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Equations of state for complex fluids*

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INTRODUCTION

Compositions of coexisting fluids at elevated pressure-temperature conditions can be calculated by applying thermodynamics as in any other chemical equilibrium. This calculation requires the evaluation of the thermodynamic properties of the phase components i at the respective pressure P , temperature T , and the individual abundances x_i , i.e. composition. In comparison with solids, fluids normally have distinct PVT -behaviors. Furthermore, because of their disordered state and the relatively weak bonding between molecules, fluid species mix much more easily than solid-phase components. The evaluation of the thermodynamic properties of fluids requires, therefore, special treatment and procedures that differ significantly from those used for solids. For fluids, this treatment includes a distinct and different standard state than for solids and a special description of the volume V as a function of P , T (or P as a function of V and T) and x_i , i.e. an equation of state (EOS).

PRINCIPLES

For geological systems, which are usually defined by the variables P and T , the Gibbs free energy G is the function of choice to describe equilibria. At constant P and T the chemical equilibrium condition is defined by (the Table 1 lists the symbols used):

$$dG = 0 \quad (1)$$

The partial derivative of G with respect to P is the volume V

$$\left(\frac{\partial G}{\partial P} \right)_{T, n_i} = V \quad (2)$$

Therefore, the pressure-dependence of G is obtained by integration of Equation (2) with boundaries from the reference pressure P_r , i.e. ambient pressure of 0.1 MPa, to the required P

$$G_{(P,T)} = G_{(P_r,T)} + \int_{P_r}^P V dP \quad (3)$$

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Table 1. Notation and symbols

EOS	equation of state
<i>sub- and superscripts</i>	
o	pure phase
o^*	hypothetical standard state of an ideal gas
m	mixture
r	reference conditions ($P_r = 0.1$ MPa, $T_r = 298.15$ K)
c	critical property
i	of phase component i
<i>thermodynamic variables and properties</i>	
P	pressure
T	temperature
V, v	volume, molar volume
ρ	molar density
N_A	Avogadro's number
A, a	Helmholtz free energy, molar Helmholtz free energy
G, g	Gibbs free energy, molar Gibbs free energy
H, h	enthalpy, molar enthalpy
S, s	entropy, molar entropy
U, u	internal energy, molar internal energy
R	gas constant
a	activity
f	fugacity
x	mole fraction
n	number of moles
n_T	total number of moles
z	compressibility factor
ϕ	fugacity coefficient
μ_i	chemical potential of phase component i
k, δ	binary interaction parameter
<i>EOS specific properties</i>	
Γ	intermolecular potential
α	molecular polarizability
ϵ, σ	parameters of Lennard-Jones potential
μ	dipole moment
r	molecular distance
a, b	parameters of the van der Waals equation
B, C, D	parameters of the virial equation
y	hard-sphere parameter

For the practical treatment of mixed phases, G has to be replaced by its partial derivative with respect to composition, the chemical potential μ_i of the phase component i^l

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P, T, n_{j \neq i}} \quad (4)$$

For solids using the standard state of a pure phase component at reference conditions P_r and T_r , (i.e. 0.1 MPa, 298 K) integration over P leads to,

$$\mu_{i(P,T)} = h_{i(P_r,T)}^o - Ts_{i(P_r,T)}^o + \int_{P_r}^P v_i^o dP + RT \ln a_i \quad (5)$$

where h_i^o and s_i^o are the molar enthalpy and entropy at P_r and T , v_i^o the molar volume as a function of P at T of the pure phase component i , and a_i is its activity, which also incorporates in this case any volume effects of mixing.

However, for fluids the standard state is defined differently, and Equation (5) is not used in this form. The principal thermodynamic equations are rearranged in such a way that, at the standard state, the properties of a pure fluid are taken as if this fluid would behave like an ideal gas. For fluids, the standard state is, therefore, that of a *hypothetical ideal gas* at P_r at any required temperature T . The use of this standard state leads to the following expression,

$$\mu_{i(P,T)} = h_{i(P_r,T)}^{o*} - Ts_{i(P_r,T)}^{o*} + \int_0^P \left(\left(\frac{\partial V}{\partial n_i} \right)_{P,T,n_{j \neq i}} - \frac{RT}{P} \right) dP + RT \ln \frac{P}{P_r} + RT \ln x_i \quad (6)$$

in which the asterisk denotes the *hypothetical ideal gas* standard state properties. Details of the derivation of Equation (6), and Equation (11) in the following, can be found for example in Beattie (1955) or in Appendix A.

The integral term in Equation (6) provides the definition of the fugacity coefficient ϕ_i^m at P and T^2

$$RT \ln \phi_{i(P,T)}^m = \int_0^P \left(\left(\frac{\partial V}{\partial n_i} \right)_{P,T,n_{j \neq i}} - \frac{RT}{P} \right) dP \quad (7)$$

Thus Equation (6) can be written as

$$\mu_{i(P,T)} = h_{i(P_r,T)}^{o*} - Ts_{i(P_r,T)}^{o*} + RT \ln \frac{x_i \phi_{i(P,T)}^m P}{P_r} \quad (8)$$

and with definition of the fugacity f_i^m

¹The term *phase component* is used as a synonym for a endmember of a solution, i.e. for fluids specific species or molecules, whereas the term *component* is used in the classic thermodynamical sense.

² The lower integration boundary is strictly 0 MPa and not just some low pressure, so the fluid will behave like an ideal gas and that $f=p$ as often stated (e.g. Beattie 1955; Ferry and Baumgartner 1987; Anderson and Crerar 1993; Nordstrom and Munoz 1994; Anderson 2005). For the straightforward derivation, see Appendix A.

$$f_{i(P,T)}^m = x_i \phi_{i(P,T)}^m P \quad (9)$$

Equation (9) becomes³:

$$\mu_{i(P,T)} = h_{i(P_r,T)}^{o*} - Ts_{i(P_r,T)}^{o*} + RT \ln \frac{f_{i(P,T)}^m}{P_r} \quad (10)$$

The difference between the thermodynamic properties of a real fluid and an ideal gas is then calculated by evaluating its fugacity. It must be emphasized that a real fluid has always a fugacity coefficient not equal to 1 ($\ln \phi_i^m \neq 0$), also at P_r , but only at zero pressure and infinite volume.

The choice of the *hypothetical ideal gas* standard state, which is by no means an approximation but mathematically exact, has distinct advantages over the conventional standard state usually used for solids. First, the thermodynamic properties at standard conditions are those of an ideal gas, e.g., its heat capacity is that of an ideal gas with isolated atoms or molecules without any intermolecular interactions, which may be calculated for example by *ab initio* calculations and *molecular* simulations. Second, the evaluation of ϕ_i^m includes all excess mixing properties.

The calculation of ϕ_i^m using Equation (7) requires an EOS expression explicit in V , i.e. a function of P and T . As it will be shown below most EOS are explicit in P instead, i.e. a function of V and T , which often can not be transformed to V as a function of P and T . In that case, the following equation can be used instead (Appendix A):

$$\mu_{i(P,T)} = h_{i(P_r,T)}^{o*} - Ts_{i(P_r,T)}^{o*} + \int_V^\infty \left(\left(\frac{\partial P}{\partial n_i} \right)_{V,T,n_{i \neq j}} - \frac{RT}{V} \right) dV - RT \ln \frac{P_v}{RT} + RT \ln \frac{x_i P}{P_r} \quad (11)$$

Equation (11) is normally written using the compressibility factor z , which is defined as

$$z = \frac{P_v}{RT} \quad (12)$$

where v is the molar volume ($v=V/n_T$). Inserting (12) into (11) leads to:

$$\mu_{i(P,T)} = h_{i(P_r,T)}^{o*} - Ts_{i(P_r,T)}^{o*} + \int_V^\infty \left(\left(\frac{\partial P}{\partial n_i} \right)_{V,T,n_{i \neq j}} - \frac{RT}{V} \right) dV - RT \ln z + RT \ln \frac{x_i P}{P_r} \quad (13)$$

In this case the fugacity coefficient ϕ_i^m at V and T is defined as:

$$RT \ln \phi_{i(V,T)}^m = \int_V^\infty \left(\left(\frac{\partial P}{\partial n_i} \right)_{V,T,n_{i \neq j}} - \frac{RT}{V} \right) dV - RT \ln z \quad (14)$$

³ Note the term P_r in the denominator of equation (10). In many textbooks this is term sloppily omitted, because the pressure unit employed is *bar* and the reference pressure is set to a value of 1 bar. If, however, SI units are used, P_r is 0.1 MPa and the symbol has to be carried along.

Using Equation(14) the simplified equations

$$\mu_{i(P,T)} = h_{i(P_r,T)}^{o*} - Ts_{i(P_r,T)}^{o*} + RT \ln \frac{x_i \phi_{i(V,T)}^m P}{P_r} \quad (15)$$

and

$$\mu_{i(P,T)} = h_{i(P_r,T)}^{o*} - Ts_{i(P_r,T)}^{o*} + RT \ln \frac{f_{i(V,T)}^m}{P_r} \quad (16)$$

can be written if again the fugacity f_i is defined as:

$$f_{i(V,T)}^m = x_i \phi_{i(V,T)}^m P \quad (17)$$

For the evaluation of the fluid properties, and hence also for any calculations of possible phase separations, the expressions (7) or (14) have to be calculated for every involved phase component. This calculation requires appropriate EOS for the respective fluids.

TYPES OF EOS

Many specific articles and reviews dealing with EOS exist in the chemical and physicochemical literature, e.g., more recent reviews by Anderko (1990), Ferry and Baumgartner (1987), Prausnitz et al. (1999), Sandler (1994), Sengers et al. (2000), and Wei and Sadus (2000). In the geological literature, knowledge about EOS and its state-of-the-art is much less widespread and, therefore, a brief overview is given here.

Ideal gas

The simplest EOS is that of an ideal gas,

$$V = \frac{n_T RT}{P} \quad (18)$$

or,

$$P = \frac{n_T RT}{V} \quad (19)$$

where R is the universal gas constant and n_T the total number of molecules. An ideal gas is characterized by the absence of any intermolecular forces and the particles themselves have zero volume. As such, the volume of an ideal gas is able to approach zero at a temperature of 0 K. Because of the non-existing intermolecular forces, an ideal gas never condenses, liquids can not be described and, as a consequence, fluid separation is not possible. Hence, the EOS assigns for each pressure only one specific volume (Figure 1a). Furthermore because of the lack of intermolecular interaction, mixtures of ideal gases also mix ideally.

Virial equation

The ideal gas law can be expanded in a MacLaurien series in powers of volume,

$$P = \frac{n_T RT}{V} \left(1 + \frac{n_T B_{(T)}}{V} + \frac{n_T^2 C_{(T)}}{V^2} + \frac{n_T^3 D_{(T)}}{V^3} \dots \right) \quad (20)$$

in which B , C , D , $\dots$ are volume-independent but temperature-dependent coefficients. The virial EOS has a rigorous theoretical foundation in statistical thermodynamics. The virial coefficients are directly related to interactions between isolated molecule clusters. The parameter B represents interaction between molecule pairs, C represents interaction of three molecules, D for four molecules, and so forth. The parameters for a fluid are either determined using experimental results or calculated by statistical mechanic methods. Whereas the virial equation is theoretically sound, its applicability is limited to fluids at conditions of low and medium densities.

Figure 1. vT -relationships for a) an ideal gas and b) for a van der Waals fluid. For temperatures below the critical temperature in certain pressure regions, the van der Waals equation provides two valid solutions for v . The pressure P_e , at which liquid and vapor are in equilibrium can be calculated by considering Equation (26). The dashed curve designates the boundary of the field of two coexisting fluids.

Using the compressibility factor z (see Eqn. 12), Equation (20) can be expressed also as:

$$z = 1 + \frac{n_T B_{(T)}}{V} + \frac{n_T^2 C_{(T)}}{V^2} + \frac{n_T^3 D_{(T)}}{V^3} \dots \quad (21)$$

Another form of the virial equation can be written if z is expressed as a power series of P

$$z = 1 + B'P + C'P^2 + D'P^3 + \dots \quad (22)$$

The parameters in Equations (21) and (22) are related if they are determined from experimental results for z which were determined for V going to infinity and P to zero, respectively (see also Prausnitz et al. 1999, Appendix C).

In that case the following relationships hold:

$$B' = \frac{B}{RT}, \quad C' = \frac{C - B^2}{(RT)^2}, \quad D' = \frac{D - 3BC + 2B^3}{(RT)^3} \quad (23)$$

More details concerning the virial EOS are given for example in Trusler (2000).

Cubic EOS

The first equation that was able to reasonably describe the properties of both a vapor and a liquid phase was proposed by van der Waals (1873)

$$P = \frac{n_T RT}{V - n_T b} - \frac{n_T^2 a}{V^2} \quad (24)$$

In this equation, the volume available to the particles is reduced by a characteristic co-volume b , which is related to the volume required by the particles themselves. This parameter stands for repulsion forces between particles. Additionally, the pressure is decreased by intermolecular interaction, i.e. attractive forces, by the term $n_T^2 a / V^2$. In this case a is the characteristic interaction parameter for the respective fluid.

Equation (24) can be arranged to yield a cubic form in V ,

$$-PV^3 + (n_T b P + n_T RT)V^2 - n_T^2 a V + a b n_T^3 = 0 \quad (25)$$

therefore, an EOS, such as the van der Waals equation, is also called a cubic EOS. The cubic form of Equation (25) has the property that analytical solutions for the three roots in V exist. For certain regions in P and T , two of these roots are imaginary. Figure 1b illustrates this result. For temperatures above the critical temperature T_c , there always exists only one real root, and for each pressure, only one real volume. Below T_c there are pressure regions in which all three roots are real as, for example, in Figure 1b for pressures between P_1 and P_2 . However, only one pressure in this interval, i.e. P_e , yields the valid saturated vapor pressure for the specific fluid at a chosen temperature. To calculate P_e , an additional condition has to be met. The volume work at a constant temperature T during transformation from the liquid to vapor state, i.e. evaporation,

$$w = (V_v - V_l)P_e \quad (26)$$

has to be equal to the same work calculated using the van der Waals EOS

$$w = \int_{V_l}^{V_v} \left(\frac{n_T RT}{V - n_T b} - \frac{n_T^2 a}{V^2} \right) dV \quad (27)$$

Then, for coexisting phases the lowest root corresponds to the volume of the liquid and the highest to that of the vapor. At T_c , all three roots, i.e. volumes, are identical.

If a is a special function of T , a further advantage of a cubic EOS is, that the parameters a and b for each pure fluid can be extracted from its critical data. The critical point (P_c and T_c) is defined by the following conditions:

$$\left(\frac{\partial P}{\partial v}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0 \quad (28)$$

If Equation (28) is applied to a pure fluid the parameters a and b can be determined if P_c and T_c are known. In the case of the van der Waals equation a and b are:

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c} \quad (29)$$

$$b = \frac{1}{8} \frac{RT_c}{P_c} \quad (30)$$

The van der Waals parameters a and b are also related to the second virial coefficient B :

$$B = \frac{bV}{V - n_T b} - \frac{a}{RT} \quad (31)$$

B , however, should only be a function of T . This can be accomplished if the relation $V \gg n_T b$ in Equation (31) is used, which is at least valid for low P and large V

$$B = b - \frac{a}{RT} \quad (32)$$

Whereas the van der Waal EOS is capable of predicting vapor-liquid equilibria qualitatively, it is not suitable for quantitatively evaluating phase equilibria. Therefore a wide range of modifications of the attractive part of the van der Waals EOS exists in the literature (e.g. Anderko 2000; Wei and Sadus 2000).

Redlich and Kwong (1949) introduced successfully a temperature dependence to the attractive interaction term

$$P = \frac{n_T RT}{V - n_T b} - \frac{n_T^2 a}{\sqrt{T} V (V + n_T b)} \quad (33)$$

Because of the success of the Redlich-Kwong equation, Soave (1972) proposed a more generalized form of the attractive term than used in Equation (33),

$$P = \frac{n_T RT}{V - n_T b} - \frac{n_T^2 a(T)}{V(V + n_T b)} \quad (34)$$

with

$$a(T) = 0.4275 \left(\frac{R^2 T_c^2}{P_c} \right) \left(1 + m \left(1 - \left(\frac{T}{T_c} \right)^{\frac{1}{2}} \right) \right)^2 \quad (35)$$

$$m = 0.480 + 1.574\omega - 0.175\omega^2 \quad (36)$$

$$b = 0.08664 \left(\frac{RT_c}{P_c} \right) \quad (37)$$

within which the constants in Equations (35) and (37) are derived from the critical parameters using Equation (28) as for the van der Waals equation, and ω is an empirical parameter describing the acentric factor of the molecules, i.e. deviation from a spherical form.

