1. If more than one liquid, heavy compound is used, these quantities must be averaged. Henry coefficients are averaged by:

$$\ln (H_{SCF,mix}) = \sum_{j}^{n} (x_j * \ln (H_{SCF,j})) \qquad (50)$$

The mole fraction x_j should been seen as SCF-free mole fractions. In estimating the molar volumes at infinite dilution of the SCF, the averaging of the contributions to both compressibilty and integral $C^{\infty}_{SCF,i}$ become:

The right hand of equation (33) is called C^{∞}_{ii}.

$$C^{\infty}_{m} = \sum_{i}^{n} x_i^2 * C^{\infty}_{ii} \qquad (51)$$

$$C^{\infty}_{SCF,m} = \sum_{i}^{n} x_i * C^{\infty}_{SCF,i} \qquad (52)$$

With these averaged properties, the molar volume at infinite dilution for the SCF can be evaluated when the liquid phase consists of more than one heavy compound.

Averaging vapour pressures in the Poynting factor is not relevant, because for heavy compounds they are very small compared to operating pressure, so the term $(p-p_i^{sat})$ can be set equal to p.

3.3 Fugacity Coefficients from Equations of State

Fugacity coefficients are quantities that are used in phase equilibria calculations. They represent deviations from ideal behaviour. In this case, the fugacity coefficient is included in order to calculate deviations from both ideal mixture behaviour for the liquid phase and ideal gas behaviour for the vapour phase.

When two phases are in equilibrium, the temperature, the pressure and the chemical potential of the two phases are equal. Phase equilibria at high pressure are calculated by equation (1) or (2).

Equation (1) will be repeated here:

$$\phi_i^L * x_i = \phi_i^V * y_i \tag{1}$$

The fugacity coefficients are deviations from ideal behaviour, so it would be logical that they are some function of the chosen EOS. An EOS represents the ideal gas law with certain added parameters: it is a model to calculate p-V-T behaviour, deviating from ideal gas law behaviour.

Fugacity coefficients are related to the chosen EOS by the following equation:

$$R*T*\ln(\phi_i^F) = -\int_{\infty}^{V^F} \left\{ \left[\frac{\partial p}{\partial n_i}\right]_{T,V^F,n_j} - R*T/V^F \right\} dV^F - R*T*\ln(Z^F) \tag{53}$$

In equation (53) the partial derivative of p towards the number of moles of component i is calculated from the chosen EOS, for example equation (3), combined with the classical mixing rules.

Differentiating this equation, T, V and the number of moles of the other components in the mixture are to be held constant. The superscript F refers to the phase which is considered. V and Z in phase F can be calculated directly as has been shown from the EOS at fixed p and T. It can be seen from equation (53) that the fugacity coefficient of component i in a mixture is a function of pressure, temperature, composition and the molar volume in phase F (or the compressiblity factor in phase F).

For the Peng Robinson EOS the solution of equation (53) becomes finally, using classical mixing rules:

$$\begin{aligned} \ln(\phi_i^F) = {} & (B_i^*/B^*)*(Z^F-1) - \ln(Z^F-B^*) + [A^*/(2.828*B^*)]* \\ & [\, B_i^*/B^* - 2*\sum_j^n\{ y_i*(a_i(T)*a_j(T))^{0.5}*(1-k_{ij}) \}/a_m(T) \,]* \\ & \ln\{(Z^F+2.414*B^*)/(Z^F-0.414*B^*)\} \end{aligned} \qquad (54)$$

In equation (54) all used variables were already discussed.

Equations (53) and (54) have been derived in Appendix A.

When the virial EOS is used the result is less comprehensive. De Swaan Arons [12] derived all equations needed to calculate the phase equilibrium assuming that the supercritical phase consists of only SCF as far as mixing rules are concerned, i.e. in estimating virial coefficients for the mixture. The same assumption can be made while also invoking the third virial coefficient. The result is shown below, while the derivation is also incorporated in Appendix A:

$$(y\,/\,x)_i = K_i =$$

$$\gamma_i * \frac{P_i^{sat} * POY_i}{R * T} * (\,1\,/\,\rho_{SCF}\,) * ENHANCEMENT_{vap} \qquad (55)$$

This ENHANCEMENT can be regarded as follows. The concentration of the heavy compound in the supercritical phase calculated by the virial EOS devided by this concentration calculated by the ideal gas law (Raoult's Law) is defined as the ENHANCEMENT factor. As can be seen in (55) only vapour phase's non-ideality has been invoked in this ENHANCEMENT, while liquid phase's non-ideality has already been encountered by means of the activity coefficient. This is refered to by means of the subscript 'vap'. The solubility of the heavy compounds in the supercritical phase is enhanced with respect to ideal gas law behaviour, due to intermolecular forces. These intermolecular forces increase of course with pressure causing the gas mixture to become denser. It can be shown that this enhancement factor varies exponentially with the density of the SCF (B-truncated virial EOS). The term $\mathrm{ENHANCEMENT}_{vap}$ in (55) equals (see Appendix A for elucidation):

$$\mathrm{ENHANCEMENT}_{vap} = \exp(-2*B_{12}*\rho_1 - 1.5*C_{112}*\rho_1^2) \qquad (56)$$

When the B-truncated virial EOS is used, C_{112} becomes zero and (56) and the result is the same as De Swaan Arons derived [12]. Logically, when the ideal gas law is used as EOS, both B_{12} and C_{112} become zero, causing the ENHANCEMENT to be zero in complete harmony with its definition.

3.4 Calculation of Phase Equilibria Using One Equation of State

At fixed temperature, pressure and composition the EOS result in one equation with only one variable. This variable is either the molar volume or the compressibility factor, depending on how the equation has been written. It is wanted to use equation (54), so it is logical to use the EOS written like equation (9). Any cubic EOS result finally in a third order equation in Z or V.

For the liquid phase, Z^L will be the smallest root of this third order equation, depending on pressure, temperature and composition x_i. Z^V will be the largest root, depending on pressure, temperature and composition y_i. Convergence problems may occur because it is very well possible to have a so called trivial root problem [2]. Even when there are three roots for the system, one root could be the result of iterations, because slight changes in initial compositions and binary interaction parameters can have extreme consequences for the iteration. This problem can be avoided by choosing the intial values for composition in a dedicated manner. This is not so easy as it looks like. It is a great disadvantage in using the cubic EOS, which makes the virial EOS more popular in use, because the virial EOS does not require any iteration at all if the corresponding states correlations reviewed in section 3.1 are used. The major disadvantage of the virial equation is its limitation of not being valid at pressures which are too high. For example, when carbon dioxide is used as SCF, the virial EOS cannot be used with much accuracy above 125-130 bar, depending on temperature (e.g. about 70 °C).

When, finally the phase equilibrium has been modelled, the result can be used in dimensing separation columns. This is reviewed in section 4. In this section a complete analysis of degrees of freedom will be made, because it is important to know, which variables and parameters are important to know and which variables and parameters are not relevant to measure or estimate. Therefore the analysis of degrees of freedom concerning the phase equilibrium modelling will be made.

For the cubic equations of state:

If the total number of components is c, there are c equilibrium conditions (1), 2*c fugacity coefficient equations (53) for the liquid and vapour phase. For both phases the EOS is also valid and the condition that $\Sigma x=1$ and $\Sigma y=1$ must also be satisfied, involving 4 more equations.

In total there are 3c+4 equations.

There are 4*c variables because of the fugacity coefficients and mole fractions of both phases. Pressure, temperature and compressibility factors of both phases cause the total number of variables to be: 4c+4. Other quantities are considered to be parameters and they are known: they are not variables.

Finally, it is found that there are c degrees of freedom.

For the virial EOS and Henry's Law:
The virial coefficients, vapour pressures, critical properties, Henry coefficients and binary parameters in both the virial EOS mixing rules and activity coefficients are regarded as parameters and are known. Pressure, temperature and composition of both phases are variables (2c+2).

The model results in three equation for the distribution coefficients (= y_i / x_i) for all compounds (Henry's Law estimates the distribution coefficient of the SCF, while the virial EOS estimates the distribution-coefficients of all heavy compounds). So there are c equations for the distribution coefficients. The restriction that Σx and Σy must equal one results in a total of c+2 equations.

Finally it is found that there are c degress of freedom, like has been found for cubic equations of state. This means that when equations of state are considered as black boxes, the two proposed models require the same input variables two results in the same output variables, but they of course differ in magnitude.

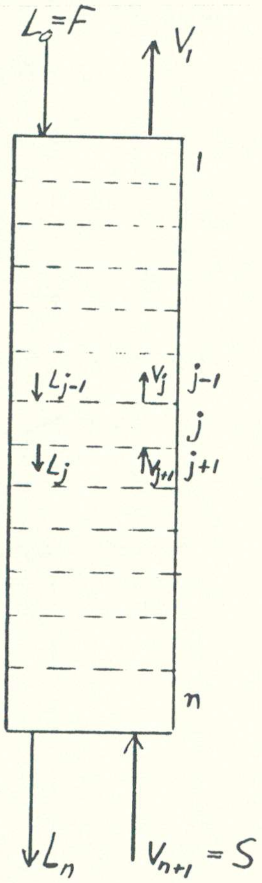


Figure I 1: Flowsheet for the extraction column without reflux.

4. Modelling Separation Columns

In this section the column will be modelled by the stage to stage calculation method. The column is considered to be a number of stages in series. In every stage equilibrium will be reached between the vapour and liquid phase. The column can be used in several ways.

It can be used without reflux: the column will be a normal extraction column, as shown in figure I, with the liquid feed coming in at the top of the column.

It is also possible to operate the column with reflux, while the feed can be added at several places to the column. This is shown in figure II.

First the column without reflux will be considered, afterwards the refluxed operation.

