

Second
Edition

THERMODYNAMIC MODELS: FUNDAMENTALS & COMPUTATIONAL ASPECTS

Michael L. Michelsen
Jørgen M. Mollerup

TIE-LINE PUBLICATIONS

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Thermodynamic Models: Fundamentals & Computational Aspects

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Educational software

Supplementary material can be downloaded from the publisher's web site:
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A Fortran source module for calculation of fugacity coefficients and all associated derivatives from standard cubic equations of state. The module includes a small component data base and provides the reader with a helpful starting point for implementing and applying the algorithms described in the text.

A list of exercises for some of the book chapters. These exercises are intended to let the students build programs of increasing complexity based on the recommendations in the text.

An executable file, capable of performing calculations of two-phase and multiphase equilibrium at constant temperature and pressure as well as calculating the phase envelope for a mixture, using the database from the source module. The executable file enables the students to verify whether their own programs function correctly.

This material will be updated on the web site.

Preface

The aim of this book is to provide the researcher and the practising engineer with the tools to implement algorithms for modelling and calculating phase equilibrium. This includes a methodology for efficient coding of procedures for calculation of thermodynamic properties, in particular when these properties are derived from an equation of state.

More than twenty years of experience with the development of algorithms for calculation of phase equilibrium has convinced us that the best combination of speed and reliability is offered by second order convergence methods. This implies that the equation of state must be able to provide, in addition to density, enthalpy and fugacity coefficients, the derivatives of these properties with respect to temperature, pressure and mixture composition. We aim to demonstrate that these derivatives can in general be calculated for a very modest additional effort, even in complex models that incorporate chemical theory.

Traditional successive substitution procedures based on the ideal solution approximation still have their place for convergence of 'easy' problems and for providing initial estimates for more difficult problems, and the numerical approach that we advocate is to start with the classical substitution approach but to switch to a second order method if convergence with the simpler method does not occur rapidly.

Finally, we emphasise the use of stability analysis, combined with a minimization approach for efficient and reliable solution of a range of practically important equilibrium calculations.

The material in this book has for a number of years been used as the basis for a PhD-level 3-week course in numerical calculation of phase equilibrium. The first two weeks of the course are used for lectures and individual computer exercises, where the students write their own algorithms (in Fortran) for performing equilibrium calculations, such as two-phase and multiphase isothermal flash, saturation points, and chemical equilibrium. For this pur-

pose they are provided with routines for calculating thermodynamic properties and their derivatives. The third week of the course is used for working on individual projects on which the report grade is based.

Co-workers at Institut for Kemiteknik, and in particular the IVC-SEP group, have contributed over the years, and we gratefully acknowledge their contribution. In addition much inspiration has come from external contacts, and we would in particular like to thank Prof. Robert A. Heidemann from University of Calgary, Canada, Dr. Hans Kirstenmacher from Linde AG, Germany, Dr. Eric Hendriks from Shell Global Solutions, and Dr. Karen Schou Pedersen from Calsep A/S, Denmark.

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Chapter 1

An Outline of the Classical Thermodynamics

Introduction

The purpose of this chapter is to review the framework of the classical thermodynamics with special emphasis on the Helmholtz energy and its first and second derivatives. We are not concerned with any particular model of the Helmholtz energy. This is not important in this context since the framework of the classical thermodynamics is not concerned with models except for the Helmholtz energy for the perfect gas mixture which is in accord with many experimental facts, but ultimately it is a postulate. In this outline we summarise the consequences of the laws and of Euler's theorem of homogeneous functions and set up the rules for the development of consistent models and calculation of derived properties by combining partial derivatives of the Helmholtz state function.

1 The first and the second law and other basic concepts

The two laws of thermodynamics are a result of numerous observations and simply summarise a vast amount of human experience in a long historical development. They are neither proofs nor definitions, but exist as postulates because of the absence of an experience that disproves or contradicts them. The foundation of the formal structure of the two laws as a phenomenological theory was laid from the early 19th century to the beginning of the 20th century.

The classical thermodynamics is concerned with a system where changes within the system at equilibrium are described by state functions. A thermodynamic system is a physical or mental collection of matter or entities.

Entities not belonging to the system are denoted the surroundings. The system may be complex in nature whereas the surroundings can always be made simple. A state function is singly valued and continuously differentiable that is, at a given set of state variables the function has one and only one value and this value is independent of how we arrive at that particular state. The thermodynamic state of the system is thus uniquely defined by a set of variables that are time independent and defines the thermodynamic state at equilibrium. The thermodynamic state functions are zero or first order homogeneous functions. The properties of a state of a homogeneous system are divided into intensive properties and extensive properties. The intensive properties are zero order homogeneous functions, non-additive and uniform throughout a homogeneous system at equilibrium; for example, the pressure, temperature, concentrations, partial molar properties, chemical potentials and electric potential are intensive properties. The extensive properties are first order homogeneous functions, additive and proportional to the extent of the system; for example, the volume, surface area, number of moles, entropy and internal energy.

The existence of an equilibrium state and the properties at equilibrium are closely connected with the second law of thermodynamics. The equilibrium is a state that the system tends towards spontaneously, and any spontaneous process leads to an increase in the total entropy of the system and its surroundings. The intensive state variables of a homogeneous system at equilibrium are constant for all time and have the same magnitude at any position in the system. A reversible or quasi-static process is a process where every state in the process represents an equilibrium state. Therefore a reversible process is neither time nor path dependent and gradients of the state variables are absent.

The first law

The empirical foundation of the first law is the experimental demonstration of the equivalence principle of heat and mechanical work known as Joule's experiment and the formulation of the energy principle. As a result it is postulated that a state function U denoted the internal energy exists and that the total internal energy of a system and its surroundings is conserved. In a closed system the state function has the property that

$$\Delta U = Q + W \tag{1}$$

where Q is the heat absorbed by the system and W the work done on the system. Heat is defined as the entity which flows between regions of different

temperatures solely because of a temperature gradient. Heat and work are in general not state functions.

The second law

The first explicit formulation of the second law was given by W. Thomson (Lord Kelvin) in 1851 based on the work of Carnot, Joule, and Clausius. The concept of entropy was introduced a few years later by Clausius.

The second law postulates the existence of a state function S denoted the entropy which for a closed system has the property that for a change from equilibrium state 1 to equilibrium state 2 the change in entropy ΔS is calculable as

$$\Delta S = \int_1^2 \frac{\delta Q_{rev}}{T} \quad (2)$$

where δQ_{rev} is a differential change in the heat added to the system and the subscript *rev* designates that Q is for a reversible process. If the path from equilibrium state 1 to equilibrium state 2 is irreversible, the change in the entropy will be the same because S is a state function but eqn. (2) does no longer apply.

Furthermore, the second law postulates that the total change in the entropy of a system and its surroundings resulting from a reversible process is zero whereas it is positive for an irreversible process

$$\Delta S_{total} \geq 0 \quad (3)$$

When the process is reversible, that is, when every state in the process represents equilibrium states, it follows from eqn. (2) that

$$\Delta S = \frac{Q_{rev}}{T} \quad (4)$$

otherwise, the direction of a spontaneous irreversible process must satisfy Clausius' inequality

$$\Delta S > \frac{Q}{T} \quad (5)$$

An isolated system is a system that neither exchanges heat, work nor matter with the surroundings. If the isolated system is at equilibrium, no spontaneous process will take place, but if it is in a non-equilibrium state, a spontaneous process towards the equilibrium state must increase the entropy of the system. This means that the state of the system at equilibrium is a state where the entropy of an isolated system is a maximum. That is

$$\Delta S_{isolated} \geq 0 \quad (6)$$

where the equality holds at equilibrium.

Work

Various forces can act on the system and perform work on the system. These can be body forces like gravity, electric or magnetic forces or surface forces like external pressure and surface tension.

When a surrounding pressure performs work on a volume element of a fluid, the rate of work done is the product of the force times the velocity of which the surface of the fluid expands or contracts. Let \vec{n} be the normal vector to and \vec{u} the velocity of the differential surface element $d\mathfrak{A}$, then the rate of reversible conversion of work into

$$\frac{W_{rev}}{\Delta t} = \int_{surface} (-P(\vec{n} \cdot \vec{u}) d\mathfrak{A}) = -P \frac{\Delta V}{\Delta t} \quad (7)$$

where V is the total volume of the system.

A closed system is a system that only exchanges heat and work but not matter with the surroundings. If the only force acting on a closed system is the external pressure P , we can by combining eqns. (1), (4) and (7) derive the following simple expression for a reversible change in the internal energy of the system

$$\Delta U = T \Delta S - P \Delta V \quad (8)$$

Eqn. (8) is incomplete since a number of contributions to the internal energy are not included. When we change the volume of the system, we inevitably change the surface area of the system and thus the internal energy of the system. Similarly, if the system is converted from a closed system into an open system that exchanges matter with the surroundings, this will contribute to a change in the internal energy. If some of the matter in the system is charged and the system is moving in an electric field of potential ψ , work will be performed and change the internal energy of the system. We will analyse that in the next passage.

The internal energy

The first law states that the change in the internal energy equals the heat absorbed by the system and the work done on the system. The heat absorbed by the system is not a useful external variable since it is not a state function, but by means of the entropy, defined by the second law of thermodynamics, we replaced heat by entropy as shown in eqn. (8). The work done on the system is caused by the forces acting on the system and it is calculable from basic physical principles and depends on the forces and the physical properties associated with the matter in the system like the volume V , the surface area \mathfrak{A} , the amount of matter n , and the charges of the matter $q = \sum_i q_i$. These

properties are extensive variables. The system is isotropic. The internal energy is a function of these extensive variables, that is

$$U(S, V, \mathfrak{A}, \mathbf{n}, q) \quad (9)$$

From this rather formal expression we will derive several well-known equations.