Experimentally observed z -values (Equation 12), at the critical point of pure fluids, i.e. z_c , with geological relevance, range between 0.229 for H_2O and 0.306 for H_2 (Poling et al. 2000). In contrast, the van der Waals EOS generally predicts a z_c -value of 0.375 and the Redlich-Kwong and Soave EOS a z_c of 0.333, which are too large. Peng and Robinson (1976) altered the attractive part of the van der Waals EOS in such a way that z_c becomes 0.307:

$$P = \frac{n_T RT}{V - n_T b} - \frac{n_T^2 a}{V(V - n_T b) + n_T b(V + n_T b)} \quad (38)$$

With:

$$a(T) = 0.45724 \left(\frac{R^2 T_c^2}{P_c} \right) \left(1 + m \left(1 - \left(\frac{T}{T_c} \right)^{\frac{1}{2}} \right) \right)^2 \quad (39)$$

$$m = 0.37464 + 1.5422\omega - 0.26922\omega^2 \quad (40)$$

$$b = 0.07780 \left(\frac{RT_c}{P_c} \right) \quad (41)$$

The Peng-Robinson EOS seems to be better suited for hydrocarbons than the Soave EOS down to intermediate values for the acentric factor.

Abbott (1979) showed that any cubic EOS, with the appropriate asymptotic behavior as V approaches b , can be written in a generic form

$$P = \frac{n_T RT}{V - n_T b} - \frac{n_T^2 \theta (V - n_T \eta)}{(V - n_T b)(V^2 + \delta n_T V + n_T^2 \epsilon)} \quad (42)$$

in which the parameters b , δ , ϵ , θ , and η depend generally on T and composition and are individual for each fluid species. Equation (42) can be considered as a generalization of the van der Waals equation, and EOS such as (24), (33), (34), and (38) can be expressed by Equation (42) using a proper choice for the parameters b , δ , ϵ , θ , and η .

Further cubic EOS with three and more parameters are discussed in Anderko (2000).

Hard-sphere extension of the EOS

A notable and quite successful modification of the repulsive term is the accurate and rigorous hard-sphere extension by Carnahan and Starling (1969). The result of their computer simulations by treating the molecules as hard spheres yielded as a result the following term for the repulsive interaction:

$$P = \frac{n_T RT}{V} \left(\frac{1 + y + y^2 - y^3}{(1 - y)^3} \right) \quad (43)$$

With:

$$y = \frac{n_T b}{4V} = \frac{b}{4v} \quad (44)$$

Equation (43) can be combined with the different attractive terms of the cubic EOS. In such a way a modified van der Waals EOS

$$P = \frac{n_T RT}{V} \left(\frac{1 + y + y^2 - y^3}{(1 - y)^3} \right) - \frac{n_T^2 a}{V^2} \quad (45)$$

or modified Redlich-Kwong EOS

$$P = \frac{n_T RT}{V} \left(\frac{1 + y + y^2 - y^3}{(1 - y)^3} \right) - \frac{n_T^2 a_{(T)}}{V(V + n_T b)} \quad (46)$$

can be formulated. Equations such as (45) or (46) are, however, no longer cubic equations in volume, but rather expressions to the power of 5. As a consequence, no analytical roots for V exist anymore, instead they have to be searched for numerically. However, with the computer power available today, this search is not a problem.

Integrated EOS

Another approach to derive an EOS is to consider the Helmholtz free energy A of a fluid directly. Thereby, the intermolecular potentials Γ are used in their integrated and averaged form. Figure 2 illustrates some simple potentials. The simplest potential for repulsion is that of hard spheres (Figure 2a):

$$\Gamma_{(r)} = \begin{cases} \infty & \text{for } r \leq \sigma \\ 0 & \text{for } r > \sigma \end{cases} \quad (47)$$

This function just means that the potential is infinity for an intermolecular distance r below σ , which is the collision diameter. Carnahan and Starling (1969) have shown that, for this potential, an exact solution exists (see Eqn. 43).

A very simplified attraction term can be added to this potential, (Figure 2b), which describes a potential with a minimum of ε between σ and $R\sigma$. Mathematically such a square-well potential can be described by:

$$\Gamma_{(r)} = \begin{cases} \infty & \text{for } r \leq \sigma \\ -\varepsilon & \text{for } \sigma < r \leq R\sigma \\ 0 & \text{for } r > R\sigma \end{cases} \quad (48)$$

More realistic is the Lennard-Jones potential (Figure 2c):

Figure 2. Intermolecular potentials: a) hard sphere, b) square well, and c) Lennard-Jones. For discussion see text.

$$\Gamma_{(r)} = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right) \quad (49)$$

In the Lennard-Jones potential, the repulsive wall is not vertical but goes with the power of 12 and allows some, but energetically costly, penetration of the two molecules. The attraction goes with the power of 6 and models the dispersion forces.

As for the cubic EOS, the individual contributions to A are added. For the simplest case A is just the sum of the contribution of the ideal gas A^{ideal} and some residual term $A^{residual}$

$$A = A^{ideal} + A^{residual} \quad (50)$$

Whereas the ideal contribution is calculated using the ideal standard state properties by integrating the ideal gas law, the residual term is split into well-known contributions, which are treated as the reference frame and a term which should describe the rest, the perturbation term,

$$A^{residual} = A^{reference} + A^{perturbation} \quad (51)$$

such that:

$$A = A^{ideal} + A^{reference} + A^{perturbation} \quad (52)$$

Possible terms for $A^{residual}$, besides others, are those from hard-sphere repulsion, dispersion, electrostatic interactions like dipole-dipole, induced dipole-dipole, quadrupole-quadrupole, dipole-quadrupole, and induced dipole-quadrupole interactions. Empirical terms can also be formulated

$$A^{residual} = A^{hs} + A^{dis} + A^{dip-dip} + A^{ind-dip} + A^{quad-quad} + A^{quad-dip} + A^{ind-quad} + \dots + A^{empirical} \quad (53)$$

Perturbation theory is often used (e.g. Boublík 2000) in conjunction with integrated EOS from which the term $A^{\text{perturbation}}$ is named. In an oversimplified manner, the perturbation terms stem from series expansions of a well-known reference frame.

An example for an A^{residual} -term is the application of the hard-sphere potential from Equation (43). Subtraction of the ideal gas part and integration over the proper boundaries yields the expression A^{hs}

$$A^{\text{hs}} = n_T a^{\text{hs}} = \int_V \left(\frac{n_T RT}{V} \left(\frac{1+y+y^2-y^3}{(1-y)^3} \right) - \frac{n_T RT}{V} \right) dV = n_T RT \frac{4y-3y^2}{(1-y)^2} \quad (54)$$

In conjunction with an integrated EOS, A is often expressed as a molar function a using the molar volume v or ρ like $a(\rho, T, x_i)$ or $a(v, T, x_i)$ as in (54) instead of $A(V, T, n_i)$. In that case the fugacity coefficient ϕ_i^m can be calculated for use in Equation (15) with

$$\ln \phi_{i(V,T,x_i)}^m = \left(\frac{\partial n_T a_{(\rho \text{ or } v, T, x)}^{\text{residual}} / RT}{\partial n_i} \right)_{\rho \text{ or } v, T, n_{j \neq i}} - \ln z + z - 1 \quad (55)$$

instead of Equation (14). Details and derivation are in Appendix A.

MIXING AND COMBINING RULES

The subject of this volume is fluid mixtures and their possible segregation of separate phases. The phase rule predicts that, in a fluid consisting of two and more phase components, at constant P and T , coexistence of fluids with different compositions is in principle possible. As a result the thermodynamic evaluation of phase equilibria requires EOS of such mixtures. Such an EOS for fluid mixtures can be obtained for example if, for the required phase components, i.e. species or molecules, the respective EOS for the pure phase components are available, which have the same mathematical form. In this case, at least in principle, the necessary EOS parameters of each pure species can be combined in one way or another, and parameters for the respective mixtures may be obtained.

The question arises as to how the EOS parameters should be combined. The respective hints come from the theory behind the virial EOS (Eqn. 20) which is theoretically rigorous. As described above the parameters B , C , D , and so forth represent the 2-, 3-, 4-, and higher body interactions in a virial EOS. It is evident that in mixtures the number of these interactions depend on the quantities of the actual species. It can be shown that the virial interaction parameters in a mixture have to be calculated by summing over all products of the probabilities of the respective species combinations times its interaction parameter

$$B_{(T,x)} = \sum_i \sum_j x_i x_j B_{ij(T)} \quad (56)$$

$$C_{(T,x)} = \sum_i \sum_j \sum_k x_i x_j x_k C_{ijk(T)} \quad (57)$$

$$D_{(T,x)} = \sum_i \sum_j \sum_k \sum_l x_i x_j x_k x_l D_{ijkl(T)} \quad (58)$$

⋮

Because Equations (56) to (58) are exact and the virial EOS has been proven to work well at least at middle and low densities, the such predicted behavior for mixtures should be considered at least as the low-pressure boundary condition for other types of EOS when expanded to the virial form (Sandler and Orbey 2000). However, these equations provide no information *per se* about the way in which the mixed species parameters such as B_{ij} , C_{ijk} , and D_{ijkl} are related to the respective parameters of the pure species, i.e. B_{ii} , B_{jj} or C_{iii} , C_{jjj} , C_{kkk} and so forth.

Mathematically it can be shown that the van der Waals equation can be expressed as a Taylor series:

$$\frac{PV}{n_T RT} = \sum_{m=0}^{\infty} \left(\frac{n_T b}{V} \right)^m - \frac{n_T a}{RTV} \quad (59)$$

As in Equation (32), Equation (59) shows the relationship between the virial equation (Eqn. 20) and the van der Waals equation (24). If Equation (59) is expanded up to $m=1$ then:

$$B_{(T,x)} = \sum_i \sum_j x_i x_j B_{ij(T)} = b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \quad (60)$$

Equation (60) implies that:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (61)$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (62)$$

However, if Equation (59) is expanded to higher order terms then:

$$C_{(T,x)} = \sum_i \sum_j \sum_k x_i x_j x_k C_{ijk(T)} = b^2 \quad (63)$$

$$D_{(T,x)} = \sum_i \sum_j \sum_k \sum_l x_i x_j x_k x_l D_{ijkl(T)} = b^3 \quad (64)$$

⋮

It is obvious that there exists no compositional dependence for b that satisfies Equations (62), (63), (64) and so on, simultaneously. In other words, for the van der Waals EOS, the compositional dependence of Equations (63), (64) and all higher order components are not consistent with Equation (62).

As stated above, the virial equation provides no clue for combining rules to extract values for the parameters such as B_{ij} , C_{ijk} , and D_{ijkl} . As a consequence, there is no immediate hint for the calculation of a_{ij} and b_{ij} for the van der Waals equation or any other EOS for application to mixtures.

Practically, the most commonly used combining rules for the van der Waals and other EOS are,

$$a_{ij} = (a_i a_j)^{\frac{1}{2}} (1 - k_{ij}) \quad (65)$$

$$b_{ij} = \frac{1}{2} (b_i + b_j) (1 - \delta_{ij}) \quad (66)$$

where k_{ij} and δ_{ij} are binary-interaction parameters which are usually obtained by fitting the EOS to experimental results. For the case that k_{ij} and δ_{ij} are 0, Equations (61) and (62) become:

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{\frac{1}{2}} \quad (67)$$

$$b = \sum_i x_i b_i \quad (68)$$

Equations (67) and (68), the geometric mean and arithmetic mean, respectively, are the classical van der Waals mixing rules that are often also used for parameters occurring in cubic and other EOS. They are, however, only usable for moderate non-idealities.

The justification for Equations (65) and (66) is difficult. Whereas the mixed intermolecular interaction parameter a_{ij} in Equation (65) is related to and may be deduced from intermolecular potential theory, Equation (66) describes the excluded-volume parameter b_{ij} as if the molecules are hard spheres and δ_{ij} is 0. Equation (66) is, however, not unequivocal and it can be argued that even for hard spheres, the diameter is of importance and not the volume (Sandler and Orbey 2000). In that case b_{ij} would be:

$$b_{ij} = (b_i^{1/3} + b_j^{1/3})^3 \quad (69)$$

Also with the proper arguments, other combining rules are possible.

Boublík (1970) and Mansoori et al. (1971) extended the hard-sphere concept to mixtures and derived the following expression which replaces Equation (43) for mixtures

$$P = \frac{n_T RT}{V} \left(\frac{1 + \left(3 \frac{DE}{F} - 2 \right) y + \left(3 \frac{E^3}{F^2} - 3 \frac{DE}{F} + 1 \right) y^2 - \left(\frac{E^3}{F^2} \right) y^3}{(1 - y)^3} \right) \quad (70)$$

With y defined as in Equation (44) and:

$$D = \sum_{i=1}^m x_i \sigma_i, \quad E = \sum_{i=1}^m x_i \sigma_i^2, \text{ and } F = \sum_{i=1}^m x_i \sigma_i^3 \quad (71)$$

Additionally:

$$b = \frac{2}{3} \pi N_a F \quad (72)$$

Here σ_i is the hard-sphere diameter. The integrated form of the hard-sphere repulsion term is then

$$A^{hs} = n_T RT \left(\frac{\frac{3DE}{F} y - \frac{E^3}{F^2}}{1-y} + \frac{\frac{E^3}{F^2}}{(1-y)^2} + \left(\frac{E^3}{F^2} - 1 \right) \ln(1-y) \right) \quad (73)$$

with y defined as in Equation (44). For mixtures, Equation (73) can be used instead of Equation (54).

More detailed reviews dealing with EOS parameters in mixtures and combining rules can be found in Matteoli et al. (2000) and Sandler and Orbey (2000).

SPECIFIC EOS FOR MIXTURES APPLICABLE TO GEOLOGIC SETTINGS

For the calculation of fugacity coefficients, the integrals in the Equations (7) or (14) have to be solved or the respective Helmholtz free energy expressions for Equation (53) are required, both of which need appropriate EOS. However, not all EOS are equal. There exist EOS in the literature that are tuned for special purposes, e.g. EOS which reproduce precise *PVT*-relationships only in restricted regions, for example for fluid inclusion research or EOS for studies of critical behavior. Such EOS are ill-suited for use in the Equations (7) or (14), because any appropriate EOS must cover the whole range from 0 to the required P .

This volume covers coexisting fluids, and as stated before, for equilibrium calculations EOS that are able to deal with fluid mixtures are required. But in any case, the necessary boundary conditions are that any such EOS must also equally well deal with the respective pure phase components. This requirement can easily be checked with accurate EOS for pure phase components (species) which are available in the literature. For example, for H₂O, CO₂, CH₄, O₂, N₂, and Ar, accurate EOS are available from Wagner and Pruß (2002), Span and Wagner (1996), Setzmann and Wagner (1991), Schmidt and Wagner (1984), Span et al. (2000), and Tegeler et al. (1999), respectively⁴. These dedicated EOS for distinct species cannot be used for mixtures, however, except if ideal mixing is assumed or the mixing properties are determined and available otherwise. Ideal mixing does not induce phase separation, however.

For geologic, geochemical, and petrologic applications useful EOS should cover the occurring species and be valid up to the relevant P and T conditions. In the following the here presented EOS⁵ cover mostly combinations of the phase components H₂O, CO₂, CH₄, CO, H₂, O₂, N₂, Ar, He, Ne, NaCl, and KCl. EOS for hydrocarbons are handled in detail in Pedersen and Christensen (2007). The applicable maximum pressure should be at least 100 MPa or higher and maximum temperatures should be above 800°C. In the following, emphasis is

⁴ For many discussed EOS, programs running with *Mathematica*[®] are provided in conjunction with this volume as electronic supplements.

⁵ The available EOS are numerous and the following presentation can hardly be complete.

placed on the background and kind of formulation of the EOS, quality and success of the EOS are hard to evaluate and may vary with the specific requirements of applications.

Holloway (1976), Holloway (1981)

Phase components: H₂O, CO₂, CH₄, CO, H₂, N₂, H₂S, SO₂.

Applicable range given by the author: 723-2073 K, up to 4 GPa.

Based on the work of De Santis et al. (1974), Holloway proposed an EOS using a modified Redlich-Kwong equation in which the a parameter is also a function of T

$$P = \frac{n_T RT}{V - n_T b} - \frac{n_T^2 a_{(T)}}{\sqrt{T} V (V + n_T b)} \quad (74)$$

The parameter a is split into a constant a_0 and polynomial a_1

$$a_{(T)} = a^0 + a_{(T)}^1 \quad (75)$$

The mixing and the combining rules are those from Equations (67) and (68), except for the subsystem H₂O-CO₂ for which a modified expression of the type of Equation (65) is used

$$a_{\text{H}_2\text{O-CO}_2} = \left(a_{\text{H}_2\text{O}}^0 a_{\text{CO}_2}^0 \right)^{\frac{1}{2}} + \frac{1}{2} R^2 T^{5/2} K \quad (76)$$

Here K is the equilibrium constant describing the observed complex formation between H₂O and CO₂. For combinations of H₂O or CO₂ with other species the cross term is defined as:

$$a_{\text{H}_2\text{O-}j} = \left(a_{\text{H}_2\text{O}}^0 a_j \right)^{\frac{1}{2}} \quad \text{or} \quad a_{\text{CO}_2-j} = \left(a_{\text{CO}_2}^0 a_j \right)^{\frac{1}{2}} \quad (77)$$

Using this EOS, considerable deviations from ideal mixing for the system H₂O-CO₂ have been calculated by Holloway (1976), but no unmixing seems to be predicted in the EOS validity range. Flowers (1979) pointed out that the equation used by Holloway (1976) to calculate the fugacity coefficients did not obey the Gibbs-Duhem relation and was in error. The corrected EOS predicts considerable more ideal fugacity coefficients than the uncorrected EOS.