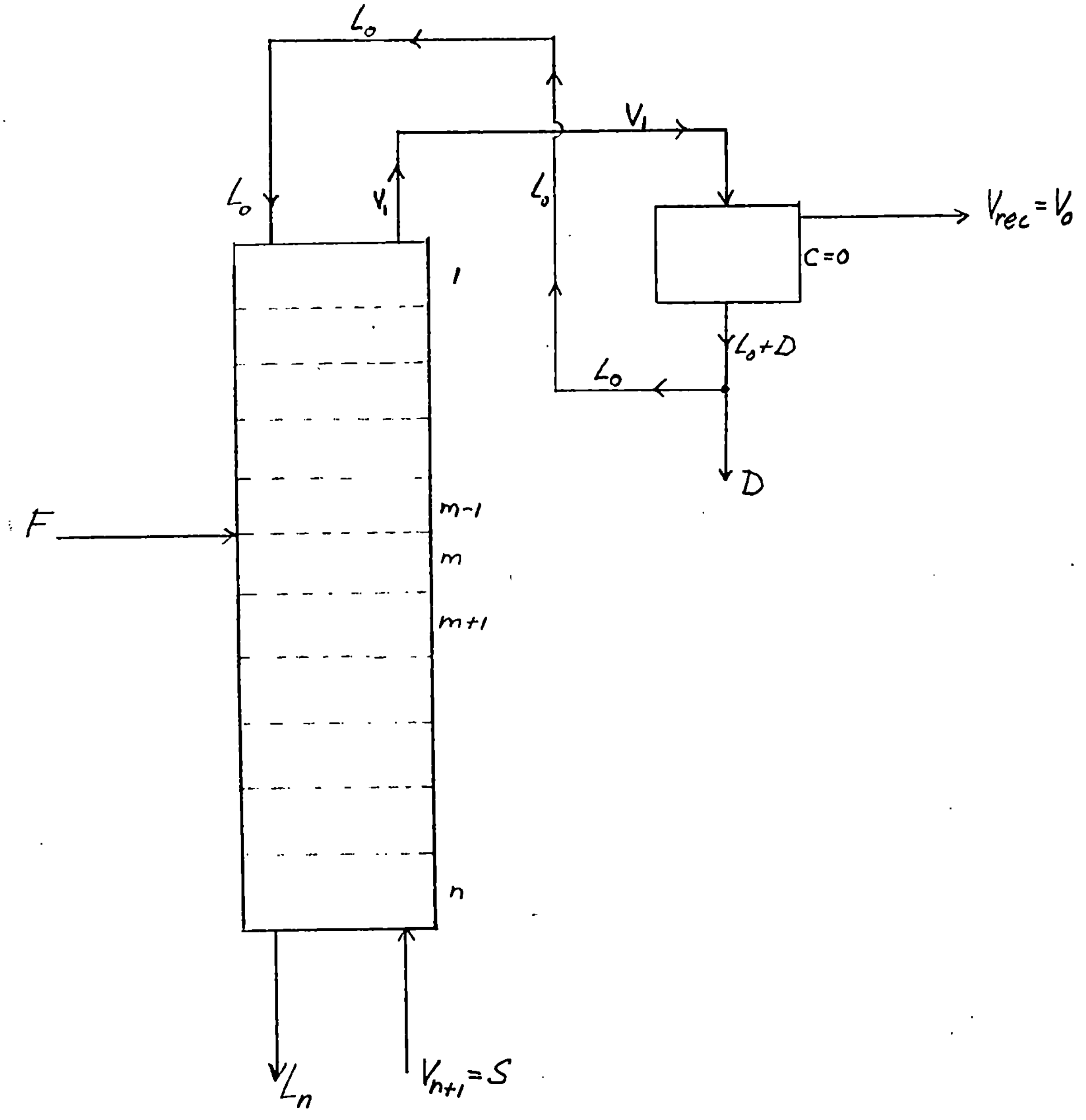


Figure II : Flowsheet for the extraction column with reflux.

4.1 Modelling the Extraction Column without Reflux

The operation is schematically shown in figure I. Two flows, that come into 1 theoretical stage, are mixed and two flows leave the same stage. The leaving flows are a vapour and a liquid stream which are thermodynamically in equilibrium. This equilibrium has already been modelled in section 3. The mass balance (when no accumulation occurs) for component i over stage j is:

IN = OUT

$$x_{i,j-1}{}^{*}L_{j-1} + y_{i,j+1}{}^{*}V_{j+1} = x_{i}{}^{*}L_{i} + y_{i}{}^{*}V_{i} \qquad (57)$$

The subscript j-1 refers to the stage above stage j, j+1 refers to the stage below stage j, see figure I. L and V symbolize the flow rates of respectively liquid and vapour phase.

In order to know the temperature at stage j for the equilibrium calculation, a heat balance also must be satisfied. In the heat balance, which will not be given here, it would be necessary to know the latent heat of each component. This is the heat that must be added in order to establish a phase transition of the liquid phase to the vapour phase. In pure vapour liquid contacting devices this would be the heat of vaporization. A supercritical phase can neither be considered to be a vapour phase nor a liquid phase. In liquid-liquid contacting devices the latent heat would be approximately zero. It is clear that the latent heat for liquid-SCF transition must be known.

In the heat balance also heat capacities or specific heats occur. These could be calculated from the chosen EOS. Further it could be possible to extract or add some amount of heat by external coolers or heaters.

In the column heaters are used in order to establish phase transitions. Heat losses to surroundings also have to be included in the heat balance.

A heat balance will not be given here, because the heat added by the external heater is in such an amount that the temperature in the column will remain constant. In other words, the temperature is controled in the entire column to be a certain value which must be fixed. It is clear now that a heat balance does not have to be taken into consideration: the extraction process will occur at constant temperature.

In order to know the pressure at stage j it is necessary to know the pressure drop in the column. Knowing the type of packing material it is possible to calculate the pressure drop over one stage. There is an empirical relation available [9] which relates the pressure drop to the liquid hold up and the gas flow at stage j. For Berl-Saddles, for example, it has been found:

$$\Delta p_j = [1 - 2.5*1.36*\{u_{L,j}^2/(d_r*g)\}^{1/3}]^{-3}* 0.29*F_p*(H/n)*\rho_{V,j}*u_{V,j}^2 \quad (58)$$

In equation (58) d_r is the diameter of one element of the package, g is the gravitational acceleration constant. $U_{L,j}$ and $u_{V,j}$ stand for respectively the liquid phase and vapour phase superficial velocity at stage j. H is the height of the package, $\rho_{V,j}$ symbolizes the density of the vapour phase at stage j. F_p is a package constant and depends purely on the geometric properties of the package.

The pressure at stage j can then be calculated:

$$p_j = p_{j+1} - \Delta p_j \tag{59}$$

Equation (58) consists of a number of new variables not discussed sofar. d_r, g, H are known: they are parameters. The value of F_p is not known: it must be specified by pressure drop data correlation. The superficial velocities contain the same information as the flows L_j and V_j. They are only written in another way:

$$u_{V,j} = V_j*M_{V,j}/\{ \rho_{V,j}* (0.25*\pi*D^2) \} \tag{60}$$

and similarly,

$$u_{L,j} = L_j*M_{L,j}/\{ \rho_{L,j}* (0.25*\pi*D^2) \} \tag{61}$$

In equations (60) and (61) M stand for molar mass and D is the diameter of the column. π is a constant.

The parameter D is known, while M can be calculated by:

$$M_{V,j} = \sum_{i}^{c}(y_{i,j}*M_i) \tag{62}$$

$$M_{L,j} = \sum_{i}^{c}(x_{i,j}*M_i) \tag{63}$$

M_i is the molar mass of component i and is constant: this is a parameter.

The densities used in equations (58) through (61) are rewritten quantities of the compressibility factor of the considered phase:

$$\rho_{V,j} = p_j * M_{V,j}/(R*T*Z^V) \quad (64)$$

$$\rho_{L,j} = p_j * M_{L,j}/(R*T*Z^L) \quad (65)$$

Now the pressure at stage j can be calculated as function of F_p, when the value of p_{n+1} has been given. This is the pressure of the pure SCF flow added at the bottom of the column.

The pressure of the liquid stream added at the top can be assumed to be equal to the pressure at stage 0. This can be made plausible by considering the pump which is used to put in the liquid feed. If the pressure at stage 0 equals p_0, the pump builds up a pressure in the liquid income pipe that is only a slight fraction higher than p_0. If the pressure in the liquid income pipe is somewhat higher then p_0, the liquid feed will flow into the column. By means of the gravitation force the liquid will fall down in the column because its density is higher than the SCF's density. This will be so when the vapour flow in the column is not high enough to cause flooding to occur. At the flooding border the liquid neither falls down nor will escape at the top: it stays constantly at the same place. Somewhat above the flooding border, the input of liquid feed is greater than the liquid flow coming out of the bottom. All liquid escapes then over the top: no separation has been accomplished.

It is useful to make an analysis of the number of the degrees of freedom in the total system.

For every stage and for every component the mass balance (57) is valid involving c*n equations. The pressure drop correlation (58) can also be applied to all stages including the relation for the explicit pressure (59): 2*n equations. Equations (60) through (65) are also valid for every stage: 6*n equations. So, totally we have added a number of n*(c+8) equations.

In this model there have been used a set of new variables, which are listed here: $x_{i,0}$, $y_{i,n+1}$, V_j, V_{n+1}, L_j, L_0, $u_{L,j}$, $u_{V,j}$, $\rho_{V,j}$, $\rho_{L,j}$, Δp_j, p_{n+1}, F_p, n, $M_{V,j}$, $M_{L,j}$.

All variables with subscript i have to be included c times; all variables with subscript j have to be included n times. Totally it is found that there are 2c+9n+5 new variables.

Thermodynamics showed that pro stage there are c degrees of freedom. So for n stages this will be a number of c*n. Temperature is constant so we can write n-1 more equations:

$$T_{j-1}=T_j=T_{j+1} \qquad (66)$$

Because of the fact that there are 2*c more mole fractions used in the total system ($x_{i,0}$ and $y_{1,n+1}$) than already have been used in the section concerning thermodynamics, two more equations can be added: $\Sigma x_{i,0}=1$ and $\Sigma y_{i,n+1}=1$, which are summation conditions.

Now the total number of degrees of freedom for the extraction column can be calculated:

DegrFr = cn+2c+9n+5-n(c+8)-2-(n-1) = 2c+4.

Let us confirm this result. When the packing factor and the number of equilibrium stages would be known, the complete system must be known specifying the complete input. The input variables are all $x_{i,0}$ minus 1, all $y_{i,n+1}$ minus 1 (because the last $x_{i,0}$ and $y_{i,n+1}$ can be calculated from the summation conditions for mole fractions), the operation temperature, pressure of the incoming SCF flow and total flows $L_0=F$ and $V_{n+1}=S$. Summing up these variables it is found that there are:

$2*(c-1) + 4 = 2c+2$ input variables. Input of n and F_p would result in a total number of variables which are externally specified of $2c+4$ which is exactly the same as the number of degrees of freedom that was derived. Thus: the number of degrees of freedom of $2c+4$ is correct.

The above modelling is valid, when no accumulation occurs. This means that all derivatives towards time equal zero. As indicated before, the model can only be applied below the flooding border. The flooding border can be determined experimentally, but can also be estimated by figure 7, page 89 in [9]. The disadvantage of this estimation procedure is that viscosities of both phases have to be known. At high pressures it could very well be possible that the relations [9] are not valid. Another remark can be made about this correlation: it can be applied for L-V systems, while here no V - phase is present, but a supercritical phase. It is thus very dangerous to use these correlations. Little is known about flooding borders for column-types while operated at high pressures.