The derivation is based on the fact that the thermodynamic functions are first order homogeneous functions in the extensive variables. All the independent variables of the internal energy are extensive variables and we will explore the consequences of applying Euler's theorem of homogeneous functions to the internal energy, eqn. (9). Since $m = 1$, eqn. (A2) in the appendix to this chapter, page 50, provides us with the following expression for the internal energy.

$$U(\mathbf{b}) = \sum_i b_i \left(\frac{\partial U}{\partial b_i} \right)_{b_j} \quad (A2)$$

where \mathbf{b} are the extensive variables $\mathbf{b} = (S, V, A, \mathbf{n}, q)$. The partial derivatives of U

$$U_i = \left(\frac{\partial U}{\partial b_i} \right)_{b_j} \quad (10)$$

define the intensive variables of the system. U_i and b_i are conjugated properties. Thus Euler's theorem provides the following expression of the internal energy

$$\begin{aligned} U = & S \left(\frac{\partial U}{\partial S} \right)_{V, \mathfrak{A}, \mathbf{n}, q} + V \left(\frac{\partial U}{\partial V} \right)_{S, \mathfrak{A}, \mathbf{n}, q} + \mathfrak{A} \left(\frac{\partial U}{\partial \mathfrak{A}} \right)_{S, V, \mathbf{n}, q} \\ & + \sum_i n_i \left(\frac{\partial U}{\partial n_i} \right)_{V, S, \mathfrak{A}, q} + q \left(\frac{\partial U}{\partial q} \right)_{V, S, \mathfrak{A}, \mathbf{n}} \end{aligned} \quad (11)$$

The partial derivatives of the internal energy define a number of important intensive properties of the system, that is,

Temperature

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, \mathfrak{A}, \mathbf{n}, q} \quad (12)$$

Pressure

$$P = - \left(\frac{\partial U}{\partial V} \right)_{S, \mathfrak{A}, \mathbf{n}, q} \quad (13)$$

The derivatives of the internal energy with respect to entropy and volume conform to eqn. (8).

Surface energy or surface tension

$$\sigma = \left(\frac{\partial U}{\partial \mathfrak{A}} \right)_{S,V,n,q} \quad (14)$$

The classical chemical potentials

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{V,S,\mathfrak{A},q} \quad (15)$$

and finally the electric potential

$$\psi = \left(\frac{\partial U}{\partial q} \right)_{V,S,\mathfrak{A},n} \quad (16)$$

The charges are $q = \sum_i n_i z_i F$ where z_i is the charge number and F is Faraday's constant.

It is common practice to write eqn. (A2) in the following manner

$$U = \sum_i U_i b_i \quad (17)$$

If we insert eqns. (12)-(16) in eqn. (17), we obtain the following expression for the internal energy which is a little more informative than eqn. (9)

$$U = TS - PV + \sigma \mathfrak{A} + \sum_i \mu_i n_i + \psi q \quad (18)$$

The term TS represents the heat and all the other terms are terms that represent various forms of the internal energy associated with work done on the system. The term $\sigma \mathfrak{A}$ is important in small systems where the ratio of the surface area to the volume becomes large. This ratio is six divided by the diameter of a sphere and six divided by the length of the edge of a cube. The term will contribute to the potential of a nucleus and therefore a nucleus will have a larger potential than a large crystal. The last term will contribute to chemical potential of a charged molecule by an amount $z_i F \psi$ per mole of substance. We will explore that in the Chapter 6. Actually, the last term is the scalar product of the electric field strength and the total polarisation of the dielectric that in our case simplifies to ψq . The subject is analysed by Münster (1970) in Chapter IX: "Systems in an electric field" and Chapter XI: "Electrochemical systems". We have not included neither kinetic nor potential energy in eqn. (18) because they are not needed in any of the applications presented in this book.

We cannot calculate an absolute value of internal energy from eqn. (18) because absolute values of the entropy cannot be obtained from the first and the second laws. In most engineering calculations the choice of a reference for the entropy and the derived properties, the chemical potentials and the electric potential, is a matter of convenience since we are usually concerned with changes in the thermodynamic functions, only.

Euler's theorem of homogeneous functions can provide us with another important equation. We will demonstrate the application of eqn. (A11) in the appendix to this chapter. Because all the independent variables of the internal energy are extensive variables, the terms in the first summation cancel which will result in the constraint

$$\sum_i b_i d \left(\frac{\partial U}{\partial b_i} \right)_{b_j} = \sum_i b_i dU_i = 0 \quad (\text{A11})$$

where \mathbf{b} are the extensive variables $\mathbf{b} = (S, V, \mathfrak{A}, \mathbf{n}, q)$, that is

$$S dT - V dP + \mathfrak{A} d\sigma + \sum_i n_i d\mu_i + q d\psi = 0 \quad (19)$$

The expression of the exact differential of a homogeneous function of degree one is shown in eqn. (A10) in the appendix to this chapter and it corresponds to the exact differential of eqn. (A2). When $m = 1$, the result is

$$dU = \sum_i b_i d \left(\frac{\partial U}{\partial b_i} \right)_{b_j} + \sum_i \left(\frac{\partial U}{\partial b_i} \right)_{b_j} db_i \quad (\text{A10})$$

The first term on the right-hand side of eqn. (A10) is zero due to the constraint expressed in eqn. (A11). Therefore

$$dU = \sum_i \left(\frac{\partial U}{\partial b_i} \right)_{b_j} db_i = \sum_i U_i db_i \quad (20)$$

When we apply this equation to the internal energy, eqn. (18), the result is

$$dU = T dS - P dV + \sigma d\mathfrak{A} + \sum_i \mu_i dn_i + \psi dq \quad (21)$$

Eqn. (21) is of course in accord with the general expression for the exact differential of a function $F(\mathbf{x})$

$$dF(\mathbf{x}) = \sum_i \left(\frac{\partial F}{\partial x_i} \right)_{x_j} dx_i \quad (22)$$

Eqn. (18) is a fundamental equation. It is the sum of the products of an extensive property and its conjugated intensive property. The conjugated intensive property is the partial derivative of the internal energy with respect to the extensive variable as indicated in eqn. (10). The conjugated parameters are summarised in Table 1.

Table 1: Extensive and conjugated intensive variables of the internal energy.

Extensive property		Conjugated intensive property	
S	entropy	T	temperature
V	volume	$-P$	pressure
\mathfrak{A}	surface area	σ	surface tension
n_i	mole numbers	μ_i	chemical potentials
q	charge	ψ	electrical potential

If a homogeneous system is not at equilibrium, gradients in the intensive variables exist. These gradients will give rise to transport of extensive properties because a gradient in an intensive property is a driving force of flow of its conjugated extensive property. That is, diffusion is not caused by gradients in the compositions but by gradients in the chemical potentials.

When the surface area energy contributes little to the internal energy and the system carries no charges, we can simplify eqns. (18), (19), and (21). The expression for the internal energy becomes

$$U(\mathbf{b}) = \sum_i U_i b_i = TS - PV + \sum_i \mu_i n_i \quad (23)$$

U_i is, in eqn. (10), defined as the partial derivative of U with respect to the conjugated extensive parameter. The extensive parameters are $\mathbf{b} = (S, V, \mathbf{n})$. Eqn. (17) will assume a more familiar form known as the Gibbs-Duhem equation

$$\sum_i b_i dU_i = S dT - V dP + \sum_i n_i d\mu_i = 0 \quad (24)$$

and finally

$$dU = \sum_i U_i db_i = T dS - P dV + \sum_i \mu_i dn_i \quad (25)$$

In the remaining part of this chapter we will use eqns. (23)-(25).

A thorough discussion of the applications of the first and the second laws of thermodynamics and their applications are given in the book of Bett et al. (1975).

2 Other thermodynamic functions

The equation for the internal energy is a characteristic function; i.e. one which contains every statement that the thermodynamics can make about the system at equilibrium because the function and its derivatives are sufficient to characterise the state of a thermodynamic system completely. However, it is often expedient to use alternative ways of characterising a system than the one offered by the (U, S, V, \mathbf{n}) surface. Usually T and P are more accessible variables than S .

Other state functions can be derived from the internal energy by replacing an extensive variable by its conjugated intensive variable. The mathematical transformations are

$$\begin{aligned} M(\mathbf{x}) &= U - U_k b_k \\ &= \sum_i U_i b_i - U_k b_k = \sum_{i \neq k} U_i b_i \end{aligned} \quad (26)$$

and therefore the differential of the function M is

$$\begin{aligned} dM &= dU - U_k db_k - b_k dU_k \\ &= \sum_i U_i db_i - U_k db_k - b_k dU_k \\ &= \sum_{i \neq k} U_i db_i - b_k dU_k \end{aligned} \quad (27)$$

And for purely mathematical reasons we can write the differential of M as

$$dM = \left(\frac{\partial M}{\partial x_s} \right)_{x_r} dx_s \quad (28)$$

Eqns. (27) and (28) give rise to identities

$$\left(\frac{\partial M}{\partial b_i} \right)_{b_j \neq k, U_k} = U_i \quad (29)$$

and

$$\left(\frac{\partial U}{\partial b_k} \right)_{b_j} = -b_k \quad (30)$$

Furthermore, by comparing eqns. (27) and (28) we can conclude that the new state function is a function of the variables

$$M(\mathbf{x}) = M(U_k, \mathbf{b} \setminus b_k) \quad (31)$$

We have thus replaced the extensive variable b_k by its conjugated intensive variable U_k which ensures that the new state function becomes a characteristic function, i.e. it contains every statement that the thermodynamics can make about the system. We can of course replace more than one extensive variable by the corresponding conjugated intensive variables. A detailed discussion is given by Münster (1970).

We define three thermodynamic state functions, the enthalpy H , the Helmholtz energy A , and the Gibbs energy G .