Bowers and Helgeson (1983)

Phase components: H₂O, CO₂, NaCl.

Applicable range given by the authors: between 623 and 873 K, above 50 MPa and no particular maximum P given, maximum $x_{\text{NaCl}} = 0.14$ (35 wt%) relative to H₂O+NaCl.

This EOS is very similar to the approach taken by Holloway (1976). It uses a modified Redlich-Kwong equation like Equation (74). Differences are in the calculation of the cross terms with H₂O when applying the Equations (61) and (62). The $a_{\text{H}_2\text{O}}$ parameter is split into a pure function $a_{\text{H}_2\text{O}}^0$ and a cross term function $a_{\text{H}_2\text{O}}^0$, both of which depend on temperature. Together with the parameter $b_{\text{H}_2\text{O}}$ these are also functions of w , where w corresponds to the weight fraction of NaCl relative to H₂O+NaCl. The $a_{\text{H}_2\text{O CO}_2}$ term is calculated according Equation (76). The EOS does consider the phase component NaCl only implicitly using the parameter w , and does not use terms such as a_{NaCl} , a_{NaCl}^0 , or b_{NaCl} . For this reason, the EOS is

not a true ternary EOS. Whereas the EOS reproduces the molar volumes in its validity region well, it turns out that it can not be applied to calculate phase relations in the ternary. As a consequence, calculated values for ϕ_i^m are also doubtful. A FORTRAN program to calculate fluid properties using this EOS is provided by Bowers and Helgeson (1985). Bakker (1999) extended this EOS and added the phase components CH_4 and N_2 .

Kerrick and Jacobs (1981), Jacobs and Kerrick (1981a,b)

Phase components: H_2O , CO_2 , CH_4 .

Applicable range given by the authors: up to 573-1323 K, at least 2 GPa.

This EOS uses a modified Redlich-Kwong equation including a hard-sphere term and the parameter a is a function of V and T

$$P = \frac{n_T RT}{V} \left(\frac{1 + y + y^2 - y^3}{(1 - y)^3} \right) - \frac{n_T^2 a_{(V,T)}}{V(V + n_T b)} \quad (78)$$

With:

$$a_{(V,T)} = c + \frac{n_T d}{V} + \frac{n_T^2 e}{V^2} \quad (79)$$

Here the parameters c , d , and e are cubic equations of T , and y is defined according to Equation (44). The mixing rules are claimed to be according to Equations (67) and (68). But from the Appendix in Kerrick and Jacobs (1981) and the program provided by Jacobs and Kerrick (1981a) it is evident that for the cross terms instead of Equation (67) relations of the type

$$c_{ij} = (c_i c_j)^{1/2}, \quad d_{ij} = (d_i d_j)^{1/2}, \quad e_{ij} = (e_i e_j)^{1/2} \quad (80)$$

are used. Thus polynomial cross terms were calculated instead. For mixtures this calculation produces a significantly different numerator in Equation (78) than using the appropriate van der Waals mixing rule. Furthermore, because Equation (79) is an arbitrary polynomial, and the attractive interaction a is always positive, some of the parameters c , d , and e might be negative. There is the inherent possibility, that as a side effect, for mixtures the cross terms in Equation (80) will result in a negative root and will be therefore imaginary. Furthermore, if for two phase components the specific parameters are both negative, according to Equation (80) inconsistent positive cross terms will result. Applying this cross terms to a pure phase with a negative c_{ii} , d_{ii} , or e_{ii} will result in a positive one. Kerrick and Jacobs (1981) took care that the problem did not arise by making sure that the parameters c , d , and e are positive in the validity region of the EOS. However, extrapolation and extension by adding additional species is error-prone besides the used rules are not the van der Waals mixing rules.

The calculated activity coefficients using this EOS show significant positive deviations from ideal mixing at elevated pressures, and unmixing is implied at temperatures $< 400^\circ\text{C}$.

Rimbach and Chatterjee (1987)

Phase components: H_2O , H_2 .

Applicable range given by the authors: above 273 K, up to 10 and 20 GPa for H_2 and H_2O , respectively.

This EOS uses a modified Redlich-Kwong in which the parameter a is a function of P and T and b only of P

$$P = \frac{n_T RT}{V - n_T b_{(P)}} - \frac{n_T^2 a_{(P,T)}}{\sqrt{T} V (V + n_T b_{(P)})} \quad (81)$$

The chosen mixing and combining rules are those of Equations (61), (62), (65), and (66) using fitted values for k_{ij} and δ_{ij} .

Grevel and Chatterjee (1992)

Phase components: H_2O , H_2 .

Applicable range given by the authors: above 673 K and at least 3300 K, at least 10 GPa.

This EOS is based on the approach taken by Halbach and Chatterjee (1982) for pure H_2O and uses a modified Redlich-Kwong equation in which the parameters a and b are functions of P and T

$$P = \frac{n_T RT}{V - n_T b_{(P,T)}} - \frac{n_T^2 a_{(P,T)}}{\sqrt{T} V (V + n_T b_{(P,T)})} \quad (82)$$

For the phase component H_2O the PT -space is split into two regions. For temperatures below 400 °C the vapor saturation curve and for temperatures above a linear relationship is used as a divider. In each region different functions for a and b were added to the function derived by Halbach and Chatterjee (1982). For H_2 single functions for a and b were derived. Van der Waals mixing rules according to Equations (67) and (68) were applied for the mixtures.

The choice to make a and b a function of P , as in Rimbach and Chatterjee (1987) and Halbach and Chatterjee (1982), makes integration not straightforward, because the EOS can not be solved either for P or V and must be therefore performed numerically. As a result of the different PT -regions for a and b used for H_2O , discontinuities in V are created which are also not advantageous for the calculation of fluid properties such as fugacity coefficients, and introduces systematic errors for pure as well as mixture properties.

Grevel (1993)

Phase components: H_2O , CH_4 .

Applicable range given by the author: above 150 K and at least 2273 K, up to 23 GPa.

Like the EOS of Grevel and Chatterjee (1992), Grevel (1993) uses a modified Redlich-Kwong equation in which both parameters a and b are functions of P and T

$$P = \frac{n_T RT}{V - n_T b_{(P,T)}} - \frac{n_T^2 a_{(P,T)}}{\sqrt{T} V (V + n_T b_{(P,T)})} \quad (83)$$

As for H_2O in Grevel and Chatterjee (1992), the PT -space is split into several regions for CH_4 with different functional dependencies for the parameter a . For higher P and T the parameter a_{CH_4} becomes negative. Therefore instead of the actual van der Waals mixing rules (67) and (68) for $a_{\text{H}_2\text{O}-\text{CH}_4}$ the relation

$$a_{H_2O-CH_4} = |a_{H_2O}a_{CH_4}|^{1/2} \quad (84)$$

is used. This choice is arbitrary and introduces discontinuities in slopes of isochores. Furthermore, mixed and pure systems do not converge. The significance of the calculated ϕ_i^m -values is therefore questionable.

Spycher and Reed (1988)

Phase components: H₂O, CO₂, CH₄.

Applicable range given by the authors: up to 1273 K, up to 50 MPa for mixtures.

The EOS is based on a virial expansion in P

$$z = 1 + B'_{(T)}P + C'_{(T)}P^2 \quad (85)$$

in which the parameters B' and C' are polynomial functions of T . As mixing rules, Equations (56) and (57) were used and the required cross terms were fitted to experimental results as functions of T . It must be noted that the mixing rules (56) and (57) are sensu stricto valid only for virial equations of the type of Equation (21), and not for Equation (85) as used here.

Saxena and Fei (1987, 1988)

Phase components: H₂O, CO₂, CH₄, CO, H₂, O₂

Applicable range given by the authors: above 400 K for all but for H₂O (>673 K), no explicit pressure and temperature limit is provided but according to Saxena and Fei (1987), the EOS is valid for crustal conditions.

The properties of the pure phase components and those of the mixture are calculated separately. The pure components are treated with a virial EOS which uses the reduced pressure $P_r = P/P_c$ as the variable (Saxena and Fei 1987),

$$z = A'_{(T_r)} + B'_{(T_r)}P_r + C'_{(T_r)}P_r^2 \quad (86)$$

in which the parameters A' , B' , and C' are functions of the reduced temperature $T_r = T/T_c$. P_c and T_c are the critical pressure and temperature for each pure phase component.

For non-polar molecules the mixture properties are calculated using a Kihara potential,

$$\Gamma_{(r)} = \begin{cases} \infty & \text{for } r < 2a \\ 4\varepsilon \left(\left(\frac{\sigma - 2a}{r - 2a} \right)^{12} - \left(\frac{\sigma - 2a}{r - 2a} \right)^6 \right) & \text{for } r \geq 2a \end{cases} \quad (87)$$

which is similar to the Lennard-Jones potential described previously, but does not theoretically allow complete penetration of the molecules. The parameter $2a$ is the spherical molecular core diameter which describes the maximum penetration depth. For interactions with involvement of polar molecules, a Stockmayer potential is used

$$\Gamma_{(r)} = 4\varepsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right) - \frac{\mu^2}{r^3} F(\theta_1, \theta_2, \theta_3) \quad (88)$$

The Stockmayer potential is a modified Lennard-Jones potential which considers the direction $(\theta_1, \theta_2, \theta_3)$ dependent dipole-dipole interactions and includes the dipole moment μ of the polar species.

The mixing rules for the pure non-polar and pure polar interactions are:

$$r_{ij} = \frac{1}{2}(r_i + r_j), \quad \sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j), \quad \varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}, \quad \mu_{ij} = (\mu_i \mu_j)^{1/2} \quad (89)$$

For a pair of polar (i) and non-polar (j) molecules, the following relation is used:

$$\sigma_{ij} = \frac{(\sigma_i + \sigma_j)}{2 \left(1 + \frac{\alpha_{jj} \mu_{ii} (\varepsilon_{ii} / \varepsilon_{jj})^{1/2}}{4 \sigma_{jj}^3 (\varepsilon_{ii} \sigma_{ii}^3)^{1/2}} \right)^{1/6}} \quad (90)$$

in which α is the polarizability of the non-polar molecule.

The calculated mixing properties for each binary system are expressed by a van Laar equation using a binary interaction parameter W_{ij} and the molar volumes of the pure phase components v_k^o ,

$$G_{ij}^{excess} = \frac{n_T W_{ij} x_i x_j v_i^o v_j^o}{(v_i^o + v_j^o)(x_i v_i^o + x_j v_j^o)} \quad (91)$$

which in turn can be combined to ternary and higher systems. Because the calculated energies are two-body interactions, ternary and higher parameters are neglected. Appropriate differentiation in respect to n_i yields the required expressions for the activity constants.

Shi and Saxena (1992)

Phase components: H_2O , CO_2 , CH_4 , CO , O_2 , H_2 , S_2 , SO_2 , COS , H_2S .

Applicable range given by the authors: up to 2500 K, up to 2 GPa.

The calculation of the pure and mixed fluid properties is, with slight modifications, identical to Saxena and Fei (1987, 1988) described above. For pure CO_2 , CH_4 , CO , O_2 , H_2 , S_2 , SO_2 , COS , and H_2S a virial equation of the type

$$z = A'_{(T_r)} + B'_{(T_r)} P_r + C'_{(T_r)} P_r^2 + D'_{(T_r)} P_r^3 \quad (92)$$

is used, in which the parameters A' , B' , C' , and D' are functions of T_r . The chosen functional dependence for each parameter is

$$Q_{(T)} = Q_1 + Q_2 T_r^{-1} + Q_3 T_r^{-3/2} + Q_4 T_r^{-3} + Q_5 T_r^{-4} \quad (93)$$

for $P < 100$ MPa and

$$Q_{(T)} = Q_1 + Q_2 T_r + Q_3 T_r^{-1} + Q_4 T_r^2 + Q_5 T_r^{-2} + Q_6 T_r^3 + Q_7 T_r^{-3} + Q_8 \ln T_r \quad (94)$$

or $P \geq 100$ MPa. The properties of H_2O are calculated using the EOS of Saul and Wagner (1989).

The properties of the fluid mixtures are calculated with the approach given by Saxena and Fei (1988), as described above.

Belonoshko and Saxena (1992c), Belonoshko et al. (1992)

Phase components: H_2O , CO_2 , CH_4 , CO , O_2 , H_2 , S_2 , SO_2 , COS , H_2S , N_2 , NH_3 , Ar.

Applicable range given by the authors: up to 2273 K for 100 MPa, 3273 K for 500 MPa, 4000 K for up to 100 GPa, lower pressure limit 500 MPa.

This EOS is based on publications of Belonoshko and Saxena (1992a,b) and does not fit into the pattern outlined in the beginning of this chapter. It is based on intermolecular potentials such as the integrated EOS, but uses results from molecular dynamical simulations as input instead. The intermolecular potential applied is of the α -Exp-6 type which is also sometimes referred to as a modified Buckingham potential,

$$\Gamma_{(r)} = \frac{\varepsilon}{\alpha - 6} \left(6 \exp \left(\alpha \left(1 - \frac{r}{r_{min}} \right) \right) - \alpha \left(\frac{r}{r_{min}} \right)^6 \right) \quad (95)$$

where ε is the minimum potential energy at the intermolecular separation r_{min} , and α determines the steepness of the repulsion wall. By applying this potential in molecular dynamical simulations large sets of PVT data were generated which were then in turn fitted to the following term which looks in part like a virial equation,

$$P_r = \left(\frac{A}{V_r - G} + \frac{B}{V_r^2} + \frac{F}{V_r^3} + \frac{C}{V_r^m} \right) \left(1 + D(\alpha - 12.75) + E(\alpha - 12.75)^2 \right) \quad (96)$$

where

$$P_r = \frac{P\sigma^3}{\varepsilon}, \quad V_r = \frac{V}{\sigma^3}, \quad T_r = \frac{kT}{\varepsilon}, \quad \sigma = \frac{r_{min}}{2^{1/6}} \quad (97)$$

and A , B , C , D , E , F , and G are either functions of only T_r or T_r and V_r , k is the Boltzmann constant and σ is the collision diameter, the distance at which the potential Γ is 0.

The applied mixing rules for ε and α are related to the Equations (61), (62), and (67), whereas the combining rule for the collision diameter σ is like Equation (69)

$$\sigma = \left(\sum_i \sum_j x_i x_j \sigma_{ij}^3 \right)^{1/3} \quad (98)$$

$$\varepsilon = \frac{\sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma_{ij}^3}{\sum_i \sum_j x_i x_j \sigma_{ij}^3} \quad (99)$$

$$\alpha = \frac{\sum_i \sum_j x_i x_j \gamma_{ij} \varepsilon_{ij} \sigma_{ij}^3}{\sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma_{ij}^3} \quad (100)$$

With:

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j), \quad \varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}, \quad \alpha_{ij} = (\alpha_i \alpha_j)^{1/2} \quad (101)$$

According to the authors, the rather high lower boundary pressure of validity (500 MPa at 400 K) is related to the use of the α -Exp-6 type potential. As a consequence for the evaluation of the fugacity coefficients using Equation (14), the integral must be split into a low and a high V part. For volumes corresponding to pressures below 500 MPa another but valid EOS has to be used to obtain satisfactory accuracies for ϕ_i^m .

For the application of this EOS and that of Shi and Saxena (1992), the authors provide a program called SUPERFLUID (Belonoshko et al. 1992).

Duan et al. (1992c, 1996)

Phase components: H₂O, CO₂, CH₄, CO, O₂, H₂, Cl₂, H₂S, N₂.

Applicable range given by the authors: up to 2800 K, up to 30 GPa.