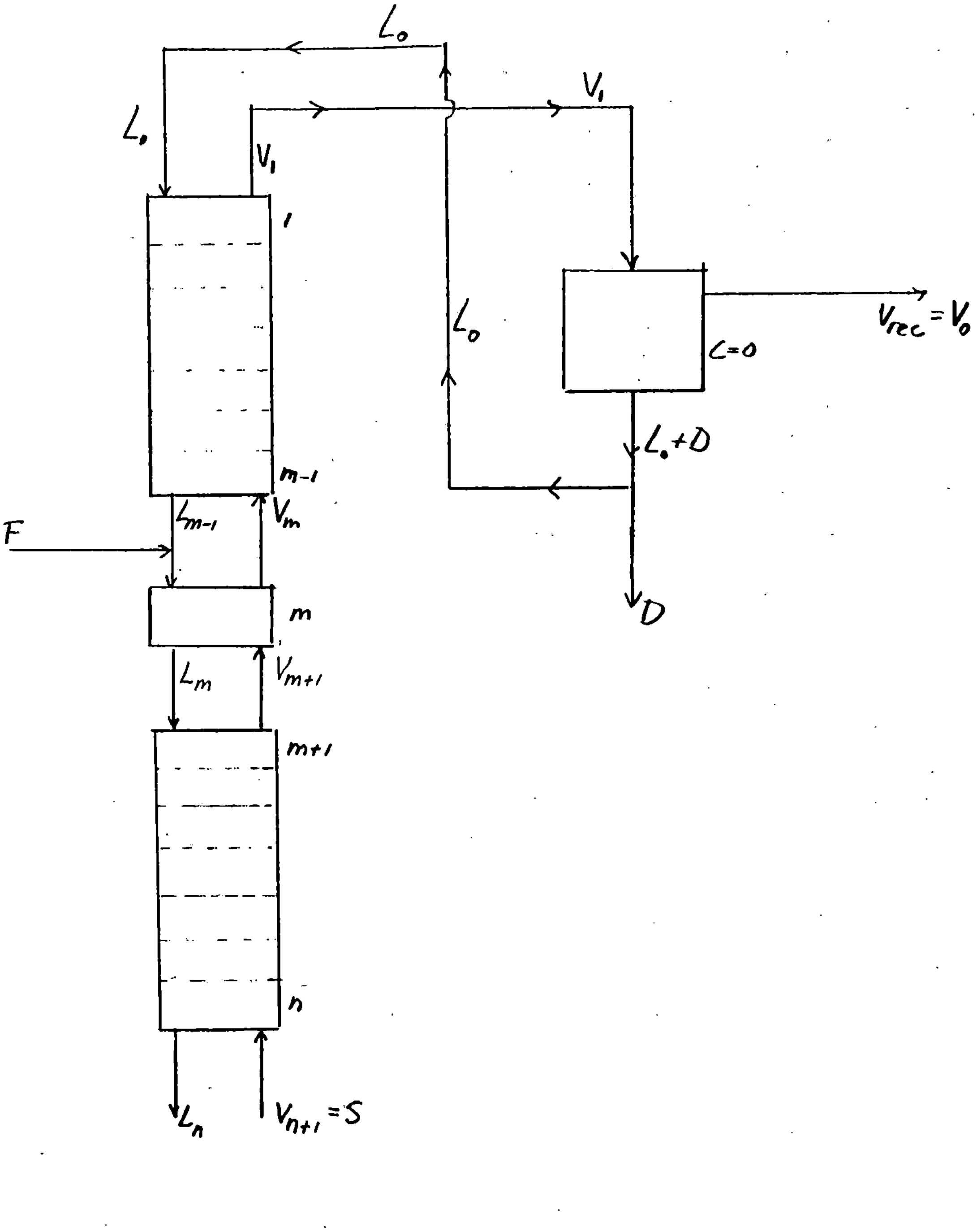


Figure III: Flowsheet for the extraction column with reflux. A scheme for the system built up in four sections. See text for elucidation.

4.2 Modelling the Extraction Column with Reflux

In this section the the extraction column will be modelled in the case that a reflux section has been included. The fresh liquid feed will now not be added at the top of the column, but somewhere between the bottom and the top. The column should be designed in such a way that fresh liquid feed can be added at several places to the column. The column has been shown schematically in figure II.

In order to model the column, it can be cut into four sections:

1. Bottom Section	: stages m+1 to n
2. Feed Stage	: stage m
3. Top Section	: stages 1 to m-1.
4. Reflux Arrangement	: stage 0 (the condensor).

This cutting has been shown in figure III.

When possible, equations which were used in section 4.1, are not rewritten. These equations will be refered to.

1. Bottom Section.

As can be seen in figure III the bottom section is exactly the same as an extraction column without reflux, which has been considered in figure II. The only difference is that there are now only (n-m) equilibrium stages and thus subscripts for mole fractions, flows and pressure at the top stage of the bottom section have been changed.

For each stage of the (n-m) stages present the mass balance is valid. The mass balance is represented by equation (57).

The pressure drop equations (58) through (65) are also valid, while temperature is controled to be constant. This indicates that equation (66) also must be included.

Let us now make an analysis of the degrees of freedom in the bottom section:

There are (n-m)*c mass balances and in the pressure drop correlations 8*(n-m) equations are present. Equation (66) can be written for (n-m) temperatures, so equation (66) represent (n-m-1) more equations. Thus, totally there are (n-m)*(c+9)-1 equations.

The variables in the mass balances, pressure drop correlations, that were not included in the thermodynamical part are: $x_{i,m}$, $y_{i,n+1}$, V_j, V_{n+1}, L_j, L_m, $u_{L,j}$, $u_{V,j}$, $\rho_{V,j}$, $\rho_{L,j}$, Δp_j, p_{n+1}, F_p, n, m, $M_{V,j}$, $M_{L,j}$.

Each variable with a subscript j is present at each stage: so there are (n-m) variables times the number of variables with subscript j. The variables with subscript i are present for each component: so there are c variables times the number of variables with subscript i.

Summing up there have to be included 2c+9(n-m)+6 variables more.

Because two more mole fractions have been included here, there also are two more equations valid for this system: $\Sigma x_{i,m}=1$ and $\Sigma y_{i,n+1}=1$.

In thermodynamics it has been found that there are c degrees of freedom pro stage, involving to be (n-m)*c in the bottom section.

The number of degrees of freedom becomes now:

$$\text{DegrFr} = 2c+9(n-m)+6-2-(n-m)(c+9)+1+(n-m)c = 2c + 5.$$

This number is one more than in the extraction column without reflux, because the new variable m has been introduced.

2. Feed Stage.

The feed stage is one equilibrium stage with an extra external input of feed as can bee seen in figure III.

The mass balance for component i over the feed stage is:

$$x_{i,m-1}{}^{*}L_{m-1} + x_{i,f}{}^{*}F + y_{i,m+1}{}^{*}V_{m+1} = x_{i}{}^{*}L_{m} + y_{i}{}^{*}V_{m} \qquad (67)$$

Equation (67) is almost the same as equation (57); only the extra feed input has been included. F symbolizes the total feed flow rate, while $x_{i,f}$ stands for the mole fraction of component i in the feed.

For the (liquid) feed the pressure can be set equal to the pressure at stage m (the feed stage). This has already been elucidated under equation (65). In that case the pressure drop correlation remains the same as equations (58) through (65), while substituting constant m for variable j.

Thermodynamics for stage m have shown that there are c degrees of freedom more.

It will be derived now what happens to the total number of degrees of freedom when the feed stage is included in the bottom section.

In equation (67) an amount of new variables occur, which has neither been included in the bottom section nor in the thermodynamical part.

These variables are:

$$x_{i,m-1}, V_{m}, L_{m-1}, F, x_{i,f}, u_{V,m}, \rho_{V,m}, \Delta p_{m}, M_{V,m}, u_{L,m}, M_{L,m}, \rho_{L,m}$$

Summing up the variables, it is found that there are 2c+10 new variables.

Of course we can write two more equations for $x_{i,m-1}$ and $x_{i,f}$. These are the summation conditions that equal 1.

It is necessary to make a correction here. The thermodynamical part also takes into consideration the summation conditions. Viewing sceptically at the above made analysis, it can be seen that the summation condition $\Sigma x_{i,m}$ has been counted twice as well as variable $x_{i,m}$.

So there are for the feed stage c mass balances, 8 equations in the pressure drop correlations and 2 more summation conditions. 1 condition has been counted twice as well as c variables. We already found that 2c+10 variables have been added and the number of degrees of freedom due to thermodynamics has been extended by c. The number of degrees of freedom for the feed stage integrated with the bottom section is now extended by

2c+10 (variables) - (c+10) (equations) + c (degrees of freedom due to thermodynamics) - c ($x_{i,m}$ counted twice) + 1 ($\Sigma x_{i,m}$ counted twice) = c+1.

The number of degrees of freedom now becomes: 3c+6.

While integrating the feed stage with the bottom section also an extra equation appears because of temperature equality (66) at stages m and m+1.

The final number of degrees of freedom in the system feed stage integrated with bottom section now becomes:

DegrFr = 3c+5.

Let us confirm this result. Total input must give total ouput. Input: mole fractions and flow rates of all input flows and the pressure of the incoming SCF flow at stage n: 3(c-1)+4 specifications. Further specification of operation temperature and the column properties F_p, m and n result in a total number of specified variables: 3(c-1)+8 = 3c+5. So the analysis of the number of degrees of freedom is correct.

3. Top Section.

The top section is again exactly the same as the extraction column without reflux which can be seen when comparing figure III with figure I. Thus, it is also the same as the bottom section, only the number of equilibrium stages is different.

The number of degrees of freedom in an extraction column without reflux is independent on the number of stages. This has been shown in the analysis of the number of degrees of freedom for both the extraction column without reflux and the bottom section.

So, the number of degrees of freedom in the top section equals 2c+4. In the bottom section it has been found that this number was 2c+5, because of the extra variable m, when being compared with the extraction column without reflux. In the top section the number of stages is only a function of variable m. The number of stages is m-1, thus independent of n.

Now it is necessary to find the number of equations and variables which have been counted twice.

The variables, which have been counted twice, can be found at the connecting point of the top section and the feed stage as well as the variables which symbolize column properties:

$x_{i,m-1}$, $y_{i,m}$, L_{m-1}, V_m, m, F_p, p_m : 2c+5

Equations which have been counted twice:

$\Sigma x_{i,m-1}=1$, $\Sigma y_{i,m}=1$: 2

Extra equation: $T_{m-1} = T_m$ (66) : 1

So the total number of degrees of freedom, which must be added when integrating the top section with the already integrated bottom section and feed stage, becomes:

$$2c+4 - (2c+5) + 2 - 1 = 0$$

Thus, the total number of degrees of freedom after integrating the top and bottom section and the feed stage has been fixed by:

DegrFr = 3c+5.

4. Reflux Arrangement.

In the reflux arrangement the outcoming SCF flow is cooled in order to establish condensation of the dissolved components. Then the nearly pure SCF can be recycled to the bottom of the column in order to perform a new extraction. The condensed components flow out of the condensor and can partly be refluxed. This can be seen in figure III.

In the condensor it can be assumed that the pressure equals the pressure at stage 1 in the column, because no pump is used between the SCF flow coming out of the column and the incoming flow in the condensor. In that case possible pressure losses due to cooling cause the incoming flow to increase to a steady state flow rate. In this situation the pressure in the condensor equals the pressure at stage 1 in the column when the pressure drop due to friction in the pipe is neglected.

The fact that the SCF flow rate coming out of the column increases until steady state is reached does not make the total model to be inaccurate. The model, as has been stated before, is applicable in the steady state situation. This consideration of increasing flow has only been made here in order to state why the pressure in the condensor equals the pressure at stage 1 in the column.

Let us now write down the equations which are valid for the reflux arrangement. The condensor can be seen as an additional equilibrium stage at which the pressure is the same as at stage 1 and the temperature is unknown. The temperature in the condensor is unknown because it is optional to what temperature the flow coming out of the column is cooled. The reflux arrangement has been shown in figure III.

Thermodynamics thus can be applied to the condensor as well as a mass balance.

The mass balance for one component over the condensor is:

$$y_{i,1}*V_1 = x_{i,c}*L_c + y_{i,rec}*V_{rec} \qquad (68)$$

In equation (68) $y_{i,rec}$ is the mole fraction of component i in the SCF flow leaving the condensor to be recycled. This flow rate is symbolized by V_{rec}. The subscript c stands for condensor.

A part of the liquid flow, L_c, is refluxed and introduced again in the column at stage 1. This part of L_c thus equals the liquid flow L_0. The part which is not refluxed equals the flow leaving the system at the reflux arrangement. This flow is symbolized by D, where D stands for distillate. Looking sceptically at figure III, it can be seen that the condensor can also be indicated as equilibrium stage 0, because the leaving liquid flow has the same composition as flow L_0 which is introduced at stage 1 at the top of the column. In that case the mass balance (68) can be rewritten in an equation which causes the condensor to be connected with the column by means of other subscripts:

$$y_{i,1}*V_1 = x_{i,0}*(L_0+D) + y_{i,0}*V_0 \qquad (69)$$

The phase equilibrium occuring at "stage 0" can be described by thermodynamics. It has been shown that thermodynamics cause the number of degrees of freedom to be extended by c.

How much liquid product leaving the condensor is refluxed can be expressed in terms of a reflux ratio, R, which is defined as:

$$R = L_0 / D \qquad (70)$$

Let us now make an analysis of the number of degrees of freedom in the total extraction column with reflux.

There are c mass balances (69) and an extension of the number of degrees of freedom due to thermodynamics of c. Also 1 equation (70) has been added.