The enthalpy equals the internal energy minus energy equivalent to the PV properties of the system. If no work is performed on the system except the PV work, the change in enthalpy equals the heat absorbed by the system at isobaric conditions. To perform the transformation from the internal energy to the enthalpy function we shall replace the extensive variable V by its conjugated intensive variable, the pressure P . The independent variables in the new thermodynamic function are (S, P, \mathbf{n}) . The enthalpy is by definition

$$H(S, P, \mathbf{n}) = U - V \left(\frac{\partial U}{\partial V} \right)_{S, \mathbf{n}} = U + PV = TS + \sum_i \mu_i n_i \quad (32)$$

and according to eqns. (27) and (28) the differential of H is

$$\begin{aligned} dH &= \left(\frac{\partial H}{\partial S} \right)_{P, \mathbf{n}} dS + \left(\frac{\partial H}{\partial P} \right)_{S, \mathbf{n}} dP + \sum_i \left(\frac{\partial H}{\partial n_i} \right)_{S, P} dn_i \\ &= T dS + V dP + \sum_i \mu_i dn_i \end{aligned} \quad (33)$$

In the Helmholtz energy the extensive variable S is replaced by its conjugated intensive variable, the temperature T . The isothermal-isochoric reversible work done on the system is equal to the increase in the Helmholtz energy. The Helmholtz energy is

$$A(T, V, \mathbf{n}) = U - S \left(\frac{\partial U}{\partial S} \right)_{V, \mathbf{n}} = U - TS = -PV + \sum_i \mu_i n_i \quad (34)$$

and according to eqns. (27) and (28) the differential of A is

$$\begin{aligned} dA &= \left(\frac{\partial A}{\partial T} \right)_{V, \mathbf{n}} dT + \left(\frac{\partial A}{\partial V} \right)_{T, \mathbf{n}} dV + \sum_i \left(\frac{\partial A}{\partial n_i} \right)_{T, V} dn_i \\ &= -S dT - P dV + \sum_i \mu_i dn_i \end{aligned} \quad (35)$$

The independent variables are (T, V, \mathbf{n}) and from a practical point of view the Helmholtz energy is the most important of the thermodynamic functions

because it is a function of three accessible variables, temperature, volume and mole numbers, and therefore calculable from the *PVT* properties of fluids.

The independent variables in the Gibbs energy are temperature, pressure and mole numbers, i.e. (T, P, \mathbf{n}) . To perform the transformation we shall replace entropy by temperature and volume by pressure. The isothermal-isobaric reversible work done on the system is equal to the increase in the Gibbs energy. The Gibbs energy is

$$\begin{aligned} G(T, P, \mathbf{n}) &= U - S \left(\frac{\partial U}{\partial S} \right)_{V, \mathbf{n}} - V \left(\frac{\partial U}{\partial V} \right)_{S, \mathbf{n}} \\ &= U - TS + PV = H - TS = \sum_i \mu_i n_i \end{aligned} \quad (36)$$

and the differential of G is

$$\begin{aligned} dG &= \left(\frac{\partial G}{\partial T} \right)_{P, \mathbf{n}} dT + \left(\frac{\partial G}{\partial P} \right)_{T, \mathbf{n}} dP + \sum_i \left(\frac{\partial G}{\partial n_i} \right)_{T, P} dn_i \\ &= -S dT + V dP + \sum_i \mu_i dn_i \end{aligned} \quad (37)$$

Like U and S , the energy functions defined by eqns. (32), (34) and (36), are state functions and each of the surfaces (H, S, P, \mathbf{n}) , (A, T, V, \mathbf{n}) , and (G, T, P, \mathbf{n}) is represented by a characteristic function.

We can derive other useful differential relations. If we solve eqn. (25) for dS , the result is

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{1}{T} \sum_i \mu_i dn_i \quad (38)$$

This differential is utilised when we, in the subsequent section, derive the conditions that must hold at equilibrium.

Furthermore we will derive two important differential relations. If we divide eqn. (36) by T and calculate the exact differential, the result is

$$d\left(\frac{G}{T}\right) = H d\left(\frac{1}{T}\right) + \frac{1}{T} dH - dS$$

We insert the differential dH from eqn. (33) in this equation and get

$$d\left(\frac{G}{T}\right) = H d\left(\frac{1}{T}\right) + \frac{1}{T} \left(T dS + V dP + \sum_i \mu_i dn_i \right) - dS$$

the entropy terms cancel and resulting equation is

$$d\left(\frac{G}{T}\right) = H d\left(\frac{1}{T}\right) + \frac{V}{T} dP + \frac{1}{T} \sum_i \mu_i dn_i \quad (39)$$

and similarly from eqns. (34) and (25) we can derive the differential relation

$$d\left(\frac{A}{T}\right) = U d\left(\frac{1}{T}\right) - \frac{P}{T} dV + \frac{1}{T} \sum_i \mu_i dn_i \quad (40)$$

This equation immediately shows that

$$\left(\frac{\partial(A/T)}{\partial(1/T)}\right)_{V,n} = U \quad (41)$$

Due to the identity shown in eqn. (29) we observe that four equivalent expressions for the chemical potential exist. They are

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P} \quad (42)$$

The last expression is the most well-known expression but the last but one is more applicable since most of the models, that we derive, turn out to be Helmholtz energy functions. Table 2 summarises the thermodynamic state functions.

Table 2: The thermodynamic state functions.

Property	$U(S, V, n)$	$H(S, P, n)$	$A(T, V, n)$	$G(T, P, n)$
S			$-\left(\frac{\partial A}{\partial T}\right)_{V,n}$	$-\left(\frac{\partial G}{\partial T}\right)_{P,n}$
V		$\left(\frac{\partial H}{\partial P}\right)_{S,n}$		$\left(\frac{\partial G}{\partial P}\right)_{T,n}$
T	$\left(\frac{\partial U}{\partial S}\right)_{V,n}$	$\left(\frac{\partial H}{\partial S}\right)_{P,n}$		
P	$-\left(\frac{\partial U}{\partial V}\right)_{S,n}$		$-\left(\frac{\partial A}{\partial V}\right)_{T,n}$	
μ_i	$\left(\frac{\partial U}{\partial n_i}\right)_{S,V}$	$\left(\frac{\partial H}{\partial n_i}\right)_{S,P}$	$\left(\frac{\partial A}{\partial n_i}\right)_{T,V}$	$\left(\frac{\partial G}{\partial n_i}\right)_{T,P}$

Several mutual relations between partial derivatives can be obtained from the equations in this section. The result is summarised in Table 3.

Table 3: Partial derivatives of the thermodynamic state functions.

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \quad (\text{I})$$

$$\left(\frac{\partial A}{\partial P}\right)_T = -P \left(\frac{\partial V}{\partial P}\right)_T \quad (\text{II})$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad (\text{III})$$

$$\left(\frac{\partial A}{\partial T}\right)_P = -S - P \left(\frac{\partial V}{\partial T}\right)_P \quad (\text{IV})$$

$$\left(\frac{\partial(A/T)}{\partial(1/T)}\right)_V = U \quad (\text{V})$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad (\text{VI})$$

$$\left(\frac{\partial U}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T \quad (\text{VII})$$

$$\left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V = C_V \quad (\text{VIII})$$

$$\begin{aligned} \left(\frac{\partial U}{\partial T}\right)_P &= C_V + \left(T \left(\frac{\partial P}{\partial T}\right)_V - P\right) \left(\frac{\partial V}{\partial T}\right)_P \\ &= T \left(\frac{\partial S}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial T}\right)_P = C_P - P \left(\frac{\partial V}{\partial T}\right)_P \end{aligned} \quad (\text{IX})$$

$$\left(\frac{\partial H}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V + V \left(\frac{\partial P}{\partial V}\right)_T \quad (\text{X})$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P \quad (\text{XI})$$

continues

$$\begin{aligned}\left(\frac{\partial H}{\partial T}\right)_V &= C_P + \left(V - T \left(\frac{\partial V}{\partial T}\right)_P\right) \left(\frac{\partial P}{\partial T}\right)_V \\ &= C_V + V \left(\frac{\partial P}{\partial T}\right)_V\end{aligned}\quad (\text{XII})$$

$$\left(\frac{\partial H}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P = C_P \quad (\text{XIII})$$

$$\left(\frac{\partial G}{\partial V}\right)_T = V \left(\frac{\partial P}{\partial V}\right)_T \quad (\text{XIV})$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad (\text{XV})$$

$$\left(\frac{\partial G}{\partial T}\right)_V = -S + V \left(\frac{\partial P}{\partial T}\right)_V \quad (\text{XVI})$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad (\text{XVII})$$

$$\left(\frac{\partial(G/T)}{\partial(1/T)}\right)_P = H \quad (\text{XVIII})$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (\text{XIX})$$

$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P \quad (\text{XX})$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad (\text{XXI})$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad (\text{XXII})$$

3 Equilibrium

It is a consequence of the second law of thermodynamics that an isolated system will approach equilibrium by increasing its entropy and that the equilibrium state is a stationary point of maximum entropy because the direction

of spontaneous processes in an isolated system must proceed so that the entropy of the system is increasing, that is $(\Delta S)_{U,V,n}$. Suppose that the isolated system consists of several phases, is non-reacting, and that the individual phases are considered as open systems that can exchange energy, work and matter with one another. Then the extensive independent properties U , V and n at equilibrium are subject to the constraints

$$\sum_j^{\pi} dU^j = 0 \quad (43)$$

$$\sum_j^{\pi} dV^j = 0 \quad (44)$$

$$\sum_j^{\pi} dn_i^j = 0, \quad i = 1, \dots, C \quad (45)$$

where i denotes the individual components $i = 1, \dots, C$ and j the individual phases $j = 1, \dots, \pi$. There are thus $\pi(C+2)$ independent variables and $C+2$ constraints. Since the differential equation, eqn. (38), relates changes taking place between equilibrium states in an isolated system, we can express the condition of equilibrium in this way

$$dS = \sum_j^{\pi} \frac{dU^j}{T^j} + \sum_j^{\pi} \frac{P^j}{T^j} dV^j - \sum_j^{\pi} \sum_i^C \frac{\mu_i^j}{T^j} dn_i^j = 0 \quad (46)$$

where the independent variables are subject to the constraints shown above. These constraints can be removed by considering the independent variables of one of the phases, say phase α , as dependent variables. When the sum of the changes of the extensive variables is zero, we can express the changes of the extensive properties of phase α in this way

$$dU^\alpha = - \sum_{j \neq \alpha}^{\pi} dU^j \quad (47)$$

$$dV^\alpha = - \sum_{j \neq \alpha}^{\pi} dV^j \quad (48)$$

$$dn_i^\alpha = - \sum_{j \neq \alpha}^{\pi} dn_i^j, \quad i = 1, \dots, C \quad (49)$$