In Duan et al. (1996) the EOS presented by Duan et al. (1992c) for pure phase components is extended to fluid mixtures. The EOS is a virial equation

$$z = \frac{P_{ref} V_{ref}}{n_T R T_{ref}} = 1 + \frac{B}{V_{ref}} + \frac{C}{V_{ref}^2} + \frac{D}{V_{ref}^4} + \frac{E}{V_{ref}^5} + \frac{F}{V_{ref}^2} \left(1 + \frac{\gamma}{V_{ref}^2} \right) \exp \left(-\frac{\gamma}{V_{ref}^2} \right) \quad (102)$$

in which P_{ref} , V_{ref} and T_{ref} are defined as follows:

$$P_{ref} = \frac{\varepsilon_{ref} \sigma_i^3 P}{\varepsilon_i \sigma_{ref}^3}, \quad V_{ref} = \frac{\sigma_{ref}^3 V}{\sigma_i^3}, \quad T_{ref} = \frac{\varepsilon_{ref} T}{\varepsilon_i} \quad (103)$$

The parameters ε and σ are those of the Lennard-Jones potential. The index *ref* signifies the pure reference fluid CH₄ for which the parameters B , C , D , E , F , and γ were determined and the index i stands for any pure fluid for which the EOS is intended to be valid. Except for γ , these parameters are functions of T_{ref} . For mixtures, the following mixing and combining rules are used:

$$\varepsilon = \sum_i \sum_j x_i x_j k_{1,ij} (\varepsilon_i \varepsilon_j)^{1/2}, \quad \sigma = \sum_i \sum_j x_i x_j k_{2,ij} \left(\frac{\sigma_i + \sigma_j}{2} \right), \quad k_{1,ii} = 1, \quad k_{2,ii} = 1 \quad (104)$$

Here the mixing parameters $k_{1,ij}$ and $k_{2,ij}$ are treated as constants and have been fitted using experimental results.

Duan et al. (2000) checked the validity of this EOS for H₂O, CO₂, CH₄, N₂ mixtures by comparing the calculated properties to experimental results and to other EOS with favorable results.

Duan et al. (1992a,b)

Phase components: H₂O, CO₂, CH₄.

Applicable range given by the authors: up to 1273 K, up to 300 MPa.

The EOS used is very similar to the approach taken by Duan et al. (1992c, 1996)

$$z = 1 + \frac{BV_c}{V} + \frac{CV_c^2}{V^2} + \frac{DV_c^4}{V^4} + \frac{EV_c^5}{V^5} + \frac{FV_c^2}{V^2} \left(\beta + \frac{\gamma V_c^2}{V^2} \right) \exp \left(-\frac{\gamma V_c^2}{V^2} \right) \quad (105)$$

and differs in the additional parameter β , and the replacement of the Lennard-Jones parameters by the critical properties of the pure phase components and uses reduced properties instead:

$$P_r = \frac{P}{P_c}, \quad V_r = \frac{V}{V_c}, \quad T_r = \frac{T}{T_c} \quad (106)$$

Accordingly the parameters B, C, D, E, F are functions of the reduced temperature T_r and the parameters β and γ are constants. Different from the approach above is the treatment of the mixing and combining rules. Mixing requires cross terms for the parameters B, C, D, E, F , and γ and also one for the critical volume V_c . However, whereas V_c for a pure phase component has a physical meaning, for a mixture it does not. Mixing rules according to Equations (56) to (58) and cross terms for each term in Equation (105), are listed below:

$$B^{mix} V_c^{mix} = \sum_i \sum_j x_i x_j B_{ij} V_{c,ij} \quad (107)$$

$$B_{ij} = \left(\frac{B_i^{1/3} + B_j^{1/3}}{2} \right)^3 k_{1,ij}, \quad V_{c,ij} = \left(\frac{V_{c,i}^{1/3} + V_{c,j}^{1/3}}{2} \right)^3, \quad k_{1,ii} = 1 \quad (108)$$

$$C^{mix} (V_c^{mix})^2 = \sum_i \sum_j \sum_k x_i x_j x_k C_{ijk} V_{c,ijk}^2 \quad (109)$$

$$C_{ijk} = \left(\frac{C_i^{1/3} + C_j^{1/3} + C_k^{1/3}}{3} \right)^3 k_{2,ijk}, \quad V_{c,ijk} = \left(\frac{V_{c,i}^{1/3} + V_{c,j}^{1/3} + V_{c,k}^{1/3}}{3} \right)^3 \quad (110)$$

$$k_{2,iii} = 1, \quad k_{2,ijj} = k_{2,iji}, \quad k_{2,ikk} = k_{2,iik}, \quad k_{2,jkk} = k_{2,jjk} \quad (111)$$

$$D^{mix} (V_c^{mix})^4 = \sum_i \sum_j \sum_k \sum_l \sum_m x_i x_j x_k x_l x_m D_{ijklm} V_{c,ijklm}^4 \quad (112)$$

$$D_{ijklm} = \left(\frac{D_i^{1/3} + D_j^{1/3} + D_k^{1/3} + D_l^{1/3} + D_m^{1/3}}{5} \right)^3 \quad (113)$$

$$V_{c,ijklm} = \left(\frac{V_{c,i}^{1/3} + V_{c,j}^{1/3} + V_{c,k}^{1/3} + V_{c,l}^{1/3} + V_{c,m}^{1/3}}{5} \right)^3 \quad (114)$$

$$E^{mix}(V_c^{mix})^5 = \sum_i \sum_j \sum_k \sum_l \sum_m \sum_n x_i x_j x_k x_l x_m x_n E_{ijklmn} V_{c,ijklmn}^5 \quad (115)$$

$$E_{ijklmn} = \left(\frac{E_i^{1/3} + E_j^{1/3} + E_k^{1/3} + E_l^{1/3} + E_m^{1/3} + E_n^{1/3}}{6} \right)^3 \quad (116)$$

$$V_{c,ijklmn} = \left(\frac{V_{c,i}^{1/3} + V_{c,j}^{1/3} + V_{c,k}^{1/3} + V_{c,l}^{1/3} + V_{c,m}^{1/3} + V_{c,n}^{1/3}}{6} \right)^3 \quad (117)$$

$$F^{mix}(V_c^{mix})^2 = \sum_i \sum_j x_i x_j F_{ij} V_{c,ij}^2 \quad (118)$$

$$F_{ij} = \left(\frac{F_i^{1/3} + F_j^{1/3}}{2} \right)^3 k_{1,ij}, \quad V_{c,ij} = \left(\frac{V_{c,i}^{1/3} + V_{c,j}^{1/3}}{2} \right)^3 \quad (119)$$

$$\beta = \sum_i x_i \beta_i \quad (120)$$

$$\gamma^{mix}(V_c^{mix})^2 = \sum_i \sum_j \sum_k x_i x_j x_k \gamma_{ijk} V_{c,ijk}^2 \quad (121)$$

$$\gamma_{ijk} = \left(\frac{\gamma_i^{1/3} + \gamma_j^{1/3} + \gamma_k^{1/3}}{3} \right)^3 k_{3,ijk} \quad (122)$$

$$k_{3,ijk} = 1 \text{ for } i = j = k, \quad k_{3,ijj} = k_{3,ijj}, \quad k_{3,ikk} = k_{3,iik}, \quad k_{3,jkk} = k_{3,jjk} \quad (123)$$

A program to calculate the fluid properties using this EOS has been published by Nieva and Barragan (2003).

Duan and Zhang (2006)

Phase components: H₂O, CO₂.

Applicable range given by the authors: up to 2573 K, up to 10 GPa.

An identical EOS to the one described above (Duan et al. 1992a,b) is used and the parameters calibrated to experimental results and volumes derived from molecular simulations.

Anderko and Pitzer (1993a,b), Duan et al. (1995)

Phase components: H₂O, NaCl, KCl and H₂O, NaCl, CO₂.

Applicable range given by the authors: between 773 and up to 1200 K and below 500 MPa for the system containing H₂O, CO₂, and NaCl. If KCl is considered as a phase component, maximum temperature is 973 K.

Anderko and Pitzer (1993a) implemented a reasonable successful EOS for H₂O-NaCl mixtures. Anderko and Pitzer (1993b) added the phase component KCl, and later Duan et al. (1995) adapted CO₂ to the base system H₂O-NaCl⁶. NaCl as well as KCl are treated as undissociated species. The foundation of this EOS is an integrated formulation of the Helmholtz free energy and adds a hard-sphere, dipole-dipole interaction and a perturbation term to the ideal gas properties:

$$A = A^{ideal} + A^{hs} + A^{dip-dip} + A^{per} \quad (124)$$

On a molar basis, the hard-sphere contribution is calculated according to Equation (73) which is derived for mixtures:

$$\frac{a^{hs}}{RT} = \frac{A^{hs}}{n_T RT} = \frac{\frac{3DE}{F} y - \frac{E^3}{F^2}}{1-y} + \frac{\frac{E^3}{F^2}}{(1-y)^2} + \left(\frac{E^3}{F^2} - 1 \right) \ln(1-y) \quad (125)$$

The definitions for y , D , E , and F are from Equations (44), (71), and (72). The dipole-dipole interaction term uses a [0,1] Padé approximation

$$\frac{a^{dip-dip}}{RT} = \frac{A^{dip-dip}}{n_T RT} = \frac{A_2}{1 - A_3/A_2}. \quad (126)$$

The required terms in Equation (126) are calculated according to the following equations:

$$A_2 = -\frac{4}{3} \sum_{i=1}^m \sum_{j=1}^m x_i x_j \frac{b_i b_j}{b_{ij}} y_{ij} \tilde{\mu}_i^2 \tilde{\mu}_j^2 I_{2(\eta)} \quad (127)$$

With:

$$y_{ij} = \frac{b_{ij}}{4v}, \quad b_{ij} = \left(\frac{b_i^{1/3} + b_j^{1/3}}{2} \right)^3 \quad (128)$$

And:

$$A_3 = \frac{10}{9} \sum_{i=1}^m \sum_{j=1}^m \sum_{k=1}^m x_i x_j x_k \frac{b_i b_j b_k}{b_{ij} b_{ik} b_{jk}} y_{ijk}^3 \tilde{\mu}_i^2 \tilde{\mu}_j^2 \tilde{\mu}_k^2 I_{3(\eta)} \quad (129)$$

With:

$$y_{ijk} = \frac{b_{ijk}}{4v} = \frac{(b_{ij} b_{ik} b_{jk})^{1/3}}{4v} \quad (130)$$

In Equations (127) and (129) $\tilde{\mu}_i$ is the reduced dipole moment,

⁶ There seems to be some frustration in the community and practical implementations of this EOS are scarce. Because of a few typing errors in the required constants, but mainly resulting from some confusion in the presented derivatives many programming efforts failed. In Appendix B, a complete set of constants and required equations is provided.

$$\tilde{\mu}_i = \left(\frac{\mu_i^2}{\sigma_i^3 kT} \right)^{1/2} \quad (131)$$

and the functions $I_{2(\eta)}$ and $I_{3(\eta)}$ are integrals over pair and triple distribution functions and depend on η :

$$\eta = \frac{1}{4v} \sum_{i=1} \sum_{j=1} x_i x_j b_{ij} \quad (132)$$

The perturbation term is a virial expansion of the form:

$$\frac{a^{per}}{RT} = \frac{A^{per}}{n_T RT} = -\frac{1}{RT} \left(\frac{a}{v} + \frac{acb}{4v^2} + \frac{adb^2}{16v^3} + \frac{aeb^3}{64v^4} \right) \quad (133)$$

In this equation, the quantities a , acb , adb^2 , and aeb^3 are related to the second, third, fourth, and fifth virial coefficients, respectively. Accordingly, the second virial coefficient is a quadratic function of composition, the third a cubic, and so on. Besides the co-volume b relevant for 2, 3, 4, and 5 body interactions, the respective quantities involve mixing parameters characteristic for each considered binary join, which in turn are functions of T .

Using this EOS binary and ternary fluid phase equilibria can be successfully calculated. Figure 3 shows an example that illustrates the phase relationships in the system $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ as a function of P and T . In Heinrich (2007) further isothermal-isobaric phase equilibria are presented.

Duan et al. (2003)

Phase components: H_2O , CH_4 , NaCl and H_2O , CO_2 , CH_4 , NaCl .

Applicable range given by the authors: 573 to 1300 K, up to 500 MPa.

The approach used by Anderko and Pitzer (1993a) and later taken up by Duan et al. (1995) has been augmented in this publication further by the phase component CH_4 .

Jiang and Pitzer (1996), Duan et al. (2006)

Phase components: H_2O , CaCl_2 and H_2O , MgCl_2 .

Applicable range given by the authors: 523 to 973 K, up to 150 MPa.

Jiang and Pitzer (1996) presented an EOS for the system $\text{H}_2\text{O}-\text{CaCl}_2$ and Duan et al. (2006) for the systems $\text{H}_2\text{O}-\text{CaCl}_2$ and $\text{H}_2\text{O}-\text{MgCl}_2$, which are based on the approach taken by Anderko and Pitzer (1993a), except that dipole-quadrupole and quadrupole-quadrupole interactions were additionally taken into account. The respective Helmholtz free energy is then:

$$A = A^{ideal} + A^{hs} + A^{dip-dip} + A^{dip-quad} + A^{quad-quad} + A^{per} \quad (134)$$

Figure 3. Phase relationships in the system $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ as function of P and T . The ternary phase boundaries, including the tie lines connecting coexisting fluids, are calculated using the EOS by Duan et al. (1995). [Used by permission of Springer, from Heinrich et al. (2004), *Contributions to Mineralogy and Petrology*, Vol. 148, Fig. 1, p. 133]

Churakov and Gottschalk (2003a,b)

Phase components: H_2O , CO_2 , CH_4 , CO , H_2 , O_2 , N_2 , Ar , He , Ne and 88 other organic and inorganic phase components.

Applicable range given by the authors: at least 2000 K and up to 10 GPa.

This EOS is based on perturbation theory and uses the following expression for the Helmholtz free energy,

$$A = A^{\text{ideal}} + A^{\text{LJ}} + A^{\text{dip-dip}} + A^{\text{ind-dip}} \quad (135)$$

which considers expressions derived from intermolecular potentials according to the Lennard-Jones, dipole-dipole and induced dipole-dipole interaction. A^{LJ} is split into terms for the hard-sphere, high temperature and random phase approximation (see also Shmulovich et al. 1982)

$$A^{LJ} = A^{hs} + A^{hta} + A^{rpa} \quad (136)$$

As in Anderko and Pitzer (1993a), for $A^{dip-dip}$, a [0,1] Padé approximation is used.

$$A^{dip-dip} = \frac{A_2^{dip-dip}}{\left(1 - A_3^{dip-dip} / A_2^{dip-dip}\right)} \quad (137)$$

With:

$$A_2^{dip-dip} = -\frac{2\pi N_A^2 \rho}{3kT} \sum_{i=1}^m \sum_{j=1}^m x_i x_j \frac{\mu_i^2 \mu_j^2}{\sigma_{ij}^3} J_{ij} \quad (138)$$

$$A_3^{dip-dip} = \frac{32\pi^3 N_A^3 \rho^2}{135(kT)^2} \left(\frac{14\pi}{5}\right)^{1/2} \sum_{i=1}^m \sum_{j=1}^m \sum_{k=1}^m x_i x_j x_k \frac{\mu_i^2 \mu_j^2 \mu_k^2}{\sigma_{ij} \sigma_{ik} \sigma_{jk}} K_{ijk} \quad (139)$$

And:

$$A_2^{ind-dip} = -2\pi N_A^2 \rho \sum_{i=1}^m \sum_{j=1}^m x_i x_j \frac{\alpha_j \mu_i^2 + \alpha_i \mu_j^2}{\sigma_{ij}^3} J_{ij} \quad (140)$$

Here N_A is the Avogadro's number, μ_i the dipole moment and α_i the polarizability of the molecule i , k the Boltzmann constant, and J_{ij} and K_{ijk} are the integrals over pair and triple distribution functions of the reference Lennard-Jones fluid. For the Equations (138) to (140), the following combining rules are applied:

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j), \quad \varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2} \quad (141)$$

The mixing rules for the Lennard-Jones contributions are:

$$\sigma_{mix}^3 = \sum_{i=1}^m \sum_{j=1}^m x_i x_j \sigma_{ij}^3 \quad (142)$$

$$\varepsilon_{mix} = \frac{1}{\sigma_{mix}^3} \sum_{i=1}^m \sum_{j=1}^m x_i x_j \varepsilon_{ij} \sigma_{ij}^3 \quad (143)$$

Figure 4 shows calculated fluid-vapor phase equilibria using this EOS for the system H₂O-Xe, H₂O-CH₄ and H₂O-CO₂ in the range between 523-633 K and 0-300 MPa and compares them to interpolated experimental results. For the polar - non-polar systems H₂O-Xe and H₂O-CH₄, the calculated and the experimental results are in good agreement despite using parameters only for pure phase components. Larger deviations are observed for the system H₂O-CO₂, which results from the fact that the EOS does not treat dipole-quadrupole interactions, an important type of interaction in this system. In Figure 5, equilibria of coexisting fluids in the systems H₂O-N₂, H₂O-Ar, and H₂O-CH₄ are plotted for pressures up to 6 GPa and shows that considerable ranges of fluid unmixing is predicted in these systems. Whereas with this EOS, the quality of the calculated properties for the smaller molecules is very good, because of the involvement of only three constants (ε , σ , μ or α) for each phase

component, for complicated molecules these have to be evaluated carefully before being applied.