The new variables, which have neither been included in thermodynamics nor in the top and bottom sections nor in feed stage, are:

R, D, V_0 : 3 variables.

The variable $x_{i,0}$ has been counted twice as well as its summation condition, $\Sigma x_{i,0}=1$.

We can write an additional equation:

$$p_0 = p_{condensor} = p_1 \tag{71}$$

So the number of degrees of freedom due to the reflux arrangement, has to be extended by:

$$3 - (c+1) + c - c + 1 - 1 = 2 - c$$

Integrating the reflux arrangement to the top and bottom section and the feed stage, it is found the the total number of degrees of freedom in the extraction column with reflux is:

$$\text{DegrFr} = 3c+5 + 2-c = 2c+7$$

Let us confirm this final result.

Specification of all input variables must determine all output variables.

Specification of composition and flow rate of the incoming feed F and the incoming pure SCF, V_{n+1}: 2(c-1)+2 specified variables.

Specification of the geometrical properties of the column, F_p, n, m: 3 specified variables.

Specification of operation temperature and pressure of the incoming pure SCF: 2 specified variables.

There are now 2c+5 variables specified, leaving two to be specified in order to fix the total system to be k equations with k unknown variables. These last variables must be specified by other external inputs, for example the reflux ratio and the temperature in the condensor. Also the mole fraction of the SCF in the SCF flow that is recycled can be set equal to 1, causing all other mole fraction to equal zero.

5. Discussion of Models

In section 3 models were presented to calculate the phase equilibrium as function of temperature, pressure and composition. It has been shown that only using one equation of state (EOS) the total phase equilibrium can be determined at certain temperature, pressure and composition. In that case mixing rules must be known as well as binary interaction parameters. The a(T) and b parameters for a pure substance in an EOS must also be known. They can either be a function of the critical properties of the substance or a function of the liquid density at 20 °C as has been pointed out in section 3.

The second model that has been proposed was an EOS for the supercritical phase and a measure for gas solubilities (Henry constants) for the liquid phase. All parameters can be estimated, except for Henry coefficients. Vapour pressure data are often available, so no estimation method for vapour pressures have been evaluated here.

The major difference in use between the two proposed models are calculation time and convergence problems. The latter model can readily be used, without comprehensive knowledge of numerical iterative methods. The first model, however, is more often used, because of its wider range of applicance. The second model can not be used at densities of the SCF above half the critical density (B-truncated virial EOS) or three fourths the critical density (C-truncated virial EOS). When the B-truncated virial EOS is used above 0.5 times the critical density, the model will yield solubilities of the heavy compounds in the supercritical phase to be too high. The chemical interactions, that become important in dense gases, are estimated too high: the B-coefficient exaggerates the effect [12].

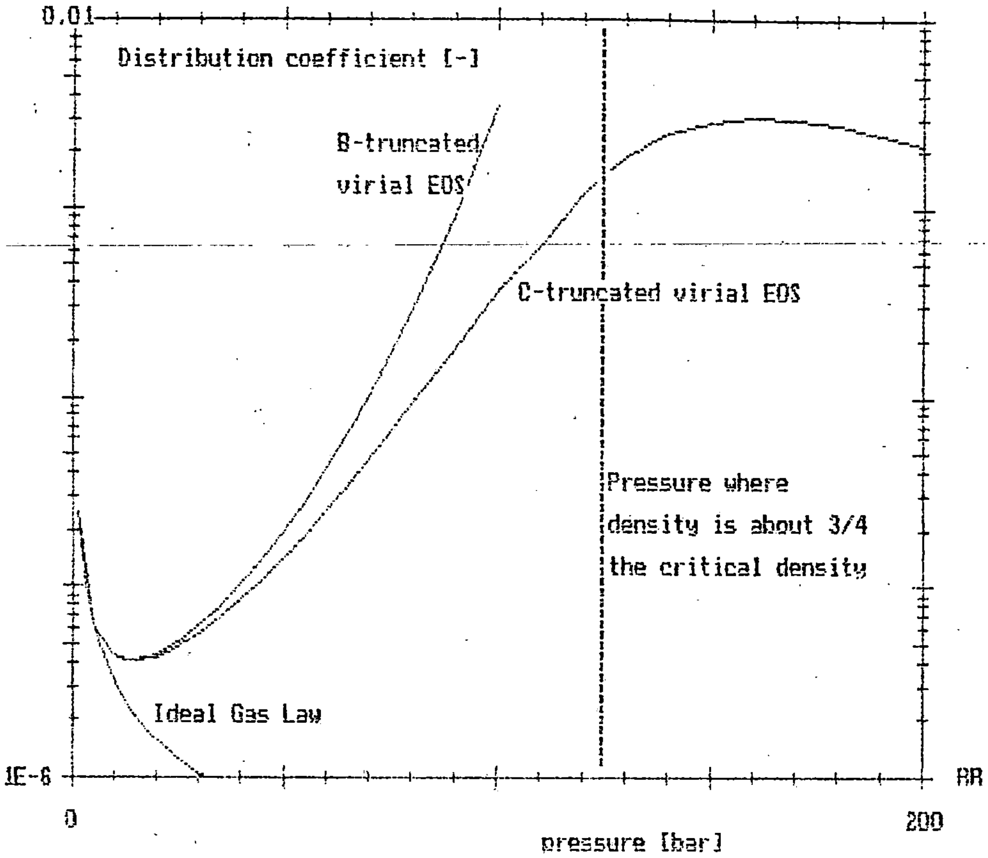


Figure IV : Distribution coefficient as function of pressure. B-truncated as well as C-truncated virial EOS has been shown. The ideal gas law has been plotted in order to see the enhancement-factor concept. This graph is the calculation result for the system ~~hexadecanol~~ and carbon dioxide. No non-ideality of liquid phase has been invoked. The binary parameters were estimated. No link to reported data in literature has been made. The graph should just be seen as an illustrative view for the effect of the virial coefficients. See text for further elucidaton.

n-octadecane

From that moment the C-coefficient becomes important. It pulls the effect of B back to result in results that are in more agreement with reality. At about three fourths the critical density this pulling back effect of C becomes too large and the model will estimate the solubility of the heavy compounds in the supercritical phase to be too small. This can be seen in figure IV. Because no corresponding states correlations are available in literature, no extension of the model to higher densities can be made.

Scientifically seen, the second model is somewhat more educative and easier to evaluate. Chemical interactions and the heavy compound's own volatility can be regarded separately, while these effects are completely strangled in cubic equations of state. In getting first feelings about equilibria of certain systems the second model could be prefered. Cubic equations of state can be used in a later stadium, to make the model applicable to a greater range of densities of the SCF.

For cubic equations of state:

Summarizing, three cases are important in fixing the phase equilibrium:

- choose an appropriate equation of state,
- choose an appropriate model to determine the pure substance parameters a(T) and b,
- choose appropriate mixing rules,
- knowledge of the binary interaction parameters.

The first three items are choices to be made. Combination of these three choices must describe the phase equilibrium in the best way.

The values for the binary interaction parameters can be determined by means of solubility experiments or can be known out of literature: it could be possible that solubility experiments have already been done by another person. The values for k_{ij}'s are dependent on the three chosen items EOS, a(T) and b, mixing rules.

The model which describes the technology of the column calculates at each equilibrium stage incoming and leaving mole fractions as well as the flow rates. Thus, it can be called a stage to stage calculation procedure. The calculation procedure will be iterative because external specifications are not known at the same stage. In case of an extraction column without reflux, the input specifications are to be set at stage 1 and stage n. So knowledge of mathematics is also needed in order to solve the equations.

The stage to stage calculation model which has been discussed is only valid at steady state: no accumulation has been assumed to occur.

Normally equilibrium will not be reached in a real stage, but since there are no real stages present this is no problem. The packed column can be assumed to be built up of n theoretical equilibrium stages in series.

6. Conclusion

In section 3 phase equilibria were modelled where a supercritical fluidum was involved. This means that there has to be dealt with high pressures. Two models for describing phase equilibria at high pressure (where a supercritical fluidum is involved) have been presented. Advantages and disadvantages have comprehensively been discussed in section 5.

It has been shown that due to corresponding states correlations many relevant properties such as virial coefficients can be estimated. Because of its simplicity the virial equation of state can provide fast and reasonably good estimates of these types of phase equilibria. Further knowledge of Henry constants and vapour pressure data provides the calculation of complete phase equilibria. No iterations are required, even for systems consisting of many components.

Applying phase equilibria in industries, it is desired to connect these models to technological models that describe in- and output flow in a separation column. These types of phase equilibria are applied in supercritical extraction processes (or: supercritical entrainment distillation processes). In section 4 an analysis of degrees of freedom has been made when a continuously operated separation column is used.

7. Notation

First a list (in alphabetical order) will be given of the variables, followed by a number of Greek variables, without taking into consideration their sub- and superscripts. The latter will be listed afterwards. Finally, a list of abbreviations will be given.

Symbol	Description	Units
a and a(T)	pure substance parameter in EOS	$J*m^3/mol^2$
A^*	dimensionless form of parameter a(T)	-
b	pure substance parameter in EOS	m^3/mol
B^* 1.	dimensionless form of parameter b	-
2.	second virial coefficient	m^3/mol
C	third virial coefficient	m^6/mol^2
D	flow rate of distillate	mol/s
DegrFr	number of degrees of freedom	-
F	flow rate of feed	mol/s
F_p	packing factor	-
H	Henry constant	Pa
k_{ij}	binary interaction parameter	-
L	flow rate of liquid phase	mol/s
m	number of feed stage	-
M	molar mass	kg/mol
n	number of stages in column	-
p	pressure	Pa
R	reflux ratio	-
S	flow rate of SCF = V_{n+1}	mol/s
T	absolute temperature	K

V	1.	molar volume	m^3/mol
	2.	flow rate of vapour (=SCF) phase	mol/s
u		superficial velocity	m/s
x		mole fraction in liquid phase	-
x_0		variable used in Brunner's method to determine a(T) and b	-
y		mole fraction in vapour (=SCF) phase	-
Z		compressibility factor	-

Greek symbols:

Δp	pressure drop	Pa
ρ	density	kg/m^3
ϕ	fugacity coefficient	-
ω	Pitzer's acentric factor	-
γ	(acentric) activity coefficient	-

Sub- and Superscripts used:

c	1.	condensor
	2.	critical
f		feed
F		phase
i		component
j	1.	component
	2.	stage
k		component
L		Liquid phase
m	1.	number of feed stage
	2.	mixture
rec		recycle
sat		saturated (used in vapour pressure notation)
V		Vapour (=SCF) phase

Abbreviations:

EOS	equation of state
HETP	height equivalent to one theoretical plate
SCE	supercritical extraction
SCF	supercritical fluidum
CSC	corresponding states correlation

8. Literature

[1] Delamine, Brochure of Akzo Salt and Bsic Chemicals Nederland b.v. about Ethylene Amines, Delfzijl (August 1985).

[2] Prausnitz J.M.; Reid, R.C.; Poling, B.E., The Properties of Gases and Liquids, 4th ed., McGraw-Hill, New York (1987).

[3] De Loos, Th.W.; Van der Kooi, H.J., Toegepaste Thermodynamica en fasenleer, Handout for Lecture st79, Delft University of Technology, University Press.

[4] McHugh, M.A.; Krukonis V.J., Supercritical Fluid Extraction, Principles and Practice, Butterworth Publishers, Boston (1986).

[5] Brunner, G.; Dohrn, R., Empirische Korrelationen zur Bestimmung der Reinstoffparameter der Peng-Robinson-Zustandsgleichung und ihre Anwendung zur Phasengleichwichtsberechnung, Chem. Ing. Tech., 60 (12), 1059-1061 (1988).