We can now replace the changes of the dependent variables, the extensive properties of phase α , in eqn. (46) with these expressions to obtain an equation where all extensive variables are independent variables. The eventual

result is

$$\sum_{j \neq \alpha}^{\pi} \left(\frac{1}{T^j} - \frac{1}{T^\alpha} \right) dU^j + \sum_{j \neq \alpha}^{\pi} \left(\frac{P^j}{T^j} - \frac{P^\alpha}{T^\alpha} \right) dV^j - \sum_{j \neq \alpha}^{\pi} \sum_i^C \left(\frac{\mu_i^j}{T^j} - \frac{\mu_i^\alpha}{T^\alpha} \right) dn_i^j = 0 \quad (50)$$

Since the extensive properties are now independent variables, this equation must be satisfied for any changes in the independent variables, therefore the terms in each of the brackets must be zero. That is,

$$T^j = T^\alpha, \quad j \neq \alpha \quad (51)$$

$$P^j = P^\alpha, \quad j \neq \alpha \quad (52)$$

$$\mu_i^j = \mu_i^\alpha, \quad j \neq \alpha \quad \text{and} \quad i = 1, \dots, C \quad (53)$$

Because α can be any phase in the system, the equations imply that the temperature and the pressure must be uniform throughout the system and that the chemical potentials of component i are the same in all the phases of the system at equilibrium. But the chemical potentials of the individual components are of course not identical.

The system considered is an isolated multiphase system where the individual phases are open systems that can exchange energy, work and matter with one another and the conditions of equilibrium do only apply to such a system. If two or more of the phases are separated by semi-permeable membranes, the conditions of equilibrium must be modified. Eqn. (51) will most often apply because many systems are isothermal. Eqn. (52) will no longer apply, and eqn. (53) will only apply to components that can diffuse through the membranes.

In many cases we do not use U , V and n as our independent variables therefore it is desirable to derive equivalent criteria using more accessible variables like T , P , V and n for instance. To do so we shall assume, that the departures from equilibrium are sufficiently small, that temperature and pressure are uniform throughout the system, and, that the thermodynamic quantities can be defined by the corresponding relations for systems at equilibrium. Because spontaneous processes do occur the increase in entropy must be larger than the corresponding reversible change, that is $\delta S > (\Delta S)_{rev}$, and therefore we must replace the equality of eqn. (8) by an inequality and the reversible changes by the increments δ that is

$$\delta U < T \delta S - P \delta V \quad (54)$$

We assume that the increments of the Gibbs energy is calculable from an equation similar to eqn. (36)

$$\delta G = \delta U + \delta(PV) - \delta(TS) \quad (55)$$

When we replace δU in this equation by the two terms on the right-hand side of the inequality, eqn. (54), we obtain an inequality for the increment of δG of a spontaneous process

$$\delta G < T \delta S - P \delta V + \delta(PV) - \delta(TS) \quad (56)$$

If the temperature and pressure of the system are constant, a spontaneous process must proceed in such a way that

$$(\delta G)_{T,P} < 0 \quad (57)$$

This inequality shows that a closed system at constant temperature and pressure will approach equilibrium when the Gibbs energy is decreasing and thus the stationary point is a global minimum of the Gibbs energy.

Similarly, we calculate the increments of the Helmholtz energy from an equation similar to eqn. (34)

$$\delta A = \delta U - \delta(TS) \quad (58)$$

and as before we replace δU in this equation by the two terms on the right-hand side of the inequality, eqn. (54), to obtain an inequality for the increment of δA of a spontaneous process

$$\delta A < T \delta S - P \delta V - \delta(TS) \quad (59)$$

If the temperature and volume of the system are constant, a spontaneous process must proceed in such a way that

$$(\delta A)_{T,V} < 0 \quad (60)$$

This inequality shows that a closed system at constant temperature and volume will approach equilibrium when the Helmholtz energy is decreasing and thus the stationary point is a global minimum of the Helmholtz energy.

When a system is subject to other constraints other but equivalent criteria can be derived. Table 4 summarises the criteria. As an example, the table shows that we can specify enthalpy, pressure and the number of moles and calculate the state of the system at equilibrium by maximizing the entropy, but we cannot necessarily calculate a unique state of the system if we specify enthalpy, temperature and the mole numbers

Table 4: Equilibrium criteria of a closed system

Independent variables	State function to be minimised
S, V, n	U
U, S, n or A, T, n	V
S, P, n	H
T, P, n	G
T, V, n	A
H, P, n or U, V, n	$-S$

4 Phase stability

Consider a closed multi-component system comprised of any number of phases. The individual phases are open systems where changes can take place in a way that the independent variables for the total system remain fixed. We assume that the departures from local equilibrium are sufficiently small that the thermodynamic quantities shall be defined locally by the corresponding relations for systems at equilibrium. Select a single phase initially having the Gibbs energy $G(T, P, n)$. The chemical potentials μ_i correspond to the partial derivatives of G with respect to the variables n . A new phase is formed by removing a differential amount of matter δn . This process changes the initial system, but we assume that the changes in the independent variables of the initial phase are so small that the chemical potentials μ_i of the initial system remain unchanged. The change in the Gibbs energy of the initial phase is

$$\delta G = - \sum_i \mu_i \delta n_i \quad (61)$$

and the Gibbs energy of the new phase becomes

$$\delta G' = \sum_i \mu'_i \delta n_i \quad (62)$$

where μ'_i are the chemical potentials of the new phase. The initial phase is stable if the formation of a new phase does not lead to a decrease in the Gibbs energy of the whole system; that is if

$$\Delta G = \delta G' + \delta G = \sum_i (\mu'_i - \mu_i) \delta n_i > 0 \quad (63)$$

for any changes of the independent variables $\delta\mathbf{n}$.

Similar stability criteria can be derived for each pair of independent variables of Table 4. Table 5 summarises some of the criteria. The independent variables, which must remain fixed for the total system, are shown in brackets, i.e. $U(S, V, \mathbf{n})$ denotes that S , V and \mathbf{n} of the selected phase are treated as independent variables. The prime denotes an intensive or extensive property of the segregated phase and δ denotes the quantity of extensive property transferred to the new phase. The phase examined is stable if the inequality is fully satisfied at any change in the independent variables.

Table 5: Selected stability criteria of a single phase.

$$\Delta U(S, V, \mathbf{n}) = (T' - T) \delta S - (P' - P) \delta V$$

$$+ \sum_i (\mu'_i - \mu_i) \delta n_i > 0 \quad (\text{I})$$

$$\Delta H(S, P, \mathbf{n}) = (T' - T) \delta S + \sum_i (\mu'_i - \mu_i) \delta n_i > 0 \quad (\text{II})$$

$$\Delta S(H, P, \mathbf{n}) = \left(\frac{1}{T'} - \frac{1}{T} \right) \delta H - \sum_i \left(\frac{\mu'_i}{T'} - \frac{\mu_i}{T} \right) \delta n_i < 0 \quad (\text{III})$$

$$\Delta G(T, P, \mathbf{n}) = \sum_i (\mu'_i - \mu_i) \delta n_i > 0 \quad (\text{IV})$$

$$\Delta A(T, V, \mathbf{n}) = -(P' - P) \delta V + \sum_i (\mu'_i - \mu_i) \delta n_i > 0 \quad (\text{V})$$

5 Partial molar properties

Let M be a homogeneous function of degree one. The derivative $\partial M / \partial n_i$ at constant temperature and pressure is by definition a partial molar property of M

$$\bar{M}_i \equiv \left(\frac{\partial M}{\partial n_i} \right)_{T, P, \mathbf{n}_j} \quad (64)$$

From the discussion of Euler's theorem in appendix to this chapter we know that for any homogeneous function of degree one $M(\mathbf{a}, \mathbf{b})$ where $\mathbf{a} = (T, P)$ and $\mathbf{b} = \mathbf{n}$ we can calculate M from the partial molar properties because

according to eqn. (A12) of the appendix to this chapter

$$M = \sum_i n_i \left(\frac{\partial M}{\partial n_i} \right)_{T,P} = \sum_i n_i \bar{M}_i \quad (65)$$

If M is the Gibbs energy, then $\mathbf{a} = (T, P)$ and $\mathbf{b} = \mathbf{n}$ and the result is

$$G = \sum_i n_i \mu_i \quad (66)$$

If we calculate the derivative of the Gibbs energy in eqn. (66) with respect to the pressure, the result is

$$\begin{aligned} V &= \left(\frac{\partial G}{\partial P} \right)_{T,\mathbf{n}} = \sum_i n_i \left(\frac{\partial \mu_i}{\partial P} \right)_{T,\mathbf{n}} = \sum_i n_i \frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial P} \right)_{T,\mathbf{n}} \\ &= \sum_i n_i \left(\frac{\partial V}{\partial n_i} \right)_{T,P} = \sum_i n_i \bar{V}_i \end{aligned} \quad (67)$$

$$\begin{aligned} S &= - \left(\frac{\partial G}{\partial T} \right)_{P,\mathbf{n}} = - \sum_i n_i \left(\frac{\partial \mu_i}{\partial T} \right)_{P,\mathbf{n}} = - \sum_i n_i \frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial T} \right)_{P,\mathbf{n}} \\ &= \sum_i n_i \left(\frac{\partial S}{\partial n_i} \right)_{T,P} = \sum_i n_i \bar{S}_i \end{aligned} \quad (68)$$