Figure 4. Subcritical phase relationships in the system a) H_2O -Xe, b) H_2O - CH_4 , and c) H_2O - CO_2 . Lines are calculated isotherms using the EOS by Churakov and Gottschalk (2003a,b). Stippled lines are interpolated experimental results from Welsch (1973), Welsch (1973), Franck et al. (1974) and Shmonov et al. (1993) (H_2O -Xe and H_2O - CH_4) and Tödheide and Frank (1963) (H_2O - CO_2). [Used by permission of Elsevier, from Churakov and Gottschalk (2003), *Geochimica et Cosmochimica Acta*, Vol. 67, Fig. 9, 10 and 11, p. 2422-2423]

Figure 5. Predicted high-pressure phase equilibria, using the EOS by Churakov and Gottschalk (2003a,b) in the systems a) H_2O - N_2 , b) H_2O -Ar, and c) H_2O - CH_4 . [Used by permission of Elsevier, from Churakov and Gottschalk (2003), *Geochimica et Cosmochimica Acta*, Vol. 67, Fig. 12, p. 2423]

CALCULATION OF PHASE EQUILIBRIA

For the compositional evaluation of coexisting fluids the respective phase equilibria have to be calculated. Generally the equilibrium conditions are, that for all phase components the chemical potentials have to be at constant P and T equal in all coexisting phases:

$$\mu_i^I = \mu_i^{II} \quad (144)$$

For binary systems, this is relatively easily accomplished by solving two equations simultaneously. For ternary and higher systems, numerical and practical problems become evident and equilibrium calculations are increasingly difficult.

A better approach and the method of choice is the minimization of the Gibbs free energy. This method is also able to handle saturated solids, i.e. change of fluid bulk compositions can be treated. The development of minimization algorithms is, however, an art itself. Such programs are mostly proprietary to specific scientific groups or available only commercially. Even if such programs are obtained, it is hard if not impossible to adapt them, so that the required EOS can be applied with it. However, a promising minimization approach is that of Karpov et al. (1997), which can be programmed, at least in principle, just using the equations provided in the publication⁷.

CONCLUSIONS

Numerous equations of state are available for mixtures of non-polar and polar fluids, mainly for crustal P and T conditions. For the calculation of fluid equilibria in the mantle even for relatively low T conditions in subducting slabs, the situation becomes much less comfortable. Missing are especially EOS at such conditions which treat salts such as NaCl, KCl, and CaCl₂ as phase components. Furthermore, all the EOS described above treat these salts as undissociated species, which very probably does not describe the real situation. EOS handling total or partially dissociated brines at high P and T do not exist to my knowledge.

At elevated conditions the differences between fluids and melts vanish (see Hack et al. 2007). Fluids and melts become indistinguishable. Thus all major elements become phase components in fluids. An ultimate EOS should handle these. Since the last review in this series by Ferry and Baumgartner (1987) concerning EOS for fluids, the focus has been shifted from deriving EOS by fitting parameters to experimental results to EOS which consider intermolecular interactions directly. The last approaches seems to be promising and with further increase in available computer power more EOS applicable to problems in geosciences can be expected.

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⁷ A free but compiled implementation can be found and downloaded from <http://les.web.psi.ch/Software/GEMS-PSI/>.

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APPENDIX A

Derivations

The thermodynamic treatment of fluids at elevated pressures and temperatures has been laid out in numerous publications (e.g. Gillespie 1925, 1936; Beattie 1930, 1949, 1955, Beattie and Stockmayer 1951). For the derivation of the general accepted forms of the fugacity the so called "general limit method" is used, which avoids basically indefinite integrals¹ if real fluids are handled using ideal gases as a reference model. In most textbooks of physical chemistry the "general limit method" is also used to introduce the term fugacity. While the reasoning and the derived equations are correct, it seems that many students and some teachers misunderstand the logic behind "general limit method", which leads to errors in textbooks, publications, and lecture notes, at least in geosciences. This problem is especially true for the necessary reference and standard conditions of fluids, which requires a sufficient low pressure P^* such that a fluid behaves as an ideal gas. This again makes it sometimes difficult for students to get a grip on the term fugacity.

In my opinion much of the confusion caused by the "general limit method" can be avoided using very similar logic, but rearranging the necessary equations. In addition no assumptions have to be made, but the principal and simple properties of an ideal gas are used directly avoiding the limit considerations. These properties are that the particles have zero volume with no acting intermolecular forces. As the resulting equations defining the fugacity are identical to the "general limit method", some intermediate results may or may not enhance the understanding of the practically used reference and standard conditions. To improve the understanding of the derivation intermediate steps are also included.

Let us start from the definitions of Helmholtz and Gibbs free energies A and G using the inner energy U , the enthalpy H and the entropy S

$$A = U - TS \quad (\text{A1})$$

$$G = H - TS \quad (\text{A2})$$

In the following the partial derivatives of A and G in respect to P and T at constant composition n_i

$$\left(\frac{\partial A}{\partial V} \right)_{T, n_i} = -P \quad (\text{A3})$$

¹ Integrals of the form $\int_0^P V dP$ are indefinite. The volume of a fluid is indefinite at a pressure of 0.

$$\left(\frac{\partial G}{\partial P}\right)_{T,n_i} = V \quad (\text{A4})$$

$$\left(\frac{\partial A}{\partial T}\right)_{V,n_i} = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} = -S \quad (\text{A5})$$

and the chemical potentials μ_i

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{j \neq i}} = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j \neq i}} \quad (\text{A6})$$

are used.

P and T as state variables

First we consider P and T as the state variables. In that case G is the appropriate state function. G as a function of P at constant T is calculated by integrating Equation (A4). The integration constant in Equation (A7) is $G_{(P_r,T)}$ at the respective reference pressure P_r and any T . The usual choice of P_r is 0.1 MPa. For any real system we have:

$$G_{(P,T)} = G_{(P_r,T)} + \int_{P_r}^P V dP \quad (\text{A7})$$

Pure fluids. For the moment, the standard state of a fluid is the real pure fluid phase component. Pure phase components are generally designated by $^\circ$. We will change the standard state for the fluid later, however. For such a real pure fluid i in its standard state, Equation (A7) becomes:

$$G_{i(P,T)}^\circ = G_{i(P_r,T)}^\circ + \int_{P_r}^P V_i^\circ dP \quad (\text{A8})$$

Now the first rearrangement of Equation (A8) uses the ideal gas law, where n_T is the total number of moles ($n_T = \sum n_i$),

$$V = \frac{n_T RT}{P} \quad (\text{A9})$$

by expanding (e.g. Gillespie 1925) the argument in the integral of Equation (A8)

$$G_{i(P,T)}^\circ = G_{i(P_r,T)}^\circ + \int_{P_r}^P \left(V_i^\circ - \frac{n_T RT}{P} \right) dP + \int_{P_r}^P \frac{n_T RT}{P} dP \quad (\text{A10})$$

Within the first integral, the volume of an ideal gas is subtracted, and it must be compensated by the second integral. Now the argument in the first integral describes the deviation of the volume of a real fluid from ideal gas behavior.

The second rearrangement concerns the lower integration boundary of the first integral in Equation (A10). Instead of P_r , the lower boundary is changed to 0, which has to be compensated again, whereas the second integral of Equation (A10) can be solved immediately

$$G_{i(P,T)}^o = G_{i(P_r,T)}^o - \int_0^{P_r} \left(V_i^o - \frac{n_T RT}{P} \right) dP + \int_0^P \left(V_i^o - \frac{n_T RT}{P} \right) dP + n_T RT \ln \frac{P}{P_r} \quad (\text{A11})$$

For pure fluids we have

$$\mu_i^o = \left(\frac{\partial G_i^o}{\partial n_i} \right)_{P,T} = \frac{G_i^o}{n_T} = g_i^o \quad (\text{A12})$$

and we get a molar quantity (molar quantities are designated here by small letters) which we can either designate as $\mu_{i(P,T)}^o$ or $g_{i(P,T)}^o$:

$$\mu_{i(P,T)}^o = g_{i(P,T)}^o = \mu_{i(P_r,T)}^o - \int_0^{P_r} \left(v_i^o - \frac{RT}{P} \right) dP + \int_0^P \left(v_i^o - \frac{RT}{P} \right) dP + RT \ln \frac{P}{P_r} \quad (\text{A13})$$

In Equation (A13), we have an infinite integral by the means of Gillespie (the lower integration boundary is 0), but which has a finite value and, therefore, is harmless and solvable if we have an EOS. Equation (A13) provides the definition of the fugacity coefficient for a pure fluid:

$$RT \ln \phi_{i(P,T)}^o = \int_0^P \left(v_i^o - \frac{RT}{P} \right) dP \quad (\text{A14})$$

Equation (A14) defines the fugacity coefficient at any pressure dependent only on the upper integration boundary, either P or P_r in Equation (A13). It is important to note that for the derivation of Equation (A14), no assumptions were necessary and no general limits have to be considered but the ideal gas law *per se*.

As in Equation (A13) we can also write

$$\mu_{i(P_r,T)}^o = g_{i(P_r,T)}^o \quad (\text{A15})$$

which leads with Equation (A14) to:

$$\mu_{i(P,T)}^o = g_{i(P_r,T)}^o - RT \ln \phi_{i(P_r,T)}^o + RT \ln \phi_{i(P,T)}^o + RT \ln \frac{P}{P_r} \quad (\text{A16})$$

Now we come to the reconsideration of the standard state. The second term of the right-hand side of Equation (A16) is the term which includes the fugacity coefficient of the fluid at T and reference pressure P_r . At a pressure of 0, it is possible to treat any fluid like an ideal gas, because neither the particle volume nor intermolecular forces play a role as the particle distances are infinite. If we recapitulate that this term represents the sum (integral) of deviations from a pure real fluid and a pure ideal gas, then the

difference of the first two terms in Equation (A16) are the thermodynamic properties of an ideal gas $g_{i(P_r, T)}^{o*}$. Ideal gas properties are designated by an asterisk.*

$$g_{i(P_r, T)}^{o*} = g_{i(P_r, T)}^o - RT \ln \phi_{i(P_r, T)}^o \quad (\text{A17})$$

In other words, if we know the thermodynamic ideal gas properties of a pure phase component and are able to calculate the fugacity coefficient at P_r (having an EOS) we know the properties of the real fluid at P_r or any other P . Most thermodynamic ideal gas properties can be obtained using, for example, *ab initio* calculations and molecular simulations. Because of the lack of intermolecular forces only single-particle properties and velocity distributions have to be considered to evaluate the inner energy u_i^{o*} and the heat capacity $c_{P,i}^{o*}$. The partitioning function or g_i^{o*} has to be calculated to obtain the entropy s_i^{o*} . For any fluid phase component, it is convenient to choose the ideal gas as its standard state. In addition, because $g_{i(P, T)}^{o*}$ in Equation (A17) is a corrected term and not a real quantity, this special choice is also called the standard state of an *hypothetical ideal gas*. As for solids the reference conditions are usually 0.1 MPa and 298.15 K.

Using Equation (A17) we can also write for Equation (A16)

$$\mu_{i(P, T)}^o = g_{i(P_r, T)}^{o*} + RT \ln \frac{\phi_{i(P, T)}^o P}{P_r} \quad (\text{A18})$$

or with Equation (A2):

$$\mu_{i(P, T)}^o = h_{i(P_r, T)}^{o*} - T s_{i(P_r, T)}^{o*} + RT \ln \frac{\phi_{i(P, T)}^o P}{P_r} \quad (\text{A19})$$

Knowing the heat capacity of the *hypothetical ideal gas* $c_{P,i}^{o*}$ as a function of T any chemical potential $\mu_{i(P, T)}^o$ can be calculated provided that we have an EOS

$$\mu_{i(P, T)}^o = h_{i(P_r, T_r)}^{o*} + \int_{T_r}^T c_{P,i}^{o*} dT - T \left(s_{i(P_r, T_r)}^{o*} + \int_{T_r}^T \frac{c_{P,i}^{o*}}{T} dT \right) + RT \ln \frac{\phi_{i(P, T)}^o P}{P_r} \quad (\text{A20})$$

Fluid mixtures. Instead of the molar quantity of pure fluids in Equation (A18) we can also write in general:

$$G_{i(P, T)}^o = G_{i(P_r, T)}^{o*} + \int_0^P \left(V_i^o - \frac{n_T RT}{P} \right) dP + n_T RT \ln \frac{P}{P_r} \quad (\text{A21})$$

If we consider mixtures this equation alters to

$$G_{(P, T)} = G_{(P_r, T)}^* + \int_0^P \left(V - \frac{n_T RT}{P} \right) dP + n_T RT \ln \frac{P}{P_r} \quad (\text{A22})$$

in which the pure are replaced by the mixed properties. If we recapitulate that $G_{i(P_r, T)}^*$ is then the property of a mixture of ideal gases we get

$$G_{(P, T)} = \sum_i n_i \left(g_{i(P_r, T)}^{o*} + RT \ln x_i \right) + \int_0^P \left(V - \frac{n_r RT}{P} \right) dP + n_r RT \ln \frac{P}{P_r}. \quad (A23)$$

Because of the missing intermolecular forces, no volume of mixing occurs and we have to consider only the ideal entropy of mixing $\left(\sum_i n_i RT \ln x_i \right)$. It is convenient to incorporate the entropy of mixing in to the last term of Equation (A23)

$$G_{(P, T)} = \sum_i n_i g_{i(P_r, T)}^{o*} + \int_0^P \left(V - \frac{n_r RT}{P} \right) dP + RT \sum_i n_i \ln \frac{x_i P}{P_r}. \quad (A24)$$

Differentiation using Equation (A6) gets the respective μ_i for each component i :

$$\mu_{i(P, T)} = g_{i(P_r, T)}^{o*} + \int_0^P \left(\left(\frac{\partial V}{\partial n_i} \right)_{P, T, n_{j \neq i}} - \frac{RT}{P} \right) dP + RT \ln \frac{x_i P}{P_r} \quad (A25)$$

So the fugacity coefficient ϕ_i^m in the mixture is defined as:

$$RT \ln \phi_{i(P, T)}^m = \int_0^P \left(\left(\frac{\partial V}{\partial n_i} \right)_{P, T, n_{j \neq i}} - \frac{RT}{P} \right) dP \quad (A26)$$

The evaluation of $\phi_{i(P, T)}^m$ requires an EOS but now for fluid mixtures. Using Equation (A26) and we get the general expression:

$$\mu_{i(P, T)} = g_{i(P_r, T)}^{o*} + RT \ln \frac{x_i \phi_{i(P, T)}^m P}{P_r} \quad (A27)$$

Or:

$$\mu_{i(P, T)} = h_{i(P_r, T)}^{o*} - Ts_{i(P_r, T)}^{o*} + RT \ln \frac{x_i \phi_{i(P, T)}^m P}{P_r} \quad (A28)$$

With the definition of the fugacity

$$f_{i(P, T)}^m = x_i \phi_{i(P, T)}^m P \quad (A29)$$

we get

$$\mu_{i(P, T)} = h_{i(P_r, T)}^{o*} - Ts_{i(P_r, T)}^{o*} + RT \ln \frac{f_{i(P, T)}^m}{P_r} \quad (A30)$$

As a result also the following relations also hold for the activity coefficient γ_i and activity a_i :

$$f_{i(P,T)}^o = \phi_{i(P,T)}^o P \quad (\text{A31})$$

$$\phi_{i(P,T)}^m = \gamma_i \phi_{i(P,T)}^o \quad (\text{A32})$$

$$f_{i(P,T)}^m = a_i f_{i(P,T)}^o \quad (\text{A33})$$

Again, for the definition of the fugacity coefficient of a phase component in a fluid mixture no other prerequisite than the ideal gas definition is needed.