[6] Brunner, G.; Dohrn, R., Programmsystem zur Berechnung von Hochdruckphasengleichwichten-Anwendung auf Stoffe mit Unbekannten Kritischen Daten, Chem. Tech. (Leipzig), 41 (2), 65-68 (1989).

[7] Johnston, K.P.; Peck, D.G.; Kim, S., REVIEWS: Modeling Supercritical Mixtures: How Predictive Is It?, Ind. Eng. Chem. Res., 28, 1115-1125 (1989).

[8] Gangadhara Rao, V.S.; Mukhopadhyay, M., Solid Solubilities in Spuercritical Fluids from Group Contributions, J. Supercrit. Fluids, 3 (2), 66-70 (1990).

[9] Zuiderweg, F.J., Fysische Scheidingsmethoden, deel I: Evenwichten, Scheidingsberekeningen, Fysische Transport Verschijnselen, Handout for Lecture st77, Delft University of Technology, University Press (1980).

[10] Brunner, G., Selectivity of Supercritical Compounds and Entrainers with Respect to Model Substances, Fluid Phase Equilib., 10, 289-298 (1983).

[11] Brunner, G.; Peter, S., Zum Stand der Extraktion mit Komprimierten Gasen, Chem Ing. Tech. 53 (7), 529-542 (1981).

[12] De Swaan Arons, J; Coorens, H.; De Loos, Th.W.; Supercritical Extraction. Prediction of the Capacity and Selectivity of Supercritical Solvents, Delft Progress Report, 12, 1988.

[13] Neau, E.; Alessi, P.; Fermeglia, M.; Kikic, I., Low-Pressure Equilibrium Data for the Prediction of Solubility in Carbon Dioxide, Chem Eng. Sci., 45 (4), 795-808 (1990).

[14] Walas, S.M., Phase Equilibria in Chemical Engineering, Butterwoth Publishers, Boston (1985).

[15] Stahl, E.; Quirin, K.W.; Gerard, D., Verdichtete Gase zur Extraktion und Raffination, Springer Verlag, Berlin (1987).

[16] Treybal, R.E., Liquid Extraction, 2nd ed., McGraw-Hill, New York (1963), in: Chemical Engineering Series.

[17] Weast, R.C., Handbook of Chemistry and Physics, 52nd ed., The Chemical Rubber Co., Cleveland (1971-1972).

[18] Perry, R.H.; Chilton, C.H., Chemical Engineers' Handbook, 5th ed., McGraw-Hill, New York (1973).

[19] Macknick, A.B.; Prausnitz, J.M., *Vapor Pressure of High Molecular-Weight Hydrocarbons*, J. Chem. Eng. Data, 24 (3), 175-178 (1979).

[20] Smith et.al., *Physical Science Data 25: Thermodynamic Data for Pure Compounds, Part B: Halogenated Hydrocarbons and Alcohols*, Elsevier, Amsterdam (1986).

[21] Zou, M.; Yu, Z.R.; Kashulines, P.; Rizvi, S.S.H., *Fluid-Liquid Phase Equilibria of Fatty Acids and Fatty Acid Methyl Esters in Supercritical Carbon Dioxide*, J. Supercrit. Fluids, 3 (1), 23-28 (1990).

[22] Orbey, H.; Vera, J.H., *Correlation for the Third Virial Coefficient Using Tc, pc and ω As Parameters*, J. AIChE., 29 (1), 107-113 (1983).

[23] Tsonopoulos, C., *An Empirical Correlation of Second Virial Coefficients*, J. AIChE., 20 (2), 263-272 (1974).

[24] De Santis, R.; Grande, B., *An Equation for Predicting Third Virial Coefficients of Nonpolar Gases*, J. AIChE., 25 (6), 931-938 (1979).

[25] Brelvi, S.W.; O'Connell, J.P., *Corresponding States Correlations for Liquid Compressibility and Partial Molal Volumes of Gases at Infinite Dilution in Liquids*, J. AIChE., 18 (6), 1239-1243 (1972).

Appendix A: Derivation of Equations (53) through (56)

At page 27, 28 and 29 in this report four formulas were used. The first (53) links any equation of state (EOS) to the fugacity coefficients of every component present in the mixture. (53) can be derived from fundamental thermodynamics: definition of certain quantities and the first and second law of thermodynamics. quation (54) is the solution for equation (53) when the Peng Robinson EOS is used. This concerns rather mathematics than fundamental thermodynamics.

Equation (55) and (56) are solutions for equation (53) when the virial equation of state is used, while the Lewis rule is applied.

This appendix has been built up of three sections, deriving all equations.

A.1. Derivation of Equation (53)

For the fugacity coefficient, ϕ_i, of component i in a mixture containing n components, a relation will be derived that relates this property to any EOS.
The fugacity, f_i, of component i in a mixture containing n components is defined by:

$$R*T*d\{\ln(f_i)\} = v_i*d\{p\} = \frac{\partial V}{\partial n_i}*d\{p\} \qquad (A1)$$

In (A1) v_i is the partial molar volume of component i, while V stands for total volume.

The chemical potential, μ_i, of component i is defined by:

$$\mu_i = \{\partial M/\partial n_i\} \quad [M= G, U, H \text{ or } A] \tag{A2}$$

In (A2) G is the free Gibbs energy, U the internal energy, H the enthalpy and A the free Helmholz energy. The internal energy of a mixture will be considered first. If heat is put into the system the internal energy of the mixture will increase, while the internal energy will decrease if the mixture performs some work. So, the increase of the internal energy of a mixture equals the difference between the heat which is added to the mixture and the work which is performed by the mixture. This consideration is known as the first law of thermodynamics. Written in formula:

$$\Delta U = Q - W \tag{A3}$$

or in differential form:

$$dU = \partial Q - \partial W \tag{A4}$$

The process of adding heat and performing work is now considered reversible, that is when the changes of the properties concerned, will take place in an infinite long time. Consider a tube in which the mixture is present with on top of the mixture in the tube a piston that can move freely. The work performed by the mixture is now defined as the force performed by the mixture multiplied by the distance the piston moved. Since the area of the tube is constant the force will be the area multiplied by the pressure of the mixture. The distance multiplied by the area will be the mixture's volume. So work is defined, remembering that area is constant:

$$\partial W = F{*}ds = p{*}A * d\,(V/A) = p{*}dV \tag{A5}$$

Considering a Carnot cycle and the second law of thermodynamics it can be concluded that entropy, S, is given by the equation:

$$\partial Q = T*dS \qquad (A6)$$

Combining (A4), (A5), and (A6) it is found that

$$dU = T*dS - p*dV \qquad (A7)$$

Enthalpy is defined as

$$H = U + P*V \quad \text{or} \quad dH = dU + p*dV + V*dp \qquad (A8)$$

Substituting (A7) in (A8) it is found that

$$dH = T*dS + V*dp \qquad (A9)$$

The free Gibbs and free Helmholz energy are defined by

$$A = U - T*S \quad \text{or } dA = dU - T*dS - S*dT \qquad (A10)$$

$$G = H - T*S \quad \text{or } dG = dH - T*dS - S*dT \qquad (A11)$$

Substituting (A7) in (A10) it can be seen that

$$dA = - S*dT - p*dV \qquad (A12)$$

In the same way, substitution of (A9) in (A11) leads to:

$$dG = V*dp - S*dT \qquad (A13)$$

Now it can be seen from (A12) and (A13) that $A=A(T,V,n)$ and $G=G(p,T,n)$. Equation (A2) represents partial differentials, so taking all other properties constant. Applying (A2) to both the free Gibbs and Helmholz energy, it is found that:

$$\{\partial A/\partial n_i\}_{T,V,n(j)} = \mu_i \tag{A14}$$

$$\{\partial G/\partial n_i\}_{p,T,n(j)} = \mu_i \tag{A15}$$

At constant temperature and composition (A12) and (A13) become:

$$dA = - p*dV \quad \text{and} \quad dG = V*dp \tag{A16}$$

If (A14) is differentiated towards volume the result will be:

$$d\mu_i = [\frac{\partial}{\partial V} \{ \frac{\partial A}{\partial n_i} \}_{T,V,n(j)}]_{T,n(j)} * dV \tag{A17}$$

If (A15) is differentiated towards pressure the result will be:

$$d\mu_i = [\frac{\partial}{\partial p} \{ \frac{\partial G}{\partial n_i} \}_{p,T,n(j)}]_{T,n(j)} * dp \tag{A18}$$

In (A17) and (A18) the differentials below the quotient sign can be exchanged:

$$d\mu_i = [\frac{\partial}{\partial n_i} \{ \frac{\partial A}{\partial V} \}_{T,n(j)}]_{T,V,n(j)} * dV \tag{A19}$$

If (A15) is differentiated towards pressure the result will be:

$$d\mu_i = [\frac{\partial}{\partial n_i} \{ \frac{\partial G}{\partial p} \}_{T,n(j)}]_{p,T,n(j)} * dp \tag{A20}$$

It follows that equation (A19) equals (A20). From equation (A16) it is found that:

$$\{ \frac{\partial G}{\partial p} \}_{T,n(j)} = V \quad \text{and} \quad \{ \frac{\partial A}{\partial V} \}_{T,n(j)} = - p \tag{A21}$$

The equality of (A19) and (A20), while substituting equation (A21) results in:

$$\left\{ \frac{\partial V}{\partial n_i} \right\}_{p,T,n(j)} * dp = - \left\{ \frac{\partial p}{\partial n_i} \right\}_{T,V,n(j)} * dV \qquad \text{(A22)}$$

This result can be substituted in equation (A1) to give:

$$R*T*d\{\ln(f_i)\} = - \left\{ \frac{\partial p}{\partial n_i} \right\}_{T,V,n(j)} * dV \qquad \text{(A23)}$$

Adding the term R*T*d{ln [V/(n*R*T)] } at both sides of A(23) it follows that:

$$R*T*d\{\ln\frac{fi*V}{n*R*T}\} = R*T*d\{\ln\frac{V}{n*R*T}\} - \left\{ \frac{\partial p}{\partial n_i} \right\}_{T,V,n(j)} * dV \qquad \text{(A24)}$$

Next, the just added term can be rewritten:

$$R*T*d\{\ln\frac{V}{n*R*T}\} = R*T*\{ 1/(V/\{n*R*T\}) \}*dV = \{R*T/V\}*dV \qquad \text{(A25)}$$

Substitution of (A25) in (A24) results in:

$$R*T*d\{\ln\frac{fi*V}{n*R*T}\} = \left[\frac{R*T}{V} - \left\{ \frac{\partial p}{\partial n_i} \right\}_{T,V,n(j)} \right] * dV \qquad \text{(A26)}$$

Equation (A26) can be integrated from V towards infinity. If $V=\infty$ than the mixture behaves like an ideal gas, because the molecules do not interact with each other. In that case the left term of (A26) becomes: $R*T*\ln y_i$, because $p_i = f_i = y_i*p$ (ideal gas behaviour).

The result becomes:

$$R*T*[\ln y_i - \ln\frac{fi*V}{n*R*T}] = \int_V^{\infty} \left[\frac{R*T}{V} - \left\{ \frac{\partial p}{\partial n_i} \right\}_{T,V,n(j)} \right] dV \qquad \text{(A27)}$$

or

$$R*T*[\ \ln(f_i/y_i)\ ] = \int_V^\infty [\ \{\ \frac{\partial p}{\partial n_i}\}_{T,V,n(j)} - \frac{R*T}{V}\ ]dV - R*T*\ln\frac{V}{n*R*T} \qquad (A28)$$

or, because of the fugacity coefficient's definition ($f_i=y_i*\phi_i*p$):

$$R*T*[\ln(\phi_i*p)] = \int_V^\infty [\ \{\ \frac{\partial p}{\partial n_i}\}_{T,V,n(j)} - \frac{R*T}{V}\ ]dV - R*T*\ln\frac{V}{n*R*T} \qquad (A29)$$

Defining the compressibility factor as $Z=p*V/(n*R*T)$ the final equation becomes

$$R*T*[\ln(\phi_i)] = \int_V^\infty [\ \{\ \frac{\partial p}{\partial n_i}\}_{T,V,n(j)} - \frac{R*T}{V}\ ]dV - R*T*\ln Z \qquad (A30)$$

Equation (A30) is the same as equation (53) at page 27 in the report. It is, thus, derived.