If M is the internal energy U , the result is

$$U = \sum_i n_i \bar{U}_i \quad (69)$$

but the partial molar internal energy is a more composite function than the chemical potential. The partial molar internal energy is calculable as

$$\begin{aligned} \left(\frac{\partial U}{\partial n_i} \right)_{T,P} &= \left(\frac{\partial U}{\partial n_i} \right)_{S,V} + \left(\frac{\partial U}{\partial S} \right)_{V,\mathbf{n}} \left(\frac{\partial S}{\partial n_i} \right)_{T,P} \\ &\quad + \left(\frac{\partial U}{\partial V} \right)_{S,\mathbf{n}} \left(\frac{\partial V}{\partial n_i} \right)_{T,P} \end{aligned} \quad (70)$$

that is

$$\bar{U}_i = \mu_i + T \bar{S}_i - P \bar{V}_i \quad (71)$$

Derivatives with respect to molarity and molality are not partial molar properties and besides they have little physical significance.

6 Residual properties

Experimentally we can measure changes in the extensive properties but an absolute value can only be calculated with an arbitrary zero of the entropy. In engineering calculations the choice of a zero is a matter of convenience since we are usually concerned with changes in the thermodynamic functions, only. One possible choice of the zero is the state of a gas at temperature T_0 and the limit of zero density and pressure. The property M at the state (T, V, n) or (T, P, n) can be calculated by mixing the gases at temperature T_0 and zero density and pressure, heating the mixture to the temperature T and then compressing it to the volume or pressure of the state. This is formally done as

$$M = \Delta M^* + \int_{T_0}^T \left(\frac{\partial M^*}{\partial T} \right)_{V=\infty, n} dT + \int_{\infty}^V \left(\frac{\partial M^*}{\partial V} \right)_{T, n} dV \quad (72)$$

or

$$M = \Delta M^* + \int_{T_0}^T \left(\frac{\partial M^*}{\partial T} \right)_{P=0, n} dT + \int_0^P \left(\frac{\partial M^*}{\partial P} \right)_{T, n} dP \quad (73)$$

where ΔM^* denotes the property change upon mixing at the temperature T_0 and zero density and pressure. The right-hand sides of eqns. (72) and (73) can be rearranged to comprise two terms, one which is the property M^* of the hypothetical perfect gas at the state (T, V, n) or (T, P, n) over the chosen zero, and a second term M^r which is the difference between the property of the state and the hypothetical perfect gas state. If the variables are (T, V, n) , the result is

$$M = M^*(T, V, n) + M^r(T, V, n) \quad (74)$$

where

$$M^*(T, V, n) = \Delta M^* + \int_{T_0}^T \left(\frac{\partial M^*}{\partial T} \right)_{V=\infty, n} dT + \int_{\infty}^V \left(\frac{\partial M^*}{\partial V} \right)_{T, n} dV \quad (75)$$

and

$$M^r(T, V, n) = \int_{\infty}^V \left(\left(\frac{\partial M}{\partial V} \right)_{T, n} - \left(\frac{\partial M^*}{\partial V} \right)_{T, n} \right) dV \quad (76)$$

$M^*(T, V, n)$ is the property of M of a hypothetical perfect gas at state (T, V, n) . The pressure of the state $M(T, V, n)$ is the pressure of the system $P = nZRT/V$ whereas the pressure of the state $M^*(T, V, n)$ is the corresponding perfect gas pressure $P^* = nRT/V$.

If the variables are (T, P, \mathbf{n}) , the result is

$$M = M^*(T, P, \mathbf{n}) + M^r(T, P, \mathbf{n}) \quad (77)$$

where

$$M^*(T, P, \mathbf{n}) = \Delta M^* + \int_{T_0}^T \left(\frac{\partial M^*}{\partial T} \right)_{P=0, \mathbf{n}} dT + \int_0^P \left(\frac{\partial M^*}{\partial P} \right)_{T, \mathbf{n}} dP \quad (78)$$

and

$$M^r(T, P, \mathbf{n}) = \int_0^P \left(\left(\frac{\partial M}{\partial P} \right)_{T, \mathbf{n}} - \left(\frac{\partial M^*}{\partial P} \right)_{T, \mathbf{n}} \right) dP \quad (79)$$

$M^*(T, P, \mathbf{n})$ is the property of M of a hypothetical perfect gas at state (T, P, \mathbf{n}) . The volume of the state $M(T, P, \mathbf{n})$ is the volume of the system $V = nZRT/P$ whereas the volume of the state $M^*(T, P, \mathbf{n})$ is the volume of the corresponding perfect gas $V^* = nRT/P$.

The difference between the two sets of residual properties is due to the difference in the hypothetical perfect gas properties at the two states (T, V, \mathbf{n}) and (T, P, \mathbf{n}) , respectively. At a perfect gas state (P_0, V_0, \mathbf{n}) which has the temperature $T = P_0V_0/nR$ the two sets of hypothetical perfect gas properties are exactly identical because the state is a perfect gas state, i.e. $A^*(T, V_0, \mathbf{n}) = A^*(T, P_0, \mathbf{n})$. The difference between the hypothetical perfect gas states $A^*(T, V, \mathbf{n})$ and $A^*(T, P, \mathbf{n})$ is calculable if we integrate from the perfect gas state to the real state using the equation of state of a perfect gas, that is

$$\begin{aligned} & A^*(T, V, \mathbf{n}) - A^*(T, P, \mathbf{n}) \\ &= \int_{V_0}^V \left(\frac{\partial A^*}{\partial V} \right)_{T, \mathbf{n}} dV - \int_{P_0}^P \left(\frac{\partial A^*}{\partial P} \right)_{T, \mathbf{n}} dP \\ &= - \int_{V_0}^V P dV + \int_{P_0}^P P \left(\frac{\partial V}{\partial P} \right)_{T, \mathbf{n}} dP \\ &= -nRT \ln \frac{V}{V_0} - nRT \ln \frac{P}{P_0} = -nRT \ln Z \end{aligned} \quad (80)$$

where $Z = PV/nRT$. The difference between the residual properties of the Helmholtz function at state (T, P, \mathbf{n}) and state (T, V, \mathbf{n}) can now be obtained from eqns. (74), (77), and (80)

$$A^r(T, P, \mathbf{n}) = A^r(T, V, \mathbf{n}) - nRT \ln Z \quad (81)$$

The residual functions are important because they allow us to calculate the thermodynamic properties of a system over that of an arbitrary hypothetical

perfect gas state. It is especially for the calculation of the derived properties most convenient to calculate the residual Helmholtz energy $A^r(T, V, n)$ and obtain other residual properties from the partial derivatives of the residual Helmholtz energy $A^r(T, V, n)$. The relationships between residual properties are summarised in Table 6.

The perfect gas

In the second part of Section 7 we will analyse the formula for the Helmholtz energy of a perfect gas and the corresponding equation of state, $PV = nRT$. Seemingly, this equation of state applies to real gases at low pressure, but strictly speaking no gas behaves like a perfect gas. The ratio $(Z - 1)/P$ is zero for a perfect gas at any pressure, whereas this ratio is non-zero for a real gas even at low pressure because

$$\lim_{P \rightarrow 0} \frac{Z - 1}{P} = \frac{B}{RT} \quad (82)$$

where B is the second virial coefficient. That is the reason why we denote the state a hypothetical perfect gas state because a real perfect gas state does not exist.

7 Fugacity and fugacity coefficient

Pure components

The isothermal change of the Gibbs energy of n moles of a perfect gas is

$$\left(\frac{\partial G^*}{\partial P} \right)_{T,n} = V = \frac{nRT}{P} \quad (83)$$

By integration of the equation we obtain the difference between the Gibbs energy of a perfect gas at an arbitrary pressure P and a fixed reference pressure P_0

$$G^*(T, P, n) - G^*(T, P_0, n) = nRT \ln \frac{P}{P_0} \quad (84)$$

Since G^* for a pure component is proportional to n , we can write eqn. (84) for one mole of pure component like this

$$\mu^*(T, P) - \mu^*(T, P_0) = RT \ln \frac{P}{P_0} \quad (85)$$

where μ^* are the chemical potentials of the pure perfect gas at the temperature T and the pressures P and P_0 , respectively.