V and T as state variables

Because most EOS are explicit in P instead of V , the Helmholtz free energy has to be used to calculate μ_i . The line of arguments is, however, identical to the one given for the Gibbs free energy. The dependence of A on V is given by integrating (A3):

$$A_{(V,T)} = A_{(V_r,T)} - \int_{V_r}^V P dV \quad (\text{A34})$$

Pure fluids. Expanding Equation (A34) using the ideal gas law for a pure phase component we get:

$$A_{i(V,T)}^o = A_{i(V_r,T)}^o - \int_{V_r^o}^{V^o} \left(P - \frac{n_T RT}{V} \right) dV - \int_{V_r^o}^{V^o} \frac{n_T RT}{V} dV \quad (\text{A35})$$

Splitting the first integral by expanding the upper integration boundary to infinity² and solving the second we get:

$$A_{i(V,T)}^o = A_{i(V_r,T)}^o - \int_{V_r^o}^{\infty} \left(P - \frac{n_T RT}{V} \right) dV + \int_{V^o}^{\infty} \left(P - \frac{n_T RT}{V} \right) dV - n_T RT \ln \frac{V_i^o}{V_{i,r}^o} \quad (\text{A36})$$

With V_r for an *hypothetical ideal gas* at reference conditions

$$V_{i,r}^o = \frac{n_T RT}{P_r} \quad (\text{A37})$$

we get

$$A_{i(V,T)}^o = A_{i(V_r,T)}^o - \int_{V_r^o}^{\infty} \left(P - \frac{n_T RT}{V} \right) dV + \int_{V^o}^{\infty} \left(P - \frac{n_T RT}{V} \right) dV - n_T RT \ln \frac{P_r V_i^o}{n_T RT} \quad (\text{A38})$$

or with $v_i^o = V_i^o/n_T$ and going to the standard state of a *hypothetical ideal gas*

² The lower and the higher integration boundaries are switched; therefore, the sign changes.

$$A_{i(V,T)}^o = A_{i(V_r,T)}^{o*} + \int_{V_i^o}^{\infty} \left(P - \frac{n_T RT}{V} \right) dV - n_T RT \ln \frac{P_r V_i^o}{RT} \quad (\text{A39})$$

Using

$$G_{i(P,T)}^{o*} = A_{i(V,T)}^{o*} + P V_i^{o*} \quad (\text{A40})$$

results in:

$$G_{i(P,T)}^o = A_{i(V_r,T)}^{o*} + \int_{V_i^o}^{\infty} \left(P - \frac{n_T RT}{V} \right) dV - n_T RT \ln \frac{P_r V_i^o}{RT} + P V_i^o \quad (\text{A41})$$

Now for a pure fluid μ_i we have

$$\mu_i^0 = \frac{G_i^0}{n_T} = g_i^0 \quad (\text{A42})$$

and Equation (A41) can be expressed by

$$g_{i(P,T)}^o = u_{i(V_r,T)}^{o*} - T s_{i(V_r,T)}^{o*} + \int_{V_i^o}^{\infty} \left(\frac{P}{n_T} - \frac{RT}{V} \right) dV - RT \ln \frac{P_r V_i^o}{RT} + P V_i^o \quad (\text{A43})$$

To extract $\varphi_{i(V,T)}^o$, we have to transform Equation (A43) a bit further. For an ideal gas we can write ($Pv=RT$)

$$h_i^{o*} = u_i^{o*} + RT \quad (\text{A44})$$

and therefore we have:

$$g_{i(P,T)}^o = h_{i(P_r,T)}^{o*} - T s_{i(P_r,T)}^{o*} + \int_{V_i^o}^{\infty} \left(\frac{P}{n_T} - \frac{RT}{V} \right) dV - RT \ln \frac{P_r V_i^o}{RT} + P V_i^o - RT \quad (\text{A45})$$

Expanding with $RT \ln(P/P_r)$ we get:

$$g_{i(P,T)}^o = h_{i(P_r,T)}^{o*} - T s_{i(P_r,T)}^{o*} + \int_{V_i^o}^{\infty} \left(\frac{P}{n_T} - \frac{RT}{V} \right) dV - RT \ln \frac{P V_i^o}{RT} + P V_i^o - RT + RT \ln \frac{P}{P_r} \quad (\text{A46})$$

With the general definition of z

$$z = \frac{Pv}{RT} \quad (\text{A47})$$

we have:

$$g_{i(P,T)}^o = h_{i(P_r,T)}^{o*} - T s_{i(P_r,T)}^{o*} + \int_{V_i^o}^{\infty} \left(\frac{P}{n_T} - \frac{RT}{V} \right) dV - RT \ln z + RT(z-1) + RT \ln \frac{P}{P_r} \quad (\text{A48})$$

From Equation (A48) we get the fugacity coefficient of a pure phase component as a function of V and T

$$\phi_{i(V,T)}^o = \int_{V_i^o}^{\infty} \left(\frac{P}{n_T} - \frac{RT}{V} \right) dV - RT \ln z + RT(z-1). \quad (\text{A49})$$

Fluid mixtures. As in (A23) for mixtures we get:

$$A_{(V,T)} = \sum_i n_i \left(a_{i(V_r,T)}^{o*} + RT \ln x_i \right) + \int_V^{\infty} \left(P - \frac{n_T RT}{V} \right) dV - n_T RT \ln \frac{V}{V_r} \quad (\text{A50})$$

As for the pure fluid, in the following some transformations of Equation (A50) are performed, which have the purpose of obtaining an expression for μ_i as a function of P and T , so the derived values are compatible with thermodynamic properties with other phase components, e.g. solids. With V_r for an *hypothetical ideal gas* mixture at reference conditions

$$V_r = \frac{n_T RT}{P_r} \quad (\text{A51})$$

we get:

$$A_{(V,T)} = \sum_i n_i \left(a_{i(V_r,T)}^{o*} + RT \ln x_i \right) + \int_V^{\infty} \left(P - \frac{n_T RT}{V} \right) dV - n_T RT \ln \frac{P_r V}{n_T RT} \quad (\text{A52})$$

Incorporation of the ideal mixing entropy into the last term of Equation (A52)

$$A_{(V,T)} = \sum_i n_i a_{i(V_r,T)}^{o*} + \int_V^{\infty} \left(P - \frac{n_T RT}{V} \right) dV - RT \sum_i n_i \ln \frac{P_r V}{x_i n_T RT} \quad (\text{A53})$$

and replacing the mole fraction x_i by its definition (n_i/n_T) we get:

$$A_{(V,T)} = \sum_i n_i a_{i(V_r,T)}^{o*} + \int_V^{\infty} \left(P - \frac{n_T RT}{V} \right) dV - RT \sum_i n_i \ln \frac{P_r V}{n_i RT} \quad (\text{A54})$$

By applying Equation (A6) we have the expression for the chemical potential

$$\mu_{i(V,T)} = a_{i(V_r,T)}^{o*} + \int_V^{\infty} \left(\left(\frac{\partial P}{\partial n_i} \right)_{V,T,n_{i \neq j}} - \frac{RT}{V} \right) dV - RT \ln \frac{P_r V}{n_i RT} + RT \quad (\text{A55})$$

Or:

$$\mu_{i(V,T)} = \mu_{i(P,T)} = u_{i(V_r,T)}^{o*} + RT - Ts_{i(V_r,T)}^{o*} + \int_V^{\infty} \left(\left(\frac{\partial P}{\partial n_i} \right)_{V,T,n_{i \neq j}} - \frac{RT}{V} \right) dV - RT \ln \frac{P_r V}{n_i RT} \quad (\text{A56})$$

Applying Equation (A44) we get:

$$\mu_{i(P,T)} = h_{i(P_r,T)}^{o*} - Ts_{i(P_r,T)}^{o*} + \int_V^\infty \left(\left(\frac{\partial P}{\partial n_i} \right)_{V,T,n_{i \neq j}} - \frac{RT}{V} \right) dV - RT \ln \frac{P_r V}{n_i RT} \quad (\text{A57})$$

Expanding with $RT \ln(P/P_r)$ and n_T

$$\mu_{i(P,T)} = h_{i(P_r,T)}^{o*} - Ts_{i(P_r,T)}^{o*} + \int_V^\infty \left(\left(\frac{\partial P}{\partial n_i} \right)_{V,T,n_{i \neq j}} - \frac{RT}{V} \right) dV - RT \ln \frac{n_T P_r V}{n_T n_i RT} + RT (\ln P - \ln P_r) \quad (\text{A58})$$

and inserting the mole fraction x_i and the molar volume $v=V/n_T$ we get:

$$\mu_{i(P,T)} = h_{i(P_r,T)}^{o*} - Ts_{i(P_r,T)}^{o*} + \int_V^\infty \left(\left(\frac{\partial P}{\partial n_i} \right)_{V,T,n_{i \neq j}} - \frac{RT}{V} \right) dV - RT \ln \frac{Pv}{RT} + RT \ln \frac{x_i P}{P_r} \quad (\text{A59})$$

Using Equation (A47) results in:

$$\mu_{i(P,T)} = h_{i(P_r,T)}^{o*} - Ts_{i(P_r,T)}^{o*} + \int_V^\infty \left(\left(\frac{\partial P}{\partial n_i} \right)_{V,T,n_{i \neq j}} - \frac{RT}{V} \right) dV - RT \ln z + RT \ln \frac{x_i P}{P_r} \quad (\text{A60})$$

From (A60) we have the definition for the fugacity coefficient for the case that the EOS needs V and T as state variables

$$RT \ln \phi_{i(V,T)} = \int_V^\infty \left(\left(\frac{\partial P}{\partial n_i} \right)_{V,T,n_{i \neq j}} - \frac{RT}{V} \right) dV - RT \ln z \quad (\text{A61})$$

As in Equation (A30), we can also write

$$\mu_{i(P,T)} = h_{i(P_r,T)}^{o*} - Ts_{i(P_r,T)}^{o*} + RT \ln \frac{x_i \phi_{i(V,T)} P}{P_r} \quad (\text{A62})$$

or with Equation (A29)

$$\mu_{i(P,T)} = h_{i(P_r,T)}^{o*} - Ts_{i(P_r,T)}^{o*} + RT \ln \frac{f_{i(V,T)}}{P_r} \quad (\text{A63})$$

Again, the only prerequisite for the definition of the fugacity coefficient is the ideal gas law. Identical relationships as in Equations (A31)-(A33) can be formulated by just replacing P by V in the subscript.

v and T as state variables

In some cases it is convenient to use molar quantities and mole fractions in the formulation of an EOS. In that case, a slightly different method can be used to calculate $\phi_{i(V,T)}$. Let us start with a slightly different form of Equation (A53)

$$A_{(V,T,n)} = \sum_i n_i a_{i(v_r,T)}^{o*} + n_T \int_v^\infty \left(P - \frac{RT}{v} \right) dv - RT \sum_i n_i \ln \frac{P_r v}{x_i RT} \quad (A64)$$

and make it molar by dividing by the total number of moles n_T

$$\frac{A_{(V,T,n)}}{n_T} = a_{(v,T,x)} = \sum_i x_i a_{i(v_r,T)}^{o*} + \int_v^\infty \left(P - \frac{RT}{v} \right) dv - RT \sum_i x_i \ln \frac{P_r v}{x_i RT} \quad (A65)$$

It is obvious that:

$$A_{(V,T,n)} = n_T a_{(v,T,x)} \quad (A66)$$

Here the molar Helmholtz free energy $a_{(v,T,x)}$ is a function of v , T , and x instead of V , T , and n . Now instead of differentiating the left side of Equation (A66), we use the right hand side and apply the product rule

$$\left(\frac{\partial A_{(V,T,n)}}{\partial n_i} \right)_{V,T,n_{j \neq i}} = \mu_{i(V,T,n)} = \left(\frac{\partial n_T a_{(v,T,x)}}{\partial n_i} \right)_{V,T,n_{j \neq i}} = a_{(v,T,x)} + n_T \left(\frac{\partial a_{(v,T,x)}}{\partial n_i} \right)_{V,T,n_{j \neq i}} \quad (A67)$$

Because x as well as v^3 are functions of n we have to apply the general chain rule for the differentiation:

$$\mu_{i(V,T,n)} = a_{(v,T,x)} + n_T \sum_j \left(\frac{\partial a_{(v,T,x)}}{\partial x_j} \right)_{v,T,x_{k \neq j}} \left(\frac{\partial x_j}{\partial n_i} \right)_{n_{k \neq i}} + n_T \left(\frac{\partial a_{(v,T,x)}}{\partial v} \right)_{T,x} \left(\frac{\partial v}{\partial n_i} \right)_{n_{k \neq i}} \quad (A68)$$

Inserting the appropriate definitions for x and v we have:

$$\mu_{i(V,T,n)} = a_{(v,T,x)} + \left(\frac{\partial a_{(v,T,x)}}{\partial x_i} \right)_{v,T,x_{k \neq i}} - \sum_j x_j \left(\frac{\partial a_{(v,T,x)}}{\partial x_j} \right)_{n_{k \neq j}} - n_T \left(\frac{\partial a_{(v,T,x)}}{\partial v} \right) \frac{v}{n_T} \quad (A69)$$

Equation (A65) can be split into an *ideal* and an *excess* term:

$$\mu_{i(V,T,n)} = \left(\frac{\partial A_{(V,T,n)}^{ideal}}{\partial n_i} \right)_{V,T,n_{j \neq i}} + \left(\frac{\partial A_{(V,T,n)}^{excess}}{\partial n_i} \right)_{V,T,n_{j \neq i}} \quad (A70)$$

Or:

³ V is the relevant thermodynamic variable and $v=V/n_T$.

$$\mu_{i(V,T,n)} = a_{i(v,T,x)}^{ideal} + a_{i(v,T,x)}^{excess} + n_T \left(\frac{\partial a_{i(v,T,x)}^{ideal}}{\partial n_i} \right)_{V,T,n_{j \neq i}} + \left(\frac{\partial a_{i(v,T,x)}^{excess}}{\partial n_i} \right)_{V,T,n_{j \neq i}} \quad (A71)$$

The *ideal* term handles the terms which use only ideal gas properties

$$\left(\frac{\partial A_{(V,T,n)}^{ideal}}{\partial n_i} \right)_{V,T,n_{j \neq i}} = a_{i(v,T,x)}^{o*} + RT \ln x_i - RT \ln \frac{P_r v}{RT} + RT \quad (A72)$$

and the excess term the rest dealing with the real properties, the integral in Equation (A65)

$$\left(\frac{\partial A_{(V,T,n)}^{excess}}{\partial n_i} \right)_{V,T,n_{j \neq i}} = a^{excess} + \left(\frac{\partial a^{excess}}{\partial x_i} \right) - \sum_j x_j \left(\frac{\partial a^{excess}}{\partial x_j} \right) + Pv - RT \quad (A73)$$

With:

$$a^{excess} = \int_v^\infty \left(P - \frac{RT}{v} \right) dv \quad (A74)$$

Equations (A72) and (A73) both use Equation (A69). So we have:

$$\begin{aligned} \mu_{i(V,T,n)} &= a_{i(v,T,x)}^{o*} + RT \ln x_i - RT \ln \frac{P_r v}{RT} + RT \\ &+ a^{excess} + \left(\frac{\partial a^{excess}}{\partial x_i} \right) - \sum_j x_j \left(\frac{\partial a^{excess}}{\partial x_j} \right) + Pv - RT \end{aligned} \quad (A75)$$

If we expand again with $RT \ln(P/P)$ and use Equation (A44) we get:

$$\begin{aligned} \mu_{i(V,T,n)} &= h_{i(v,T,x)}^{o*} - Ts_{i(v,T,x)}^{o*} + RT \ln x_i + RT \ln \frac{P}{P_r} \\ &+ a^{excess} + \left(\frac{\partial a^{excess}}{\partial x_i} \right) - \sum_j x_j \left(\frac{\partial a^{excess}}{\partial x_j} \right) - RT \ln z + Pv - RT \end{aligned} \quad (A76)$$

With the definition of z the fugacity coefficient $\phi_{i(v,T,x)}^m$ is defined as:

$$RT \ln \phi_{i(v,T,x)}^m = a^{excess} + \left(\frac{\partial a^{excess}}{\partial x_i} \right) - \sum_j x_j \left(\frac{\partial a^{excess}}{\partial x_j} \right) - RT \ln z + RT(z - 1) \quad (A77)$$

Or just as:

$$RT \ln \phi_{i(v,T,x)}^m = \left(\frac{\partial n_T a^{excess}}{\partial n_i} \right)_{v,T,n_{j \neq i}} - RT \ln z + RT(z - 1) \quad (A78)$$

ρ and T as state variables

In some cases the molar density ρ is used instead of v . In this case V is readily replaced by ρ :

$$V = \frac{n_T}{\rho} \quad (\text{A79})$$

And:

$$\frac{\partial V}{\partial \rho} = -\frac{n_T}{\rho^2} \quad (\text{A80})$$

As in Equation (A64)

$$A_{(V,T,n)} = \sum_i n_i a_{i(\rho,T)}^{o*} + n_T \int_0^\rho \frac{P - \rho RT}{\rho^2} d\rho - RT \sum_i n_i \ln \frac{P_r}{x_i \rho RT} \quad (\text{A81})$$

and make it molar by dividing by the total number of moles n_T

$$\frac{A_{(V,T,n)}}{n_T} = a_{(v,T,x)} = \sum_i x_i a_{i(\rho,T)}^{o*} + \int_0^\rho \frac{P - RT \rho}{\rho^2} d\rho - RT \sum_i x_i \ln \frac{P_r}{x_i \rho RT} \quad (\text{A82})$$