A.2 Derivation of Equation (54)

Equation (54) represents the solution of equation (53) when the Peng Robinson EOS with classical mixing rules is used. As can be seen from equation (A30) the partial derivative of pressure towards mole species i has to be calculated. Temperature and volume have to be held constant. Explicitely volume is meant because molar volume depends on composition and in that case molar volume cannot be held constant. Thus, the Peng Robinson EOS has to be written in an expression depending on V rather than molar volume like has been done in the report.

The Peng Robinson EOS in molar volume is repeated here:

$$p = \frac{R*T}{v-b} - \frac{a}{v^2 + 2*b*v - b^2} \qquad (A31)$$

substitution of $v = V/\Sigma n_j$ leads to

$$p = \frac{R*T*\Sigma n_j}{V-b*\Sigma n_j} - \frac{a*(\Sigma n_j)^2}{V^2 + 2*b*V*\Sigma n_j - (b*\Sigma n_j)^2} \qquad (A32)$$

From the classical mixing rules it follows that:

$$b = \Sigma(n_j*b_j)/\Sigma n_j \qquad (A33)$$

and

$$a = \Sigma\Sigma(n_i*n_j*a_{ij})/(\Sigma n_j)^2 \qquad (A34)$$

Substitution of (A33) and (A34) in (A32) leads to the good form of the Peng Robinson EOS that can be differentiated towards mole species i:

$$p = \frac{R*T*\Sigma n_j}{V-\Sigma(n_j*b_j)} - \frac{\Sigma\Sigma(n_i n_j*a_{ij})}{V^2 + 2*V*\Sigma(n_j*b_j) - (\Sigma(n_j*b_j))^2} \qquad (A35)$$

Knowing that

$$\frac{\partial}{\partial n_i} \{ \Sigma\Sigma(n_i*n_j*a_{ij} \} = 2 * \Sigma(n_j*a_{ij}) \qquad (A36)$$

$\partial(A35)/\partial n_j$ becomes:

$$\left\{ \frac{\partial p}{\partial n_i} \right\}_{T,V,n(j)} = \frac{R*T}{V - \Sigma(n_j*b_j)} + \frac{R*T*\Sigma n_j}{(V - \Sigma(n_j*b_j))^2} * b_i +$$

$$\frac{[\ 2*b_i*V - 2*b_i*(\Sigma(n_j*b_j))\ ]}{[\ V^2 + 2*V*\Sigma(n_j*b_j) - (\Sigma(n_j*b_j))^2\ ]^2} * \Sigma\Sigma(n_i*n_j*a_{ij})$$

$$- \frac{2*\Sigma(n_j*a_{ij})}{V^2 + 2*V*\Sigma(n_j*b_j) - (\Sigma(n_j*b_j))^2} \qquad \text{(A37)}$$

Now the differentiation towards n_i has been executed. The total absolute volume in (A37) can again be replaced by the molar volume, v, because in (A30) no further operation has to be done depending on n_i. It is found that:

$$\left\{ \frac{\partial p}{\partial n_i} \right\}_{T,V,n(j)} = \frac{R*T}{n*(v-b)} + \frac{R*T*b_i}{n*(v-b)^2} + \frac{2*b_i*a*n^2*(n*v-n*b)}{[n^2*v^2 + 2*n*v*n*b - (n*b)^2]^2} ,$$

$$- \frac{2*n*\Sigma(y_j*a_{ij})}{n^2*v^2 + 2*n*v*n*b - (n*b)^2} \qquad \text{(A38)}$$

In (A38) y_j symbolizes mole fraction of component j and is defined as n_j/n and n is defined as Σn_j.

As can be seen from (A38) the term 1/n can be set outside brackets. The final equation for the derivative becomes now:

$$\left\{ \frac{\partial p}{\partial n_i} \right\}_{T,V,n(j)} = \frac{1}{n} * \left[\frac{R*T}{v-b} + \frac{R*T*b_i}{(v-b)^2} + \frac{2*b_i*a*(v-b)}{(v^2+2*b*v-b^2)^2} - \frac{2*\Sigma(y_j*a_{ij})}{v^2+2*b*v-b^2} \right]$$

$$\text{(A39)}$$

The next thing to do is to integrate (A39) according to equation (A30). First the following integral will be solved:

$$I = \int_V^\infty \left[\left\{ \frac{\partial p}{\partial n_i} \right\}_{T,V,n(j)} - R*T/V \right] dV \qquad \text{(A40)}$$

In (A40) the new symbol I symbolizes "Integral". It can be seen that in (A40) the symbol for absolute total volume appears (V). This is also the case in equation (A30). Before substituting (A39) into (A40), (A40) first has to be rewritten in the molar volume form:

$$I = \int_V^\infty \left[\left\{ \frac{\partial p}{\partial n_i} \right\}_{T,V,n(j)} - R*T/(v*n) \right] d(n*v) \qquad \text{(A41)}$$

or

$$I = \int_V^\infty \left[n*\left\{ \frac{\partial p}{\partial n_i} \right\}_{T,V,n(j)} - R*T/v \right] dv \qquad \text{(A42)}$$

Substitution of (A39) into (A42) results in:

$$I = \int_V^\infty \left[\underbrace{\frac{R*T}{v-b}}_{A} + \underbrace{\frac{R*T*b_i}{(v-b)^2}}_{B} + \underbrace{\frac{2*b_i*a*(v-b)}{\{v^2+2*b*v-b^2\}^2}}_{C} - \underbrace{\frac{2*\Sigma(y_j*a_{ij})}{v^2+2*b*v-b^2}}_{D} - \underbrace{\frac{R*T}{v}}_{E} \right] dv \qquad \text{(A43)}$$

(A43) is the integral to be solved. It has been split up (as can be seen) into five parts, A, B, C, D, and E. First the primitive functions (function after integration without filling in the limits) of terms A, B and E will be solved:

Primitive of term	is
A	$R*T*\ln(v-b)$
E	$-\ R*T*\ln(v)$
A+E	$R*T*\ln\frac{v-b}{v}$
B	$-\ R*T*b_i/\ (v-b)$

The primitives of terms C and D are more difficult to determine. Therefore a mathematical intermezzo is given in section A.2.1

A.2.1 Mathematical Operation: Getting primitives of terms C and D

In order to get the primitives of terms C and D, standard integrals can be used. The following integrals have been listed in [17]:

$X = c*x^2 + b*x + a$ and $q = 4*a*c - b^2$ (and $q<0$)

$$\int \frac{dx}{X} = \frac{1}{\sqrt{(-q)}} * \ln \frac{2*c*x + b - \sqrt{(-q)}}{2*c*x + b + \sqrt{(-q)}} \qquad (A44)$$

$$\int \frac{dx}{X^2} = \frac{2*c*x + b}{q*X} + \frac{2*c}{q} * \int \frac{dx}{X} \qquad (A45)$$

$$\int \frac{x*dx}{X^2} = - \frac{b*x + 2*a}{q*X} - \frac{b}{q} * \int \frac{dx}{X} \qquad (A46)$$

Equations ((A44) - (A46)) can be used in order to get the primitives of terms C and D. They integrals ((A44) - (A46)) will be proofed in this section first. Starting with (A44), differentiating the right part of this equation towards x must result in 1/X. If this is so, (A44) has been proofed. Differentiating results in:

$$\frac{1}{\sqrt{(-q)}} * \left[\frac{2cx+b+\sqrt{(-q)}}{2cx+b-\sqrt{(-q)}} * \frac{2c*(2cx+b+\sqrt{(-q)} - 2c*(2cx+b-\sqrt{(-q)})}{(2cx+b+\sqrt{(-q)})^2} \right]$$

equals

$$\frac{1}{\sqrt{(-q)}} * \frac{4c*\sqrt{(-q)}}{(2cx+b-\sqrt{(-q)})*(2cx+b+\sqrt{(-q)})}$$

equals

$$\frac{4c}{4c*(cx^2+bx)+b^2+q} = \frac{4c}{4c*(cx^2+bx)+b^2+4ac-b^2} = \frac{1}{cx^2+bx+a} = \frac{1}{X}$$

So, (A44) has been proofed. Next (A45) will be proofed. Differentiating its right part must result in $1/X^2$. Differentiating gives:

$$\frac{X*2c - (2cx+b)^2}{q*X^2} + \frac{2c}{q*X} \text{ equals}$$

$$\frac{2c^2x^2+2bcx+2ac-4c^2x^2-4bcx-b^2}{q*X^2} + \frac{2c*(cx^2+bx+a)}{q*X^2} = \frac{4ac-b^2}{q*X^2} = \frac{1}{X^2}$$

Thus, (A45) has been proofed. In the same way (A46) will be proofed. Differentiating the right part must result is x/X^2:

$$-\frac{X*b-(bx+2a)*(2cx+b)}{q*X^2} - \frac{b}{q*X} \text{ equals}$$

$$-\frac{bcx^2+b^2x+ab-2bcx^2+b^2x-4acx-2ab}{q*X^2} - \frac{b*(cx^2+bx+a)}{q*X^2} = \frac{(4ac-b^2)*x}{q*X^2} = \frac{x}{X^2}$$

Now equations ((A44) - (A46)) have been proofed and can be used in determing the primitive function of terms C and D of equation (A43).

A.2 Derivation of Equation (54) (Continued)

With help of equation (A44) the primitive function of D can be found. In section A.2.1 new variables have been introduced. Before applying (A44) these variables must be linked to term D:

variable in (A44)	corresponding relation in term D
x	v
a	$-b^2$
b	$2*b$
c	1
X	$v^2 + 2*b*v - b^2$
q	$-8*b^2$

Afterwards the primitive must be multiplied by the constant $-2*\Sigma(y_j*a_{ij})$. Substituting these values in (A44) results in

$$\{(A44)\} = \frac{1}{b*\sqrt{8}} * \ln\frac{2*v + 2*b - b*\sqrt{8}}{2*v + 2*b - b*\sqrt{8}} \qquad (A47)$$

Knowing that $\sqrt{8}$ equals $2*\sqrt{2}$ and multiplying the integral with the constant results finally in the primitive for term D:

$$\mathrm{Prim}(D) = -2*\Sigma(y_j*a_{ij}) * \frac{1}{2*b*\sqrt{2}} * \ln\frac{v + b*(1+\sqrt{2})}{v + b*(1-\sqrt{2})} \qquad (A48)$$

In order to find the primitive of term C, the variables in term C also must be linked to the variables in the integral. This linking is exactly the same as the linking done for term D. The constant, which the primitive must be multiplied with afterwards, is in case of term C: $2*a*b_i$. Term C must be split:

$$\frac{2*b_i*a*(v-b)}{\{v^2+2*b*v-b^2\}^2} = 2*a*b_i*\{\frac{v}{[v2+2*b*v-b^2]^2} - \frac{b}{[v^2+2*b*v-b^2]^2}\} \qquad (A49)$$

The first term of (A49) can be solved with help of (A46); the second with help of (A45).

$$\{A(46)\} = -\frac{2*b*v-2*b^2}{8*b^2*(v^2+2*b*v-b^2)} - \frac{2*b}{8*b^2}*\{(A44)\} \qquad (A50)$$

$$\{(A45)\} = b * [\frac{2*v+2*b}{8*b^2*(v^2+2*b*v-b^2)} + \frac{2}{8*b^2}*\{(A44)\}] \qquad (A51)$$