Table 6: Residual bulk properties of fluids and fluid mixtures.

$$A^r(T, V, \mathbf{n}) = - \int_{\infty}^V \left(P - \frac{nRT}{V} \right) dV \quad (\text{I})$$

$$S^r(T, V, \mathbf{n}) = - \left(\frac{\partial A^r}{\partial T} \right)_{V, \mathbf{n}} \quad (\text{II})$$

$$C_V^r(T, V, \mathbf{n}) = -T \left(\frac{\partial^2 A^r}{\partial T^2} \right)_{V, \mathbf{n}} \quad (\text{III})$$

$$U^r(T, V, \mathbf{n}) = A^r(T, V, \mathbf{n}) + T S^r(T, V, \mathbf{n}) \quad (\text{IV})$$

$$H^r(T, V, \mathbf{n}) = U^r(T, V, \mathbf{n}) + PV - nRT \quad (\text{V})$$

$$G^r(T, V, \mathbf{n}) = A^r(T, V, \mathbf{n}) + PV - nRT \quad (\text{VI})$$

$$C_P^r(T, P, \mathbf{n}) = C_V^r(T, V, \mathbf{n}) + T \left(\frac{\partial P}{\partial T} \right)_{V, \mathbf{n}} \left(\frac{\partial V}{\partial T} \right)_{P, \mathbf{n}} - nR \quad (\text{VII})$$

$$A^r(T, P, \mathbf{n}) = A^r(T, V, \mathbf{n}) - nRT \ln Z \quad (\text{VIII})$$

$$S^r(T, P, \mathbf{n}) = S^r(T, V, \mathbf{n}) + nR \ln Z \quad (\text{IX})$$

$$C_V^r(T, P, \mathbf{n}) = C_V^r(T, V, \mathbf{n}) \quad (\text{X})$$

$$U^r(T, P, \mathbf{n}) = U^r(T, V, \mathbf{n}) \quad (\text{XI})$$

$$H^r(T, P, \mathbf{n}) = H^r(T, V, \mathbf{n}) \quad (\text{XII})$$

$$G^r(T, P, \mathbf{n}) = G^r(T, V, \mathbf{n}) - nRT \ln Z \quad (\text{XIII})$$

$$C_P^r(T, P, \mathbf{n}) = C_P^r(T, V, \mathbf{n}) \quad (\text{XIV})$$

Real fluids do not behave like perfect gases therefore we generalise eqn. (85) to define a property, the fugacity f , which for a perfect gas equals the pressure. The fugacity is defined in this way

$$RT \ln \frac{f(T, P)}{P_0} \equiv \mu(T, P) - \mu^*(T, P_0) \quad (86)$$

where $\mu(T, P)$ is the chemical potential of a pure fluid, liquid or gas. Since P in eqn. (85) is an arbitrary pressure, the definition of the fugacity does not depend on the reference pressure P_0 . By subtraction of eqn. (85) from eqn. (86) we can replace P_0 by P and obtain the expression for the fugacity coefficient $\varphi = f/P$ of a pure component

$$nRT \ln \varphi(T, P) \equiv nRT \ln \frac{f(T, P)}{P} = \mu(T, P) - \mu^*(T, P) \quad (87)$$

The fugacity coefficient of a perfect gas is unity. The expressions for the partial derivatives of the fugacity coefficient, the fugacity, and the chemical potential of a pure component are shown in Table 7.

Table 7: Derivatives of the fugacity coefficient, the fugacity, and the chemical potential of n moles of a pure component.

$$\begin{aligned} nRT \ln \varphi &= G^r(T, P, n) \\ &= A^r(T, V, n) + (PV - nRT) - nRT \ln Z \end{aligned} \quad (\text{I})$$

$$\begin{aligned} nRT \left(\frac{\partial \ln \varphi}{\partial T} \right)_P &= -\frac{A^r}{T} + \left(\frac{\partial A^r}{\partial T} \right)_V + \frac{V}{T} \left(\frac{\partial A^r}{\partial V} \right)_T \\ &= -\frac{H^r}{T} \end{aligned} \quad (\text{II})$$

$$nRT \left(\frac{\partial \ln \varphi}{\partial T} \right)_V = -\frac{H^r}{T} + V^r \left(\frac{\partial P}{\partial T} \right)_V \quad (\text{III})$$

$$nRT \left(\frac{\partial \ln \varphi}{\partial P} \right)_T = V - \frac{nRT}{P} = V^r \quad (\text{IV})$$

$$nRT \left(\frac{\partial \ln \varphi}{\partial P} \right)_V = -\frac{H^r}{T} \left(\frac{\partial T}{\partial P} \right)_V + V^r \quad (\text{V})$$

continues

$$nRT \left(\frac{\partial \ln \varphi}{\partial V} \right)_T = V^r \left(\frac{\partial P}{\partial V} \right)_T \quad (\text{VI})$$

$$nRT \left(\frac{\partial \ln \varphi}{\partial V} \right)_P = -\frac{H^r}{T} \left(\frac{\partial T}{\partial V} \right)_P \quad (\text{VII})$$

$$f = P \varphi \quad (\text{VIII})$$

$$nRT \left(\frac{\partial \ln f}{\partial T} \right)_P = -\frac{H^r}{T} \quad (\text{IX})$$

$$nRT \left(\frac{\partial \ln f}{\partial P} \right)_T = V \quad (\text{X})$$

$$\mu = \frac{G}{n} \quad (\text{XI})$$

$$\left(\frac{\partial \mu}{\partial T} \right)_P = -\frac{S}{n} = -s \quad (\text{XII})$$

$$\left(\frac{\partial \mu}{\partial P} \right)_T = \frac{V}{n} = v \quad (\text{XIII})$$

Mixtures

If we define the perfect gas mixture in terms of its equation of state $PV = nRT$, we shall have to integrate an equation similar to eqn. (83) to obtain the Gibbs energy, and we have then the problem of determining the constant of integration $\mu_i^*(T, P_0, \mathbf{n})$ which cannot be determined from the equation of state. We can evade this by defining the perfect gas mixture in terms of the Helmholtz energy $A^*(T, V, \mathbf{n})$, and then we can obtain all other properties by differentiation. The Helmholtz energy of n_i moles of a pure perfect gas of component i is

$$\begin{aligned} A_i^*(T, V, n_i) &= A_i^*(T, P, n_i) \\ &= G_i^*(T, P, n_i) - n_i RT = n_i \mu_i^*(T, P) - n_i RT \end{aligned} \quad (88)$$

When we insert $\mu_i^*(T, P)$ from eqn. (84) and use the equation of state of a perfect gas $PV = n_i RT$, the result is

$$\begin{aligned} A_i^*(T, V, n_i) &= n_i \left(\mu_i^*(T, P_0) + RT \ln \frac{P}{P_0} - RT \right) \\ &= n_i \left(\mu_i^*(T, P_0) + RT \ln \frac{n_i RT}{P_0 V} - RT \right) \end{aligned} \quad (89)$$

This is the equation we generalise in order to *define* a perfect gas mixture; it is *by definition* a mixture whose Helmholtz energy is calculable from the expression

$$A^*(T, V, n) \equiv \sum_i n_i \left(\mu_i^*(T, P_0) + RT \ln \frac{n_i RT}{P_0 V} - RT \right) \quad (90)$$

where P_0 is a fixed reference pressure, therefore μ_i^* depends on temperature, only. This definition conforms to the equation of state of a perfect gas

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T, n} = \frac{nRT}{V} \quad (91)$$

The derivative of eqn. (90) with respect the mole number of component i is the chemical potential of component i

$$\mu_i^*(T, V, n) = \left(\frac{\partial A}{\partial n_i} \right)_{T, V} = \mu_i^*(T, P_0) + RT \ln \frac{n_i RT}{P_0 V} \quad (92)$$

Furthermore, for a perfect gas mixture where $Z = 1$, we calculate $G^*(T, P, n)$ from eqns. (90) and (91)

$$\begin{aligned} G^*(T, P, n) &= A^*(T, V, n) + nRT \\ &= \sum_i n_i \left(\mu_i^*(T, P_0) + RT \ln \frac{n_i P}{n P_0} \right) \end{aligned} \quad (93)$$

and thus the chemical potential of component i is

$$\mu_i^*(T, P, n) = \left(\frac{\partial G}{\partial n_i} \right)_{T, P} = \mu_i^*(T, P_0) + RT \ln \frac{P x_i}{P_0} \quad (94)$$

where $x_i = n_i/n$ is the mole fraction of component i .

Eqn. (93) is the equation of the Gibbs energy of a perfect gas derived from the Helmholtz energy using the equation of state of a perfect gas, and eqns. (92) and (94) are the corresponding expressions of the chemical potentials.

These potentials are of course identical as long as we apply the equations to perfect gases. But when we calculate residual properties, we apply the equations of a perfect gas mixture to a real mixture, and in this case the two potentials will no longer be identical, and the properties we calculate are denoted the properties of a hypothetical perfect gas state irrespective of whether it is a gas or a liquid state.

It is sometimes convenient to replace the reference pressure P_0 in eqn. (94) by the pressure of the mixture P . We subtract eqn. (85) from eqn. (94) to obtain an equation for the chemical potential of component i in a perfect gas mixture

$$\mu_i^*(T, P, \mathbf{n}) = \mu_i^*(T, P) + RT \ln x_i \quad (95)$$

This equation has been obtained in consequence of the definition of the Helmholtz energy of a perfect gas mixture. This equation is very important because the definition of an ideal mixture shall conform to the chemical potentials of a perfect gas mixture. Ideal mixtures are not perfect gases but it would be odd if a perfect gas mixture was not considered an ideal mixture. A discussion of the ideal mixture is deferred to Section 10.

Real fluid mixtures are not perfect gas mixtures, therefore we generalise eqn. (94) to define a property \hat{f}_i , the fugacity of component i in a mixture. In the perfect gas state $\hat{f}_i = Px_i$. The definition is

$$RT \ln \frac{\hat{f}_i(T, P, \mathbf{n})}{P_0} \equiv \mu_i(T, P, \mathbf{n}) - \mu_i^*(T, P_0) \quad (96)$$

$\mu_i(T, P, \mathbf{n})$ is the chemical potential of component i in the mixture.

The expression for the fugacity coefficient $\hat{\varphi}_i = \hat{f}_i/Px_i$ of component i in a mixture is obtained by subtraction of eqn. (94) from eqn. (96)

$$\begin{aligned} RT \ln \hat{\varphi}_i(T, P, \mathbf{n}) &= RT \ln \frac{\hat{f}_i(T, P, \mathbf{n})}{Px_i} \\ &= \mu_i(T, P, \mathbf{n}) - \mu_i^*(T, P, \mathbf{n}) = \bar{G}_i^r(T, P, \mathbf{n}) \end{aligned} \quad (97)$$

The right-hand side of the equation is the partial molar residual Gibbs energy or the residual chemical potential of component i in a mixture. The fugacity coefficient holds its position in phase equilibrium calculations because we can calculate the partitioning between the phases with knowledge of the fugacity coefficients as discussed in Section 12. The fugacity coefficients of a perfect gas mixture are unity because $\hat{f}_i = Px_i$ in the perfect gas state.