Because x as well as ρ are again functions of n :

$$\mu_{i(V,T,n)} = a_{(\rho,T,x)} + n_T \sum_j \left(\frac{\partial a_{(\rho,T,x)}}{\partial x_j} \right)_{v,T,x_{k \neq j}} \left(\frac{\partial x_j}{\partial n_i} \right)_{n_{k \neq i}} + n_T \left(\frac{\partial a_{(\rho,T,x)}}{\partial \rho} \right)_{T,x} \left(\frac{\partial \rho}{\partial n_i} \right)_{n_{k \neq i}} \quad (\text{A83})$$

Inserting the appropriate definitions for x and v , we have:

$$\mu_{i(V,T,n)} = a_{(\rho,T,x)} + \left(\frac{\partial a_{(\rho,T,x)}}{\partial x_i} \right)_{v,T,x_{k \neq i}} - \sum_j x_j \left(\frac{\partial a_{(\rho,T,x)}}{\partial x_j} \right)_{n_{k \neq j}} - n_T \left(\frac{\partial a_{(\rho,T,x)}}{\partial v} \right) \frac{\rho}{n_T} \quad (\text{A84})$$

The *ideal* term handles the terms which use only ideal gas properties

$$\left(\frac{\partial A_{(V,T,n)}^{ideal}}{\partial n_i} \right)_{V,T,n_{j \neq i}} = a_{i(\rho,T,x)}^{o*} + RT \ln x_i - RT \ln \frac{P_r}{\rho RT} + RT \quad (\text{A85})$$

and the excess term handles the rest dealing with the real properties

$$\left(\frac{\partial A_{(V,T,n)}^{excess}}{\partial n_i} \right)_{V,T,n_{j \neq i}} = \int_0^\rho \frac{P - RT \rho}{\rho^2} d\rho + \left(\frac{\partial a_{(V,T,n)}^{excess}}{\partial x_i} \right) - \sum_j x_j \left(\frac{\partial a_{(V,T,n)}^{excess}}{\partial x_j} \right) + \frac{P}{\rho} - RT \quad (\text{A86})$$

With:

$$a^{excess} = \int_0^{\rho} \frac{P - RT\rho}{\rho^2} d\rho \quad (\text{A87})$$

Equations (A85) and (A86) both use Equation (A84). So we have:

$$\begin{aligned} \mu_{i(V,T,n)} &= a_{i(\rho,T,x)}^{o*} + RT \ln x_i - RT \ln \frac{P_r}{\rho RT} + RT \\ &+ a^{excess} + \left(\frac{\partial a^{excess}}{\partial x_i} \right) - \sum_j x_j \left(\frac{\partial a^{excess}}{\partial x_j} \right) + \frac{P}{\rho} - RT \end{aligned} \quad (\text{A88})$$

If we expand again with $RT \ln(P/P)$ and use (A44) we get:

$$\begin{aligned} \mu_{i(V,T,n)} &= h_{i(\rho,T,x)}^{o*} - Ts_{i(\rho,T,x)}^{o*} + RT \ln x_i + RT \ln \frac{P}{P_r} \\ &+ a^{excess} + \left(\frac{\partial a^{excess}}{\partial x_i} \right) - \sum_j x_j \left(\frac{\partial a^{excess}}{\partial x_j} \right) - RT \ln z + \frac{P}{\rho} - RT \end{aligned} \quad (\text{A89})$$

With the definition of z the fugacity coefficient $\phi_{i(\rho,T,x)}^m$ is defined as:

$$RT \ln \phi_{i(\rho,T,x)}^m = a^{excess} + \left(\frac{\partial a^{excess}}{\partial x_i} \right) - \sum_j x_j \left(\frac{\partial a^{excess}}{\partial x_j} \right) - RT \ln z + RT(z-1) \quad (\text{A90})$$

U , H , and S as a function of the state variables V , P and T

In some cases we need the properties U , H , and S as a function of the state variables for a fluid. The following partial derivatives are required

$$\left(\frac{\partial S}{\partial V} \right)_{T,n_i} = \left(\frac{\partial P}{\partial T} \right)_{V,n_i} = - \left(\frac{\partial^2 G}{\partial T \partial V} \right)_{n_i} \quad (\text{A91})$$

$$\left(\frac{\partial S}{\partial P} \right)_{T,n_i} = - \left(\frac{\partial V}{\partial T} \right)_{P,n_i} = - \left(\frac{\partial^2 G}{\partial T \partial P} \right)_{n_i} \quad (\text{A92})$$

$$\left(\frac{\partial U}{\partial V} \right)_{T,n_i} = -P + T \left(\frac{\partial P}{\partial T} \right)_{V,n_i} \quad (\text{A93})$$

$$\left(\frac{\partial H}{\partial P} \right)_{T,n_i} = V - T \left(\frac{\partial V}{\partial T} \right)_{P,n_i} \quad (\text{A94})$$

U as function of V and T . Integration of (A93) gives:

$$U_{(V,T)} = U_{(V_r,T)} + \int_{V_r}^V \left(-P + T \left(\frac{\partial P}{\partial T} \right)_{V,n_i} \right) dV \quad (\text{A95})$$

For an ideal gas:

$$\left(\frac{\partial P}{\partial T}\right)_{V,n_i} = \frac{n_T R}{V} \quad (\text{A96})$$

As a result, the integral in (A95) is zero for an ideal gas and therefore U is in this case not a function of V . This behavior is understandable, because there is no intermolecular interaction between particles. Expansion of Equation (A95), and splitting the term into an ideal gas and a deviation part like in Equation (A10) is, therefore, not necessary

$$\int_{V_r}^V \left(-P + T \left(\frac{\partial P}{\partial T}\right)_{V,n_i}\right)_{\text{ideal gas}} dV = \int_{V_r}^V \left(-\frac{n_T RT}{V} + \frac{n_T RT}{V}\right) dV = 0 \quad (\text{A97})$$

However, expansion of the integration boundaries is again useful

$$U_{(V_r,T)} = U_{(V,T)} + \int_{V_r}^{\infty} \left(-P + T \left(\frac{\partial P}{\partial T}\right)_{V,n_i}\right) dV - \int_V^{\infty} \left(-P + T \left(\frac{\partial P}{\partial T}\right)_{V,n_i}\right) dV \quad (\text{A98})$$

Combination of the first two terms of the right hand side of Equation (A98) yields U for a *hypothetical ideal gas*. In addition, for an ideal gas mixture, there is no excess U

$$U_{(V_r,T)} = U_{(V_r,T)}^{o*} + \int_{V_r}^{\infty} \left(P - T \left(\frac{\partial P}{\partial T}\right)_{V,n_i}\right) dV \quad (\text{A99})$$

$$U_{(V_r,T)} = \sum_i n_i u_{i(V_r,T)}^{o*} + \int_{V_r}^{\infty} \left(P - T \left(\frac{\partial P}{\partial T}\right)_{V,n_i}\right) dV \quad (\text{A100})$$

H as function of P and T . Integration of (A94) gives:

$$H_{(P,T)} = H_{(P_r,T)} + \int_{P_r}^P \left(V - T \left(\frac{\partial V}{\partial T}\right)_{P,n_i}\right) dP \quad (\text{A101})$$

For an ideal gas:

$$\left(\frac{\partial V}{\partial T}\right)_{P,n_i} = \frac{n_T R}{P} \quad (\text{A102})$$

As shown in (A103) the integral in (A101) is zero and H for an ideal gas is not a function of P

$$\int_{P_r}^P \left(V - T \left(\frac{\partial V}{\partial T}\right)_{P,n_i}\right)_{\text{ideal gas}} dP = \int_{P_r}^P \left(\frac{n_T RT}{P} - \frac{n_T RT}{P}\right) dP = 0 \quad (\text{A103})$$

Expanding the lower integration boundary we get:

$$H_{(P,T)} = H_{(P_r,T)} - \int_0^{P_r} \left(V - T \left(\frac{\partial V}{\partial T} \right)_{P,n_i} \right) dP + \int_0^P \left(V - T \left(\frac{\partial V}{\partial T} \right)_{P,n_i} \right) dP \quad (\text{A104})$$

Combination of the first two terms of the right hand side of (A104) yields H for a *hypothetical ideal gas*. In addition, for an ideal gas mixture there is no excess H

$$H_{(P_r,T)} = H_{(P_r,T)}^{o*} + \int_0^{P_r} \left(V - T \left(\frac{\partial V}{\partial T} \right)_{P,n_i} \right) dP \quad (\text{A105})$$

$$H_{(P_r,T)} = \sum_i n_i h_{i(P_r,T)}^{o*} + \int_0^{P_r} \left(V - T \left(\frac{\partial V}{\partial T} \right)_{P,n_i} \right) dP \quad (\text{A106})$$

S as function of V and T. For simplicity, we consider first a pure phase component i . Integration of (A91) yields

$$S_{i(V,T)}^o = S_{i(V_r,T)}^o + \int_{V_r}^V \left(\frac{\partial P}{\partial T} \right)_{V,n_i} dV \quad (\text{A107})$$

Expansion in an ideal gas and an deviation term:

$$S_{i(V,T)}^o = S_{i(V_r,T)}^o + \int_{V_r}^V \left(\left(\frac{\partial P}{\partial T} \right)_{V,n_i} - \frac{n_T R}{V} \right) dV + \int_{V_r}^V \frac{n_T R}{V} dV \quad (\text{A108})$$

Solving the last integral in (A108):

$$S_{i(V,T)}^o = S_{i(V_r,T)}^o + \int_{V_r}^V \left(\left(\frac{\partial P}{\partial T} \right)_{V,n_i} - \frac{n_T R}{V} \right) dV + n_T R \ln \frac{V}{V_r} \quad (\text{A109})$$

Extending the lower integration limit:

$$S_{i(V,T)}^o = S_{i(V_r,T)}^o + \int_{V_r}^{\infty} \left(\left(\frac{\partial P}{\partial T} \right)_{V,n_i} - \frac{n_T R}{V} \right) dV - \int_V^{\infty} \left(\left(\frac{\partial P}{\partial T} \right)_{V,n_i} - \frac{n_T R}{V} \right) dV + n_T R \ln \frac{V}{V_r} \quad (\text{A110})$$

The first two terms of (A110) are the S of an pure *hypothetical ideal gas*. If the system is a mixture ideal mixing entropy has to be added

$$S_{(V,T)} = \sum_i n_i S_{i(V_r,T)}^{o*} - \int_V^{\infty} \left(\left(\frac{\partial P}{\partial T} \right)_{V,n_i} - \frac{n_T R}{V} \right) dV + n_T R \ln \frac{V}{V_r} - R \sum_i n_i \ln x_i \quad (\text{A111})$$

S as function of P and T. Integration of (A92) again, for pure phase component yields:

$$S_{i(P,T)}^o = S_{i(P_r,T)}^o - \int_{P_r}^P \left(\frac{\partial V}{\partial T} \right)_{P,n_i} dP \quad (\text{A112})$$

Expansion in an ideal gas and a deviation term:

$$S_{i(P,T)}^o = S_{i(P_r,T)}^o - \int_{P_r}^P \left(\left(\frac{\partial V}{\partial T} \right)_{P,n_i} - \frac{n_T R}{P} \right) dP - \int_{P_r}^P \frac{n_T R}{P} dP \quad (\text{A113})$$

Solving the last integral in (A113):

$$S_{i(P,T)}^o = S_{i(P_r,T)}^o - \int_{P_r}^P \left(\left(\frac{\partial V}{\partial T} \right)_{P,n_i} - \frac{n_T R}{P} \right) dP - n_T R \ln \frac{P}{P_r} \quad (\text{A114})$$

Extending the lower integration limit:

$$S_{i(P,T)}^o = S_{i(P_r,T)}^o + \int_0^{P_r} \left(\left(\frac{\partial V}{\partial T} \right)_{P,n_i} - \frac{n_T R}{P} \right) dP - \int_0^P \left(\left(\frac{\partial V}{\partial T} \right)_{P,n_i} - \frac{n_T R}{P} \right) dP - n_T R \ln \frac{P}{P_r} \quad (\text{A115})$$

The first two terms of (A110) are the S of a pure *hypothetical ideal gas*. If the system is a mixture ideal mixing entropy has to be added

$$S_{i(P,T)} = S_{i(P,T)}^{o*} - \int_0^P \left(\left(\frac{\partial V}{\partial T} \right)_{P,n_i} - \frac{n_T R}{P} \right) dP - n_T R \ln \frac{P}{P_r} - R \sum_j n_j \ln x_j \quad (\text{A116})$$

$$S_{i(P,T)} = \sum_i n_i S_{i(P,T)}^{o*} - \int_0^P \left(\left(\frac{\partial V}{\partial T} \right)_{P,n_i} - \frac{n_T R}{P} \right) dP - n_T R \ln \frac{P}{P_r} - R \sum_j n_j \ln x_j \quad (\text{A117})$$

APPENDIX B

The EOS by Anderko and Pitzer (1993) for H₂O-NaCl and the augmentation of CO₂ by Duan et al. (1995) are valuable tools for calculation of phase relationships in the system for H₂O-CO₂-NaCl and related phase equilibria involving solids. In both publications and in some further work using this EOS, the calculation of the fugacity coefficients is laid out in the accompanying appendixes. Unfortunately, there are some inaccuracies and misunderstandings in the equations, and few errors in the constants used that lead to some frustration if someone wants to program the EOS. With some effort it was, however, possible, to extract the correct relations which I want to share in the following.¹

Fugacity coefficients

According to Appendix A to calculate the fugacity coefficient we need to solve the following equation:

$$\ln \phi_{i(v,T,x)}^m = \frac{a_{(v,T,x)}^{excess}}{RT} + \left(\frac{\partial(a_{(v,T,x)}^{excess}/RT)}{\partial x_i} \right) - \sum_j x_j \left(\frac{\partial(a_{(v,T,x)}^{excess}/RT)}{\partial x_j} \right) - \ln z + (z-1) \quad (A77)$$

To do this we need expressions for a^{excess} , z , and the derivatives of a^{excess}/RT with respect to x_i .

Excess Helmholtz free energy a^{excess}

In Anderko and Pitzer (1993) the molar Helmholtz free energy is split into an ideal, a hard-sphere, a dipole, and a perturbation contribution:

$$a = a^{ideal} + a^{rep} + a^{dip} + a^{per} \quad (B1)$$

So a^{excess} is:

$$a^{excess} = a^{rep} + a^{dip} + a^{per} \quad (B2)$$

In the Chapter above, the hard-sphere term is labeled a^{hs} . Anderko and Pitzer (1993) call it a^{rep} . To allow the comparison with Anderko and Pitzer (1993) and others, the original notation is used here. An exception is η , which is used with different definitions for the hard-sphere and for the dipole term. Therefore, y is used instead of η in the hard-sphere term. In the following the original equations from Anderko and Pitzer (1993) are listed. If needed, corrections are inserted and marked.

a^{ideal} . The ideal term a^{ideal} is:

¹ In the following equations in the Appendixes of Anderko and Pitzer (1993) and Duan et al. (1995) are labeled (Anderko xx) and (Duan xx), respectively. Corrected equations are marked with a double arrow.

$$\frac{a^{ideal}}{RT} = \frac{a_r^{o*}}{RT} - \ln \frac{v}{v_r} + \sum_{i=1} x_i \ln x_i \quad (B3)$$

a^{rep} . The repulsion term a^{rep} is:

$$\frac{a^{hs}}{RT} = \frac{a^{rep}}{RT} = \frac{\frac{3DE}{F} y - \frac{E^3}{F^2}}{1-y} + \frac{\frac{E^3}{F^2}}{(1-y)^2} + \left(\frac{E^3}{F^2} - 1 \right) \ln(1-y) \quad (B4)$$

With:

$$D = \sum_{i=1} x_i \sigma_i, \quad E = \sum_{i=1} x_i \sigma_i^2, \text{ and} \quad F = \sum_{i=1} x_i \sigma_i^3 \quad (B5)$$

$$y = \frac{b}{4v} \quad (B6)$$

$$b = \frac{2}{3} \pi N_A F \quad (B7)$$

a^{dip} . The dipole term a^{dip} is:

$$\frac{a^{dip}}{RT} = \frac{A_2}{1 - A_3/A_2} \quad (B8)$$

With:

$$A_2 = -\frac{4}{3} \sum_{i=1} \sum_{j=1} x_i x_j \frac{b_i b_j}{b_{ij}^2} \eta_{ij} \tilde{\mu}_i^2 \tilde{\mu}_j^2 I_{2(\eta)} \quad (B9)$$

$$A_3 = \frac{10}{9} \sum_{i=1} \sum_{j=1} \sum_k x_i x_j x_k \frac{b_i b_j b_k}{b_{ij} b_{ik} b_{jk}} \eta_{ijk}^2 \tilde{\mu}_i^2 \tilde{\mu}_j^2 \tilde{\mu}_k^2 I_{3(\eta)} \quad (B10)$$

$$\eta_{ij} = \frac{b_{ij}}{4v} \quad (B11)$$

$$\eta_{ijk} = \frac{b_{ijk}}{4v} = \frac{(b_{ij} b_{ik} b_{jk})^{1/3}}{4v} \quad (B12)$$

$$b_{ij} = \left(\frac{b_i^{1/3} + b_j^{1/3}}{2} \right)^3 \quad (B13)$$

$$\eta = \frac{1}{4v} \sum_{i=1} \sum_{j=1} x_i x_j b_{ij} \quad (B14)$$

$$I_{2(\eta)} = 1 + c_1 \eta + c_3 \eta^2 + c_5 \eta^3 \quad (B15)$$

$$I_{3(\eta)} = I_{2(\eta)} \left(1 + c_2 \eta + c_4 \eta^2 + c_6 \eta^3 \right) \quad (\text{B16})$$