According to (A49), (A50) and (A51) have to be substracted and multiplied by the constant $2*a*b_i$:

$$\mathrm{Prim}(C) = 2*a*b_i * [\frac{v-b}{4*b*(v^2+2*b*v-b^2)} + \frac{1}{4*b} * \{(A44)\}$$

$$+ \frac{v+b}{4*b*(v^2+2*b*v-b^2)} + \frac{1}{4*b} * \{(A44)\}] \qquad (A52)$$

or

$$\mathrm{Prim}(C) = 2*a*b_i * \left[\frac{v}{2*b*(v^2+2*b*v-b^2)} + \frac{1}{2*b} * \frac{1}{b*\sqrt{8}} * \ln\frac{v+b*(1-\sqrt{2})}{v+b*(1+\sqrt{2})}\right] \tag{A53}$$

or

$$\mathrm{Prim}(C) = a*\frac{b_i}{b} * \left[\frac{v}{v^2+2*b*v-b^2} + \frac{1}{2*b*\sqrt{2}} * \ln\frac{v+b*(1-\sqrt{2})}{v+b*(1+\sqrt{2})}\right] \tag{A54}$$

Now all primitives of all terms in (A43) have been determined and the integral I (equation (A43)) without filling in the limits becomes (notation: I'):

$$I' = R*T*\ln\frac{v-b}{v} - R*T*\frac{b_i}{v-b} - 2*\Sigma(y_j*a_{ij}) * \frac{1}{2*b*\sqrt{2}} * \ln\frac{v+b*(1+\sqrt{2})}{v+b*(1-\sqrt{2})} +$$

$$+ a*\frac{b_i}{b} * [\frac{v}{v^2+2*b*v-b^2} + \frac{1}{2*b*\sqrt{2}} * \ln\frac{v+b*(1-\sqrt{2})}{v+b*(1+\sqrt{2})} \tag{A55}$$

or

$$I' = R*T*\ln\frac{v-b}{v} - R*T*\frac{b_i}{v-b} + a*\frac{b_i}{b} * \frac{v}{v^2+2*b*v-b^2} +$$

$$\frac{a}{2*b*\sqrt{2}} * \left[\frac{b_i}{b} - \frac{2*\Sigma(y_j*a_{ij})}{a}\right] * \ln\frac{v+b*(1-\sqrt{2})}{v+b*(1+\sqrt{2})} \tag{A56}$$

Let us now fill in the limits. If v becomes very large (∞) then all terms in (A56) become zero. Thus, the solution of integral I (A43) becomes by filling in the limits in I' (A56):

$$I = R*T*\ln\frac{v}{v-b} + R*T*\frac{b_i}{v-b} - a*\frac{b_i}{b} * \frac{v}{v^2+2*b*v-b^2} +$$

$$\frac{a}{2*b*\sqrt{2}} * \left[\frac{b_i}{b} - \frac{2*\Sigma(y_j*a_{ij})}{a}\right] * \ln\frac{v+b*(1+\sqrt{2})}{v+b*(1-\sqrt{2})} \tag{A57}$$

The expression for the fugacity coefficient will be repeated here (equation (A30)):

$$R*T*[\ln(\phi_i)] = \int_V^{\infty} [\{ \frac{\partial p}{\partial n_i} \}_{T,V,n(j)} - \frac{R*T}{V}]dV - R*T*\ln Z \qquad (A30)$$

or

$$R*T*[\ln(\phi_i)] = I - R*T*\ln Z \qquad (A58)$$

where I is given by equation (A57).

Now the following term in (A57) is considered:

$$R*T*\frac{b_i}{v-b} - a*\frac{b_i}{b} * \frac{v}{v^2+2*b*v-b^2} = R*T*\frac{b_i}{v-b} - v*\frac{b_i}{b} * \frac{a}{v^2+2*b*v-b^2} \qquad (A59)$$

The term

$\frac{a}{v^2+2*b*v-b^2}$ equals $\frac{R*T}{v-b} - p$.

This can be seen with help of the Peng Robinson EOS, equation (A31). For the pressure p can be written:

$p = R*T*Z/v$ according to definition of the compressibility factor Z. Substituting these equations in (A59):

$$R*T*\frac{b_i}{v-b} - \frac{b_i}{b} * v * [\frac{R*T}{v-b} - \frac{R*T*Z}{v}] =$$

$$R*T*b_i*[\frac{1}{v-b} - \frac{v}{b} *\{\frac{1}{v-b} - \frac{Z}{v}\}] =$$

$$R*T*b_i*[\frac{1}{v-b} - \frac{v}{b*(v-b)} + \frac{Z}{b}] =$$

$$R*T*b_i*[\frac{b-v}{b*(v-b)} + \frac{Z}{b}] =$$

$$R*T*b_i*[\frac{Z}{b} - \frac{1}{b}] = R*T*\frac{b_i}{b} * (Z-1) \tag{A60}$$

The final expression for the fugacity coefficient will be found by substituting (A60) in (A57) and substituting this result in (A59):

$$R*T*[\ln(\phi_i)] = R*T*\ln\frac{v}{v-b} + R*T*\frac{b_i}{b} * (Z-1) - R*T*\ln Z +$$

$$\frac{a}{2*b*\sqrt{2}} * [\frac{b_i}{b} - \frac{2*\Sigma(y_j*a_{ij})}{a}] * \ln \frac{v+b*(1+\sqrt{2})}{v+b*(1-\sqrt{2})} \tag{A61}$$

In the report the new variables A^* and B^* were already introduced.

Substitution of

$a = A^**(R*T)^2/p$, $b = B^**R*T/p$, $b_i = B_i^**R*T/p$ and $v = R*T*Z/p$

will result in the following expression for the fugacity coefficient:

$$\ln(\phi_i) = \frac{B_i^*}{B^*} * (Z-1) - \ln(Z-B^*) +$$

$$\frac{A^*}{2*B^*\sqrt{2}} * [\frac{B_i^*}{B^*} - \frac{2*\Sigma(y_j*a_{ij})}{a}] * \ln \frac{Z+b^**(1+\sqrt{2})}{Z+B^**(1-\sqrt{2})} \tag{A62}$$

According to the classical mixing rules :

$$a_{ij} = \{ \sqrt{(a_i * a_j)} \} * (1-k_{ij}) \qquad \text{(A63)}$$

Equation (A62) combined with the mixing rule (A63) equals equation (54) in the report.

A.3 Derivation of Equation (55) and (56)

At page 28 and 29 in the report, equations (55) and (56) are mentioned. These are results of applying equation (53) and Raoult's law. First an enhancement factor is defined:

$$\text{Enh} = c_{i,SCF} \; / \; c_{i,SCF}^{ideal} \qquad \text{(A64)}$$

The enhancement factor is the factor with which the ideal concentration of the considered heavy compound in the supercritical fluidum has to be multiplied in order to yield the real concentration.

The ideal concentration is calculated from Raoult's law, extended for high pressures by the Poynting factor:

$$y_i^{ideal} * P = x_i^{ideal} * P_i^{sat} * POY_i \qquad \text{(A65)}$$

The ideal concentration follows by multiplying the mole fraction in the supercritical phase by the density of this phase. Because solubilities are very small (< 1 mass percent), the density of the supercritical phase is almost the same as the density of the supercritical fluidum as if it was pure (Lewis rule):

$$c_i^{ideal} = y_i^{ideal} * \rho_{SCF}^{ideal} \qquad \text{(A66)}$$

Combining (A65) and (A66) yields:

$$c_i^{ideal} = x_i^{ideal} * P_i^{sat} * POY_i * \rho_{SCF}^{ideal} / p \qquad (A67)$$

Because the ideal gas law is valid for this ideal concentration calculation, (A67) can be modified:

$$c_i^{ideal} = x_i^{ideal} * P_i^{sat} * POY_i / (R*T) \qquad (A68)$$

Like equation (A66) the real concentration of the heavy compound in the supercritical phase equals:

$$c_i = y_i * \rho_{SCF} \qquad (A69)$$

For the density of the supercritical fluidum considered to be an ideal gas follows:

$$\rho_{SCF}^{ideal} = p / (R * T) \qquad (A70)$$

The real density is found in the same manner by introducing the compressibility factor of the fluidum ($Z = p*v/(R*T)$):

$$\rho_{SCF} = p / (R * T * Z_{SCF}) \qquad (A71)$$

For the real situation Raoult's law has to be modified by means of fugacity and activity coefficients:

$$\phi_i * y_i * P = \gamma_i * x * P_i^{sat} * POY_i \qquad (A72)$$

Combining (A65) and (A72) yields:

$$y_i / y_i^{ideal} = (\gamma_i * x_i / x_i^{ideal}) * (1 / \phi_i) \qquad (A73)$$

Substitution of (A71) in (A69) and (A70) in (A66) results in

$$c_i^{ideal} = y_i^{ideal} * (p /(R * T)) \qquad (A74)$$

and

$$c_i = y_i * (p / (R * T * Z_{SCF})) \qquad (A75)$$

Devision of (A75) by (A74) yields:

$$c_i / c_i^{ideal} = (y_i / y_i^{ideal}) * (1 / Z_{SCF}) \qquad (A77)$$

Further subsitution of (A73) results in:

$$c_i / c_i^{ideal} = (1 / [\phi_i * Z_{SCF}]) * (\gamma_i * x_i / x_i^{ideal}) \qquad (A78)$$

This equals the enhancement factor. The result is a slight different than De Swaan Arons reported [12], because his derivation was valid for solubility of solid heavy compounds, thus no supercritical fluidum can be dissolved. Let us first consider the enhancement due to the vapour phase's non-ideality and the liquid phase's non-ideality is in first instance neglected. Later on the liquid phase's non-ideality will be incorporated. Then the similarity with De Swaan Arons's derivation becomes clear. Then the result becomes:

$$c_i = c_i^{ideal} * Enh_{vap} * \gamma_i * x_i / x_i^{ideal} \qquad (A79)$$

Substitution of (A68) in (A79) yields:

$$c_i = \gamma_i * x_i * P_i^{sat} * POY_i * Enh_{vap} / (R * T) \qquad (A80)$$

With help of (A69) it is finally found that

$$y_i / x_i = [\ \gamma_i * P_i^{sat} * POY_i / (R * T * \rho_{SCF})] * Enh_{vap} \qquad (A81)$$

which is equal to equation (55) in the report.