A most important property is the difference between the chemical potentials of a hypothetical perfect gas at the two fluid states (T, V, \mathbf{n}) and

(T, P, \mathbf{n}) . This difference can be obtained by subtraction of eqn. (94) from eqn. (92)

$$\mu_i^*(T, V, \mathbf{n}) - \mu_i^*(T, P, \mathbf{n}) = -RT \ln Z \quad (98)$$

Since the state is a real fluid state and not a perfect gas state, the compressibility factor Z is not unity. When we apply an equation for a perfect gas property to a real fluid state, we denote the calculated properties the properties of a hypothetical perfect gas. The real fluid state may be a liquid or a gas state.

Eqns. (97) and (98) show that the fugacity coefficient of component i in the mixture $\hat{\varphi}_i$ is calculable as

$$\begin{aligned} RT \ln \hat{\varphi}_i(T, P, \mathbf{n}) &= \left(\frac{\partial G^r(T, P, \mathbf{n})}{\partial n_i} \right)_{T, P} \\ &= \mu_i(T, P, \mathbf{n}) - \mu_i^*(T, P, \mathbf{n}) \\ &= \mu_i(T, V, \mathbf{n}) - \mu_i^*(T, V, \mathbf{n}) - RT \ln Z \\ &= \left(\frac{\partial A^r(T, V, \mathbf{n})}{\partial n_i} \right)_{T, V} - RT \ln Z \\ &= -\frac{\partial}{\partial n_i} \left(\int_{\infty}^V \left(P - \frac{nRT}{V} \right) dV \right) - RT \ln Z \end{aligned} \quad (99)$$

where of course $\mu_i(T, V, \mathbf{n}) = \mu_i(T, P, \mathbf{n})$ and

$$Z = 1 - \frac{V}{nRT} \left(\frac{\partial A^r(T, V, \mathbf{n})}{\partial V} \right)_{T, \mathbf{n}} \quad (100)$$

These equations demonstrate that the fugacity coefficient is most readily calculated from the derivatives of the residual Helmholtz energy at state (T, V, \mathbf{n}) . The residual Helmholtz energy is obtained from the pressure equation $P(V, T, \mathbf{n})$ by performing an integration at constant temperature and composition and once this integration has been performed all other properties are obtained by differentiation. The expressions for the partial derivatives of the fugacity coefficient, the fugacity, and the chemical potentials with respect to temperature, pressure, volume, and the mole numbers are shown in Table 8.

The frequently used expression

$$\begin{aligned} RT \ln \hat{\varphi}_i &= \int_0^P \left(\bar{V}_i - \frac{RT}{P} \right) dP \\ &= - \int_{\infty}^V \left(\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right) dV - RT \ln Z \end{aligned}$$

is of course correct, but of less practical use.

Table 8: Derivatives of the fugacity coefficients, the fugacities, and the chemical potentials of a mixture.

$$RT \ln \hat{\varphi}_i = \left(\frac{\partial A^r}{\partial n_i} \right)_{T,V} - RT \ln Z = F^{(i)} \quad (\text{I})$$

$$\begin{aligned} RT \left(\frac{\partial \ln \hat{\varphi}_i}{\partial T} \right)_{P,n} &= \left(\frac{\partial^2 A^r}{\partial T \partial n_i} \right)_V - \frac{1}{T} \left(\frac{\partial A^r}{\partial n_i} \right)_{T,V} \\ &\quad + R - \bar{V}_i \left(\frac{\partial P}{\partial T} \right)_{V,n} \\ &= - \frac{\bar{H}_i^r(T, P, n)}{T} = F_T^{(i)} \end{aligned} \quad (\text{II})$$

$$RT \left(\frac{\partial \ln \hat{\varphi}_i}{\partial P} \right)_{T,n} = \bar{V}_i - \frac{RT}{P} = F_P^{(i)} \quad (\text{III})$$

$$\begin{aligned} RT \left(\frac{\partial \ln \hat{\varphi}_i}{\partial n_j} \right)_{T,P} &= \left(\frac{\partial^2 A^r}{\partial n_i \partial n_j} \right)_{T,V} \\ &\quad + \bar{V}_i \bar{V}_j \left(\frac{\partial P}{\partial V} \right)_{T,n} + \frac{RT}{n} = F_j^{(i)} = F_i^{(j)} \end{aligned} \quad (\text{IV})$$

$$RT \left(\frac{\partial \ln \hat{\varphi}_i}{\partial T} \right)_{V,n} = F_T^{(i)} + F_P^{(i)} \left(\frac{\partial P}{\partial T} \right)_{V,n} \quad (\text{V})$$

$$RT \left(\frac{\partial \ln \hat{\varphi}_i}{\partial P} \right)_{V,n} = F_T^{(i)} \left(\frac{\partial T}{\partial P} \right)_{V,n} + F_P^{(i)} \quad (\text{VI})$$

$$RT \left(\frac{\partial \ln \hat{\varphi}_i}{\partial n_j} \right)_{T,V} = F_j^{(i)} + F_P^{(i)} \left(\frac{\partial P}{\partial n_j} \right)_{T,V} \quad (\text{VII})$$

continues

$$RT \left(\frac{\partial \ln \hat{\varphi}_i}{\partial V} \right)_{T,n} = F_P^{(i)} \left(\frac{\partial P}{\partial V} \right)_{T,n} \quad (\text{VIII})$$

$$RT \left(\frac{\partial \ln \hat{\varphi}_i}{\partial V} \right)_{P,n} = F_T^{(i)} \left(\frac{\partial T}{\partial V} \right)_{P,n} \quad (\text{IX})$$

$$RT \left(\frac{\partial \ln \hat{\varphi}_i}{\partial n_j} \right)_{P,V} = F_j^{(i)} + F_T^{(i)} \left(\frac{\partial T}{\partial n_j} \right)_{P,V} \quad (\text{X})$$

where

$$Z = \frac{PV}{nRT} \quad (\text{XI})$$

$$P = - \left(\frac{\partial A^r}{\partial V} \right)_{T,n} + \frac{nRT}{V} \quad (\text{XII})$$

$$\left(\frac{\partial P}{\partial T} \right)_{V,n} = - \left(\frac{\partial^2 A^r}{\partial V \partial T} \right)_n + \frac{nR}{V} \quad (\text{XIII})$$

$$\left(\frac{\partial P}{\partial V} \right)_{T,n} = - \left(\frac{\partial^2 A^r}{\partial V^2} \right)_{T,n} - \frac{nRT}{V^2} \quad (\text{XIV})$$

$$\left(\frac{\partial P}{\partial n_i} \right)_{T,V} = - \left(\frac{\partial^2 A^r}{\partial V \partial n_i} \right)_T + \frac{RT}{V} \quad (\text{XV})$$

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T,P} = - \left(\frac{\partial P}{\partial n_i} \right)_{T,V} / \left(\frac{\partial P}{\partial V} \right)_{T,n} \quad (\text{XVI})$$

The following identities are obtained from eqn. (99) and eqns. (II) and (III) in this table.

$$\sum_i n_i \ln \hat{\varphi}_i = \frac{G^r(T, P, n)}{RT} \quad (\text{XVII})$$

$$\sum_i n_i \left(\frac{\partial \ln \hat{\varphi}_i}{\partial T} \right)_{P,n} = - \frac{H^r(T, P, n)}{RT^2} \quad (\text{XVIII})$$

$$\sum_i n_i \left(\frac{\partial \ln \hat{\varphi}_i}{\partial P} \right)_{T,n} = \frac{(Z-1)n}{P} \quad (\text{XIX})$$

Derivatives of the fugacity

$$\left(\frac{\partial \ln \hat{f}_i}{\partial T} \right)_{P,n} = -\frac{\bar{H}_i^r(T, P, n)}{RT^2} \quad (\text{XX})$$

$$\left(\frac{\partial \ln \hat{f}_i}{\partial P} \right)_{T,n} = \frac{\bar{V}_i}{RT} \quad (\text{XXI})$$

$$\left(\frac{\partial \ln \hat{f}_i}{\partial n_j} \right)_{T,P} = \left(\frac{\partial \ln \hat{\varphi}_i}{\partial n_j} \right)_{T,P} + \left(\frac{\delta_{ij}}{n_i} - \frac{1}{n} \right) \quad (\text{XXII})$$

Derivatives of the classical chemical potential

$$\left(\frac{\partial \mu_i}{\partial T} \right)_{P,n} = -\bar{S}_i \quad (\text{XXIII})$$

$$\left(\frac{\partial \mu_i}{\partial P} \right)_{T,n} = \bar{V}_i \quad (\text{XXIV})$$

$$\left(\frac{\partial \mu_i}{\partial n_j} \right)_{T,P} = \left(\frac{\partial \mu_j}{\partial n_i} \right)_{T,V} + \bar{V}_i \bar{V}_j \left(\frac{\partial P}{\partial V} \right)_{T,n} \quad (\text{XXV})$$

$$\begin{aligned} \left(\frac{\partial \mu_i}{\partial n_j} \right)_{T,P} &= \left(\frac{\partial \mu_j}{\partial n_i} \right)_{T,P} \\ &= RT \left(\frac{\partial \ln \hat{f}_i}{\partial n_j} \right)_{T,P} = RT \left(\frac{\partial a_i}{\partial n_j} \right)_{T,P} \\ &= RT \left(\frac{\partial \ln \gamma_i}{\partial n_j} \right)_{T,P} + RT \left(\frac{\delta_{ij}}{n_i} - \frac{1}{n} \right) \end{aligned} \quad (\text{XXVI})$$

The activity a_i is defined in Section 9 and the activity coefficient γ_i is defined in Section 11.