α^{per} . The dipole term α^{per} is:

$$\frac{\alpha^{per}}{RT} = -\frac{1}{RT} \left(\frac{a}{v} + \frac{acb}{4v^2} + \frac{adb^2}{16v^3} + \frac{aeb^3}{64v^4} \right) \quad (\text{B17})$$

With:

$$a = \sum_{i=1} \sum_{j=1} x_i x_j a_{ij} \quad (\text{B18})$$

$$acb = \sum_{i=1} \sum_{j=1} \sum_{k=1} x_i x_j x_k (ac)_{ijk} b_{ijk} \quad (\text{B19})$$

$$adb^2 = \sum_{i=1} \sum_{j=1} \sum_{k=1} \sum_{l=1} x_i x_j x_k x_l (ad)_{ijkl} b_{ijkl}^2 \quad (\text{B20})$$

$$aeb^3 = \sum_{i=1} \sum_{j=1} \sum_{k=1} \sum_{l=1} \sum_{m=1} x_i x_j x_k x_l x_m (ae)_{ijklm} b_{ijklm}^3 \quad (\text{B21})$$

$$b_{ijk} = \left(\frac{b_i^{1/3} + b_j^{1/3} + b_k^{1/3}}{3} \right)^3 \quad (\text{B22})$$

$$b_{ijkl} = \left(\frac{b_i^{1/3} + b_j^{1/3} + b_k^{1/3} + b_l^{1/3}}{4} \right)^3 \quad (\text{B23})$$

$$b_{ijklm} = \left(\frac{b_i^{1/3} + b_j^{1/3} + b_k^{1/3} + b_l^{1/3} + b_m^{1/3}}{5} \right)^3 \quad (\text{B24})$$

$$a_{ij} = \left(a_i a_j \right)^{1/2} \alpha_{ij} \quad (\text{B25})$$

$$(ac)_{ijk} = \left((ac)_i (ac)_j (ac)_k \right)^{1/3} \gamma_{ijk} \quad (\text{B26})$$

Here is an inexactness. The parameter a_i is always positive, c_i is always negative, and the product $a_i c_i$ is, therefore, negative. Correct version of Equation (B26) is (B27):

$$\Rightarrow (ac)_{ijk} = - \left(\left| (ac)_i (ac)_j (ac)_k \right| \right)^{1/3} \gamma_{ijk} \quad (\text{B27})$$

$$(ad)_{ijkl} = \left((ad)_i (ad)_j (ad)_k (ad)_l \right)^{1/4} \delta_{ijkl} \quad (\text{B28})$$

$$(ae)_{ijklm} = \left((ae)_i (ae)_j (ae)_k (ae)_l (ae)_m \right)^{1/5} \epsilon_{ijklm} \quad (\text{B29})$$

The same situation as in equation (B26) arises here, e_i is always negative. Correct version of Equation (B29) is (B30):

$$\Rightarrow (ae)_{ijklm} = -\left(\left|(ae)_i(ae)_j(ae)_k(ae)_l(ae)_m\right|\right)^{1/5} \varepsilon_{ijklm} \quad (B30)$$

For H₂O and NaCl, explicit expression for a_i and c_i are given:

$$(ac)_i = a_i c_i, \quad (ad)_i = a_i d_i, \quad (ae)_i = a_i e_i \quad (B31)$$

In Duan et al (1995) for CO₂, $(ac)_{CO_2}$, $(ad)_{CO_2}$, and $(ae)_{CO_2}$ are given implicit expressions.

For the subsystem H₂O-NaCl, α , γ , δ , and ε are highly temperature dependent, and they are handled by the function τ :

$$\alpha_{ij} = \alpha_{ij}^0 \tau, \quad \gamma_{ijk} = \gamma_{ijk}^0 \tau, \quad \delta_{ijkl} = \delta_{ijkl}^0 \tau, \quad \varepsilon_{ijklm} = \varepsilon_{ijklm}^0 \tau \quad (B32)$$

The parameters b_i , μ_i , a_i , c_i , d_i , and e_i , are specific for every phase component i and they are provided by the authors.

Compressibility factor z

Also required is the compressibility factor z , which can be calculated using the following equation:

$$z = -v \left(\frac{\partial a / RT}{\partial v} \right) \quad (B33)$$

As above, the molar Helmholtz free energy can be split into its contributions:

$$z = -v \left(\frac{\partial (a^{ideal} + a^{rep} + a^{dip} + a^{per}) / RT}{\partial v} \right) = 1 - v \left(\frac{\partial (a^{rep} + a^{dip} + a^{per}) / RT}{\partial v} \right) \quad (B34)$$

$$-v \frac{\partial a^{ideal} / RT}{\partial v} = \frac{Pv}{RT} = 1 \quad (B35)$$

The differential of the ideal term is 1 and therefore the Equation (Anderko A1) should read:

$$\Rightarrow z = 1 + z^{rep} + z^{dip} + z^{per} \quad (B36)$$

z^{rep} . Anderko and Pitzer (1993) included the ideal term implicitly into the repulsion term. This choice is unfortunate because it contradicts the later use of a^{rep} .

$$z^{rep} = \frac{\left(1 + \frac{3DE}{F}\right)y - \left(2 + \frac{3DE}{F} - \frac{3E^3}{F^2}\right)y^2 - \left(\frac{E^3}{F^2} - 1\right)y^3}{(1-y)^3} \quad (B37)$$

z^{dip} . The contribution z^{dip} is:

$$z^{dip} = \eta \frac{\left(1 - \frac{2A_3}{A_2}\right) \left(\frac{\partial A_2}{\partial \eta}\right) + \left(\frac{\partial A_3}{\partial \eta}\right)}{\left(1 - \frac{A_3}{A_2}\right)^2} \quad (B38)$$

To perform the required differentiation in (B38) the Equations (B9) and (B10) have to be transformed.

$$A_2 = -\frac{4}{3} \sum_{i=1} \sum_{j=1} x_i x_j \frac{b_i b_j}{b_{ij} b^{dip}} \eta \tilde{\mu}_i^2 \tilde{\mu}_j^2 I_{2(\eta)} \quad (B39)$$

$$A_3 = \frac{10}{9} \sum_{i=1} \sum_{j=1} \sum_{k=1} x_i x_j x_k \frac{b_i b_j b_k}{b_{ij} b_{ik} b_{jk}} \frac{(b_{ij} b_{ik} b_{jk})^{2/3}}{(b^{dip})^2} \eta^2 \tilde{\mu}_i^2 \tilde{\mu}_j^2 \tilde{\mu}_k^2 I_{3(\eta)} \quad (B40)$$

It is important that in these equations that the parameter b is not that of (B7) but is linked to Equation (B14):

$$b^{dip} = \sum_{i=1} \sum_{j=1} x_i x_j b_{ij} \quad (B41)$$

In the original equations this difference is not necessarily obvious. The derivatives are then:

$$\frac{\partial A_2}{\partial \eta} = -\frac{4}{3} \sum_{i=1} \sum_{j=1} x_i x_j \frac{b_i b_j}{b_{ij} b^{dip}} \tilde{\mu}_i^2 \tilde{\mu}_j^2 \left(I_{2(\eta)} + \eta \frac{\partial I_{2(\eta)}}{\partial \eta} \right) \quad (B42)$$

$$\frac{\partial A_3}{\partial \eta} = \frac{10}{9} \sum_{i=1} \sum_{j=1} \sum_{k=1} x_i x_j x_k \frac{b_i b_j b_k}{b_{ij} b_{ik} b_{jk}} \frac{(b_{ij} b_{ik} b_{jk})^{2/3}}{(b^{dip})^2} \tilde{\mu}_i^2 \tilde{\mu}_j^2 \tilde{\mu}_k^2 \left(2\eta I_{3(\eta)} + \eta^2 \frac{\partial I_{3(\eta)}}{\partial \eta} \right) \quad (B43)$$

With:

$$\frac{\partial I_{2(\eta)}}{\partial \eta} = c_1 + 2c_3 \eta + 3c_5 \eta^2 \quad (B44)$$

$$\frac{\partial I_{3(\eta)}}{\partial \eta} = I_{2(\eta)} (c_2 + 2c_4 \eta + 3c_6 \eta^2) + \frac{\partial I_{2(\eta)}}{\partial \eta} (1 + c_2 \eta + c_4 \eta^2 + c_6 \eta^3) \quad (B45)$$

z^{per} . The contribution z^{per} is:

$$z^{per} = -\frac{1}{RT} \left(\frac{a}{v} + \frac{acb}{2v^2} + \frac{3adb^2}{16v^3} + \frac{aeb^3}{16v^4} \right) \quad (B46)$$

Derivatives of a^{excess} with respect to x_i

The remaining of the required terms are the partial derivatives with respect to the individual mole fractions.

Derivative of a^{rep} .

$$\frac{\partial(a^{rep}/RT)}{\partial x_i} = \frac{\partial(a^{rep}/RT)}{\partial D} \frac{\partial D}{\partial x_i} + \frac{\partial(a^{rep}/RT)}{\partial E} \frac{\partial E}{\partial x_i} + \frac{\partial(a^{rep}/RT)}{\partial F} \frac{\partial F}{\partial x_i} \quad (B47)$$

$$\frac{\partial(a^{rep}/RT)}{\partial D} = \frac{\frac{3E}{F}y}{1-y} \quad (B48)$$

$$\frac{\partial(a^{rep}/RT)}{\partial E} = \frac{\frac{3D}{F}y - \frac{3E^2}{F^2}}{1-y} + \frac{\frac{3E^2}{F^2}}{(1-y)^2} + \left(\frac{3E^2}{F^2} - 1 \right) \ln(1-y) \quad (B49)$$

Reminding us that y is also a function of F :

$$\frac{\partial(a^{rep}/RT)}{\partial F} = \frac{\frac{y}{F} + \frac{E^3}{F^3}(2-y)}{(1-y)} + \frac{\frac{3DE}{F^2}y^2 - \frac{E^3}{F^3}(2+y)}{(1-y)^2} + \frac{\frac{2E^3}{F^3}y}{(1-y)^3} - \frac{2E^3}{F^3} \ln(1-y) \quad (B50)$$

With:

$$\frac{\partial D}{\partial x_i} = \sigma_i, \quad \frac{\partial E}{\partial x_i} = \sigma_i^2, \quad \frac{\partial F}{\partial x_i} = \sigma_i^3 \quad (B51)$$

Derivative of a^{dip} .

Equation (Anderko A20) and (Duan A13) is:

$$\frac{\partial(n_T a^{dip}/RT)}{\partial n_i} = \frac{\left(1 - \frac{2A_3}{A_2}\right) \frac{\partial(n_T A_2)}{\partial n_i} + \frac{\partial(n_T A_3)}{\partial n_i}}{\left(1 - \frac{A_3}{A_2}\right)^2} \quad (B52)$$

Whereas this Equation (B52) is correct, the following two equations in the respective publications are not (Anderko A21, A22 and Duan A14, A15). In Anderko and Pitzer (1993), the equations are in error with respect to the running indexes and missing factors, both of which were corrected by Duan et al. (1995). But even the corrected equations are wrong in the sense that they are not the derivatives claimed to be in respect to n_i but in respect to x_i . So it is better to use:

$$\Rightarrow \frac{\partial(a^{dip}/RT)}{\partial x_i} = \frac{\left(1 - \frac{2A_3}{A_2}\right) \frac{\partial A_2}{\partial x_i} + \frac{\partial A_3}{\partial x_i}}{\left(1 - \frac{A_3}{A_2}\right)^2} \quad (B53)$$

With:

$$\Rightarrow \frac{\partial A_2}{\partial x_i} = -\frac{8}{3} I_2(\eta) \sum_{j=1} x_j \frac{b_i b_j}{b_{ij}^2} \eta_{ij} \tilde{\mu}_i^2 \tilde{\mu}_j^2 - \frac{4}{3} \frac{\partial I_2(\eta)}{\partial \eta} \sum_{j=1} \sum_{k=1} x_j x_k \frac{b_j b_k}{b_{jk}^2} \eta_{jk} \tilde{\mu}_j^2 \tilde{\mu}_k^2 \quad (B54)$$

$$\Rightarrow \frac{\partial A_2}{\partial x_i} = \frac{10}{3} I_3(\eta) \sum_{j=1} \sum_{k=1} x_j x_k \frac{b_i b_j b_k}{b_{ij} b_{ik} b_{jk}} \eta_{ijk}^2 \tilde{\mu}_i^2 \tilde{\mu}_j^2 \tilde{\mu}_k^2$$

$$+ \frac{10}{9} \frac{\partial I_3(\eta)}{\partial \eta} \frac{\partial \eta}{\partial x_i} \sum_{j=1} \sum_{k=1} \sum_{l=1} x_j x_k x_l \frac{b_j b_k b_l}{b_{jk} b_{jl} b_{lk}} \eta_{jkl}^2 \tilde{\mu}_j^2 \tilde{\mu}_k^2 \tilde{\mu}_l^2 \quad (B55)$$

$$\frac{\partial \eta}{\partial x_i} = \frac{1}{2v} \sum_{j=1} x_j b_{ij} \quad (B56)$$

It is important to note that, in Equations (B9) and (B10), the functions $I_2(\eta)$ and $I_3(\eta)$ are not part of the sum but factors, the respective terms in the derivatives (B54) and (B55) are written in front of the sums. The derivatives of $I_2(\eta)$ and $I_3(\eta)$ in respect to η are given in the Equations (B44) and (B45).

Derivative of a^{per} : The Equations (Anderko A26)-(Anderko A30) in Anderko and Pitzer (1993) and (Duan A19)-(Duan A23) in Duan et al. (1995) are in error in the given context. As above for the dipole terms, the derivatives (Anderko A27)-(Anderko A30) and (Duan A20)-(Duan A23) are not the ones claimed, but again are the derivatives with respect to x_i . The correct equations are:

$$\Rightarrow \frac{\partial(a^{per}/RT)}{\partial x_i} = -\frac{1}{RT} \left(\frac{1}{v} \frac{\partial a}{\partial x_i} + \frac{1}{4v^2} \frac{\partial acb}{\partial x_i} + \frac{1}{16v^3} \frac{\partial adb^2}{\partial x_i} + \frac{1}{64v^4} \frac{\partial aeb^3}{\partial x_i} \right) \quad (B57)$$

With:

$$\Rightarrow \frac{\partial a}{\partial x_i} = 2 \sum_j x_j a_{ij} \quad (B58)$$

$$\Rightarrow \frac{\partial acb}{\partial x_i} = 3 \sum_j \sum_k x_j x_k (ac)_{ijk} b_{ijk} \quad (B59)$$

$$\Rightarrow \frac{\partial adb^2}{\partial x_i} = 4 \sum_j \sum_k \sum_l x_j x_k x_l (ad)_{ijkl} b_{ijkl}^2 \quad (B60)$$

$$\Rightarrow \frac{\partial aeb^3}{\partial x_i} = 5 \sum_j \sum_k \sum_l \sum_m x_j x_k x_l x_m (ae)_{ijklm} b_{ijklm}^3 \quad (B61)$$

Fugacity coefficients

To calculate ϕ_i^m the Equations (B2), (B36), and the appropriate partial derivatives of a^{excess} have to be inserted into Equation (A77).

Other versions and misprints of constants in parameter functions

Two versions for the parameter a_{NaCl} seem to exist. One is that of Anderko and Pitzer (1993), and the other is an extension used in a program which A. Anderko provided to me in 1995. The extended version is:

$$\Rightarrow a_{NaCl} = (14.412 + 5.644 \exp(-0.4817(\theta - 8.959)^2) - 10 \exp(-0.6154 (\theta - 5.403)^{3.26})) \times 10^6 \quad (B62)$$

The following parameters by Anderko and Pitzer (1993) are in error. The correct parameters are:

$$\Rightarrow \gamma_{112}^o = 0.7865 + 0.1487\theta + 0.2537 \exp(-0.1162 \times 10^{-5} (\theta - 0.57315)^8) \quad (B63)$$

$$\Rightarrow \gamma_{122}^o = 1.4194 + 0.06552\theta + 0.2058 \exp(-1.604 (\theta - 5.667)^2) \quad (B64)$$