Let us now consider the vapour phase's contribution to the enhancement factor. It was already derived that

$$Enh_{vap} = 1 / (\phi_i * Z_{SCF}) \qquad (A82)$$

At this point the virial equation of state, which has been chosen, becomes important. In the report it had already been mentioned that the fugacity coefficient, ϕ_i, is denpendent of the type of equation of state that has been chosen. The virial equation of state is repeated here, truncated after the third coefficient:

$$p = (R * T / v) * (1 + B / v + C / v^2) \qquad (A83)$$

In (A30) it can be seen that (A83) should be written in terms of mole species i, knowing that $n = \Sigma n_j$. The equations for the mixture virial coefficients have already been given in the report:

$$B_m = \sum_{i}^{n}\sum_{j}^{n} y_i * y_j * B_{ij} = (1 / n^2) * \sum_{i}^{n}\sum_{j}^{n} n_i * n_j * B_{ij} \qquad (A84)$$

$$C_m = \sum_{i}^{n}\sum_{j}^{n}\sum_{k}^{n} y_i * y_j * y_k * C_{ijk} = (1 / n^3) * \sum_{i}^{n}\sum_{j}^{n}\sum_{k}^{n} n_i * n_j * n_k * C_{ijk} \qquad (A85)$$

The molar volume becomes total volume devided by n. (A83) now becomes:

$$p = (R*T*\Sigma n_j / V) * (1 + (1/(V*\Sigma n_j) * \sum_{i}^{n}\sum_{j}^{n} n_i * n_j * B_{ij} +$$

$$(1/(V^2 * \Sigma n_j) * \sum_{i}^{n}\sum_{j}^{n}\sum_{k}^{n} n_i * n_j * n_k * C_{ijk}) \qquad (A86)$$

Now the derivative $\partial p/\partial n_i$ can be obtained from (A86). (A84) and (A85) will first be written in a form where mole species i is taken outside the summation sign:

$$B_m = (n_i^2 * B_{ii} + 2 * n_i * \sum_{j\neq i} n_j * B_{ij}) / (V*\Sigma n_j) \qquad \text{(A87)}$$

$$\begin{aligned} C_m = (n_i^3 * C_{iii} &+ 3 * n_i^2 * \sum_{j\neq i} n_j * C_{iij} + \\ &3 * n_i * \sum_{j\neq i} \sum_{k\neq i} n_j * n_k * C_{ijk}) / (V^2 * \Sigma n_j) \qquad \text{(A88)} \end{aligned}$$

Differentiation pressure towards mole species i now yields:

$$\begin{aligned} \partial p/\partial n_i = &(R*T/V) * (1 + (1/(V*\Sigma n_j) * \sum_{i}^{n} \sum_{j}^{n} n_i * n_j * B_{ij} + \\ &(1/(V^2 * \Sigma n_j) * \sum_{i}^{n} \sum_{j}^{n} \sum_{k}^{n} n_i * n_j * n_k * C_{ijk}) + \\ &(R*T*\Sigma n_j/V) * \\ &\left\{ \frac{2*\sum_{j}^{n} n_j * B_{ij}}{V * \Sigma n_j} - \frac{B_m}{\Sigma n_j} - \frac{C_m}{\Sigma n_j} + \right. \\ &\left. \frac{3*n_i^2 * C_{iii} + 6*n_i * \sum_{j\neq k} n_j * C_{iij} + 3* \sum_{j\neq i} \sum_{k\neq i} n_j * n_k * C_{ijk}}{V^2 * \Sigma n_j} \right\} \qquad \text{(A89)} \end{aligned}$$

Rearrangement results in:

$$\begin{aligned} \partial p/\partial n_i = &(R*T/V) + (R*T/V) * \left[\frac{2*\sum_{j}^{n} n_j * B_{ij}}{V} + \right. \\ &\left. \frac{3*n_i^2 * C_{iii} + 6*n_i * \sum_{j\neq k} n_j * C_{iij} + 3* \sum_{j\neq i} \sum_{k\neq i} n_j * n_k * C_{ijk}}{V^2} \right] \qquad \text{(A90)} \end{aligned}$$

Equation (A90) can be rewritten in terms of mole fracions, y:

$$\partial p/\partial n_i = (R*T/V) + (R*T/V) * \left[\frac{(\Sigma n_j)*2*\sum_j^n y_j*B_{ij}}{V} + \frac{(\Sigma n_j)^2*3*y_i^2*C_{iii}+6*y_i*\sum_{j\neq k} y_j*C_{iij}+3*\sum_{j\neq i}\sum_{k\neq i} y_j*y_k*C_{ijk}}{V^2} \right] \quad (A91)$$

The term

$$3*y_i^2*C_{iii}+6*y_i*\sum_{j\neq k} y_j*C_{iij}+3*\sum_{j\neq i}\sum_{k\neq i} y_j*y_k*C_{ijk}$$

equals

$$3 * \Sigma\Sigma\, y_j y_k * C_{ijk}$$

so the final result of the derivative $\partial p/\partial n_i$ becomes:

$$\partial p/\partial n_i = (R*T/V) + (R*T/V) * \left[\frac{(\Sigma n_j)*2*\sum_j^n y_j*B_{ij}}{V} + \frac{3*\sum_j\sum_k y_j*y_k*C_{ijk}}{V^2} \right] \quad (A92)$$

The derivative (A92) must now be substituted in equation (A30). It can be seen that the integral term of (A30) becomes:

$$I = \int_{\infty}^{V} (R*T/V) * \left[\frac{(\Sigma n_j)*2*\sum_j^n y_j*B_{ij}}{V} + \frac{(\Sigma n_j)^2*3*\sum_j\sum_k y_j*y_k*C_{ijk}}{V^2} \right] dV \quad (A93)$$

The primitive of this function is rather simple:

$$\text{Prim} = - (R*T/V) * \left((\Sigma n_j)*2*\sum_j^n y_j*B_{ij} + \right.$$

$$\left. (\Sigma n_j)^2*3*\sum_{jk}\sum y_j*y_k*C_{ijk} \;/\; (2*V) \right) \qquad (A94)$$

Filling in the borders, V and ∞, and substituting the integral in (A30), while replacing total volume by molar volume, results finally in the expressing for the fugacity coefficient:

$$\ln(\phi_i) = 2*\Sigma y_i*B_{ij}/v + 1.5*\sum_{jk}\sum y_j*y_k*C_{ijk}/v^2 - \ln(Z) \qquad (A95)$$

Species i is the heavy compound. Since its mole fraction in the supercritical phase is very small (< 1 %), the molar volume of this phase can be set equal to the molar volume of the pure supercritical fluidum. For the binary system heavy compound-SCF, this assumption leads to (SCF=1 and heavy compound=2):

$$\ln(\phi_2) = 2 * B_{12} / v_1 + 1.5 * C_{122} / v_1^2 - \ln(Z) \qquad (A96)$$

Using equation (A82) and known that $\rho_{SCF} = \rho_1 = 1/v_1$, the result is:

$$Enh_{vap} = \exp\left(- 2*B_{12}*\rho_1 - 1.5*C_{112}*\rho_1^2 \right) \qquad (A97)$$

This last equation is the same as equation (57) and it is, thus, derived.

Appendix B: Estimating Binary Interaction Parameters: Peng Robinson Equation of State

In this Appendix a method will be presented that can be used in estimating binary interaction parameters. It is a sort of group contribution method in which interaction between groups of molecules are calculated from existing data of random compounds. The values which are found for the groups are used to estimate the interaction of the total compound with another molecule.

This can be expressed by the following relationship:

$$(1-k_{ij}) = \sum_{p}^{m} (n_p * K_p) \;/\; \sum_{p}^{m} (n_p) \qquad \text{(B1)}$$

In (B1) is m the number of different interactions that occur, n is the number of times that interaction p occurs. K_p is the group contribution of the occuring interaction between two groups. k_{ij} is the binary interaction parameter that is used in the mixing rules. Because it indirectly reflects interaction, it must be rewritten in $1-k_{ij}$. k_{ij} is a measure for the repulsion that occurs between two molecules, so $1-k_{ij}$ is a measure for the occuring interaction.

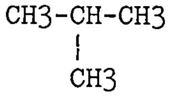
Let us apply this method for the system n-octadecane (C18), 1-hexadecanol (C16OH) and carbon dioxide (CO2) as supercritical fluidum.

It is desired to know the binary interation parameters of the interaction between C16OH-CO2, C18-CO2 and C16OH-C18.

Reference substances in order to calculate the interactions were found in the DECHEMA Data Series. First the binary interaction parameters of the systems C16OH-CO2 and C18-CO2 will be calculated. Then, C16OH-C18 will be considered.

B.1 The systems C16OH-CO2 and C18-CO2

The reference substances that are going to be used are: n-butane, carbon dioxide, n-butanol and i-butane. The following interactions were found:

			k_{ij}	$1-k_{ij}$
CO2	-	CH3-CH2-CH2-CH3	0.1333	0.8667
CO2	-	CH3-CH2-CH2-CH2OH	0.0470	0.9530
CO2	-	 $\underset{\displaystyle \mathrm{CH3}}{\mathrm{CH3\text{-}CH\text{-}CH3}}$	0.1200	0.8800

Interaction are assumed to be built up by the following groups:

CO2 - CH3 (K1)

CO2 - CH2 (K2)

CO2 - CH2OH (K3)

CO2 - CH (K4)

Carbon dioxide will show most interaction with (K3) because of its chemical affinity. This is descending in the row: (K1) > (K2) > (K4). Because interaction (K3) is relatively very large, the difference between the interactions (K2) and (K4) will be relatively small. In that case (K4)=(K2).

Filling in (B1) results in:

$$0.8667 = (2*K1 + 2*K2)/4$$

$$0.9530 = (K1 + 2*K2 + K3)/4$$

$$0.8800 = (3*K1 + K2)/4$$

These are three equations with three unknown parameters. Solving this set results in:

K1 = 0.8932 K2 = 0.8400 K3 = 1.2388

For the interaction C16OH-CO2 it can be found that:

$$(1-k_{ij}) = (\ K1 + 14*K2 + K3\ )/16 = 0.8683 \text{ ---> } k_{ij} = 0.1318$$

For the interaction C18-CO2 it can be found that:

$$(1-k_{ij}) = (2*K1 + 16*K2\ )/18 = 0.8459 \text{ ---> } k_{ij} = 0.1541$$

B.2 The system C16OH-C18

In the same way as described in section B.1 the binary interaction parameters for the system C18-C16OH can be estimated. The chosen reference substances are: n-propanol, n-hexaan, n-propaan, n-pentanol and n-heptaan. The interactions that will be focussed are:

			k_{ij}	$1-k_{ij}$
CH3-CH2-CH2OH	-	CH3-$(CH2)_4$-CH3	0.0844	0.9156
CH3-CH2-CH3	-	CH3-$(CH2)_4$-CH3	0.0007	0.9993
CH3-$(CH2)_3$-CH2OH	-	CH3-$(CH2)_5$-CH3	0.0693	0.9307

Because of small differences the interactions between CH3-CH3, CH2-CH3 and CH2-CH2 are assumed to be equal. With this assumption the following interaction are found to occur:

CH2 - CH2OH	(K1)
CH2 - CH2	(K2)
CH3 - CH2OH	(K3)

With help of (B1) it can be found that

$$0.9156 = (4*K1 + 12*K2 + 2*K3)/18$$

$$0.9993 = (\qquad 18*K2 \qquad)/18$$

$$0.9307 + (5*K1 + 28*K2 + 5*K3)/35$$

From this set the solution can be found:

$K1 = 0.1049 \quad K2 = 0.9993 \quad K3 = 2.0348$

In order to estimate the binary interaction parameter of the system C16OH-C18 it follows with help of (B1):

$$1-k_{ij} = (16*K1 + 270*K2 + 2*K3)/288 = 0.9568 \text{ ---> } k_{ij} = 0.0432$$

B.3 Summary

When the compound are indexed:

C16OH = 1 C18=2 CO2=3

then it was found that

$k_{12} = 0.0432 \quad k_{13} = 0.1318 \quad k_{23} = 0.1541$

The accuracy of these values is hard to estimate. Binary interaction parameters are normally calculated by fitting the chosen equation of state (for example the Peng Robinson EOS) on available data. In literature the following values were found:

Neau (1990) : $k_{23} = 0.161$ Walas* : $k_{HC-CO2} = 0.15$

As can be seen the found values from the presented "group contribution" method are in fair agreement with reported values.

The method has been presented because there is a theoretical fundation for the physical meaning of binary interaction parameters. Normally, however, they are used mathematical quantity in order to get experimental data described in the best possible way. Physically the quantity can be understood, so maybe it could be worth while to develop a complete group contribution method with theoretical foundation for some correction. In this review estimations were made to set some interactions equal.

S.H. Walas: In his text book "Phase Equilibria in Chemical Engineering" Walas recommends the value 0.15 for interactions between hydro carbons (HC) and carbon dioxide.