8 Application of Euler's theorem

In the appendix to this chapter, page 50, we have proved that when $M(\mathbf{a}, \mathbf{b})$ is a homogeneous function of *degree one* in variables \mathbf{b} , then the first derivatives with respect to the variables \mathbf{b} are themselves homogeneous functions of degree zero. That is

$$\sum_i b_i \left(\frac{\partial^2 M}{\partial b_i \partial b_k} \right)_{\mathbf{a}} = 0 \quad (\text{A6})$$

When we apply eqn. (A6) to the Helmholtz function, that is $M(\mathbf{a}, \mathbf{b}) = A(T, V, \mathbf{n})$, then $\mathbf{a} = T$ and $\mathbf{b} = (V, \mathbf{n})$. Therefore, we have two choices, either $b_k = n_k$ or $b_k = V$.

First, we analyse the case where $b_k = n_k$

$$\begin{aligned} & \sum_j b_j \left(\frac{\partial^2 A(T, V, \mathbf{n})}{\partial b_j \partial b_k} \right)_{T,V} \\ &= V \left(\frac{\partial^2 A(T, V, \mathbf{n})}{\partial V \partial n_k} \right)_T + \sum_j n_j \left(\frac{\partial^2 A(T, V, \mathbf{n})}{\partial n_j \partial n_k} \right)_{T,V} \\ &= -V \left(\frac{\partial P}{\partial n_k} \right)_{T,V} + \sum_j n_j \left(\frac{\partial \mu_j(T, V, \mathbf{n})}{\partial n_k} \right)_{T,V} = 0 \end{aligned} \quad (101)$$

Second, we analyse the case where $b_k = V$

$$\begin{aligned} & \sum_j b_j \left(\frac{\partial^2 A(T, V, \mathbf{n})}{\partial b_j \partial b_k} \right)_{T,V} \\ &= V \left(\frac{\partial^2 A(T, V, \mathbf{n})}{\partial V^2} \right)_{T,\mathbf{n}} + \sum_j n_j \left(\frac{\partial^2 A(T, V, \mathbf{n})}{\partial n_j \partial V} \right)_T \\ &= -V \left(\frac{\partial P}{\partial V} \right)_{T,\mathbf{n}} + \sum_j n_j \left(\frac{\partial \mu_j(T, V, \mathbf{n})}{\partial V} \right)_{T,\mathbf{n}} = 0 \end{aligned} \quad (102)$$

Eqns. (101) and (102) are very useful when checking the derivatives of the Helmholtz function.

When we apply eqn. (A6) to the Gibbs energy, that is $M(\mathbf{a}, \mathbf{b}) = G(T, P, \mathbf{n})$, then $\mathbf{a} = (T, P)$ and $\mathbf{b} = \mathbf{n}$. In the case of the Gibbs energy we only have the choice $b_k = n_k$. Therefore

$$\sum_j n_j \left(\frac{\partial^2 G(T, P, \mathbf{n})}{\partial n_j \partial n_k} \right)_{T,P} = \sum_j n_j \left(\frac{\partial \mu_j(T, P, \mathbf{n})}{\partial n_k} \right)_{T,P} = 0 \quad (103)$$

When eqn. (103) applies to the Gibbs energy, it also applies to the Gibbs energy of a perfect gas and thus also to the residual Gibbs energy which is the Gibbs energy minus the Gibbs energy of the corresponding hypothetical perfect gas.

$$\sum_j n_j \left(\frac{\partial^2 G^r(T, P, \mathbf{n})}{\partial n_j \partial n_k} \right)_{T,P} = \sum_j n_j \left(\frac{\partial \ln \phi_j(T, P, \mathbf{n})}{\partial n_k} \right)_{T,P} = 0 \quad (104)$$

And similarly for the excess Gibbs energy which is the Gibbs energy minus the Gibbs energy of the ideal mixture.

$$\sum_j n_j \left(\frac{\partial^2 G^E(T, P, \mathbf{n})}{\partial n_j \partial n_k} \right)_{T, P} = \sum_j n_j \left(\frac{\partial \ln \gamma_j(T, P, \mathbf{n})}{\partial n_k} \right)_{T, P} = 0 \quad (105)$$

The activity coefficient γ_j and the excess Gibbs energy are defined in Section 11.

For a more detailed discussion of Euler's theorem, the reader is referred to the appendix to this chapter.

9 Reference state and activity

In this section we define the reference state chemical potential and the activity. The reference state chemical potential equals the pure component chemical potential at the temperature of the solution, but the reference pressure is arbitrary. In the previous sections we defined the pure component fugacity, eqn. (86) and the fugacity of component i in a mixture, eqn. (96). If we subtract eqn. (86) from eqn. (96), the result is

$$\mu_i(T, P, \mathbf{n}) = \mu_i(T, P) + RT \ln \frac{\hat{f}_i(T, P, \mathbf{n})}{f_i(T, P)} \quad (106)$$

The ratio of the fugacity of component i in a mixture over the corresponding pure component fugacity at the same temperature and pressure *defines* the activity

$$a_i(T, P, \mathbf{n}) \equiv \frac{\hat{f}_i(T, P, \mathbf{n})}{f_i(T, P)} \quad (107)$$

The pure component chemical potential $\mu_i(T, P)$ is denoted the reference state chemical potential, the fugacity $f_i(T, P)$ is the reference state fugacity, and P and T are the reference state pressure and temperature.

The reference state temperature is the temperature of the mixture, but the reference state pressure is arbitrary. If the reference pressure is fixed, we can calculate the pure component fugacity at a reference pressure $P = P_0$ from eqn. (86). If we subtract this expression from eqn. (96), the result is

$$\mu_i(T, P, \mathbf{n}) = \mu_i(T, P_0) + RT \ln \frac{\hat{f}_i(T, P, \mathbf{n})}{f_i(T, P_0)} \quad (108)$$

The reference chemical potential is now calculated at a fixed reference pressure P_0 and one has to note that the fugacity ratio in this equation is no longer equal to the activity. If the pure component is considered to be a

perfect gas at an arbitrary pressure P or at a fixed reference pressure P_0 , then

$$\mu_i(T, P, \mathbf{n}) = \mu_i^*(T, P) + RT \ln \frac{\hat{f}_i(T, P, \mathbf{n})}{P} \quad (109)$$

or

$$\mu_i(T, P, \mathbf{n}) = \mu_i^*(T, P_0) + RT \ln \frac{\hat{f}_i(T, P, \mathbf{n})}{P_0} \quad (110)$$

Eqn. (110) is identical with eqn. (86).

10 Ideal mixtures

The ideal mixture is a convenient hypothetical state which no real solution strictly follows, but the ideal solution or the ideal mixture is a convenient reference of normal behaviour of solutions. There is no unique definition of an ideal solution, but it is most convenient that the definition conforms to the equation for the chemical potential of a perfect gas mixture, eqn. (95), that is, in view of eqn. (106) a mixture is *by definition* ideal when the activity equals the mole fraction and consequently

$$\mu_i^{id}(T, P, \mathbf{n}) \equiv \mu_i(T, P) + RT \ln x_i \quad (111)$$

and therefore

$$\hat{f}_i(T, P, \mathbf{n}) = f_i(T, P) x_i \quad (112)$$

In view of eqn. (111), the Gibbs energy of an ideal solution is

$$G^{id}(T, P, \mathbf{n}) = \sum_i n_i \mu_i(T, P) + RT \sum_i n_i \ln x_i \quad (113)$$

and consequently

$$\left(\frac{\partial G^{id}(T, P, \mathbf{n})}{\partial P} \right)_{T, \mathbf{n}} = V^{id} = \sum_i n_i v_i(T, P) = \sum_i V_i(T, P, n_i) \quad (114)$$

and

$$\begin{aligned} - \left(\frac{\partial G^{id}(T, P, \mathbf{n})}{\partial T} \right)_{P, \mathbf{n}} &= S^{id} = \sum_i n_i s_i(T, P) - R \sum_i n_i \ln x_i \\ &= \sum_i S_i(T, P, n_i) - R \sum_i n_i \ln x_i \end{aligned} \quad (115)$$

If we define a property change of mixing of an ideal solution ΔM^{id} as

$$\Delta M^{id} = M^{id} - \sum_i M_i \quad (116)$$

where M_i is the property of n_i moles of pure component, the property changes of mixing become zero except for

$$\Delta G^{id} = \Delta A^{id} = RT \sum_i n_i \ln x_i \quad (117)$$

and

$$\Delta S^{id} = -R \sum_i n_i \ln x_i \quad (118)$$

11 Non-ideal mixtures

The reference state for the symmetric activity coefficient

In the previous section we defined an ideal mixture as a solution where all the activities equal the mole fractions. To account for the non-ideality we introduce a quantity, the activity coefficient that in a non-ideal solution equals the activity divided by the mole fraction. The activity coefficient is *defined* as

$$\gamma_i(T, P, \mathbf{n}) \equiv \frac{a_i(T, P, \mathbf{n})}{x_i} = \frac{\hat{f}_i(T, P, \mathbf{n})}{x_i f_i(T, P)} = \frac{\hat{\varphi}_i(T, P, \mathbf{n})}{\varphi_i(T, P)} \quad (119)$$

The chemical potentials of the components in a fluid mixture are according to eqns. (106) and (119) calculable as

$$\begin{aligned} \mu_i(T, P, \mathbf{n}) &= \mu_i(T, P) + RT \ln a_i(T, P, \mathbf{n}) \\ &= \mu_i(T, P) + RT \ln \gamma_i(T, P, \mathbf{n}) x_i \end{aligned} \quad (120)$$

This equation and eqn. (119) are equivalent. The reference state chemical potentials shall be the chemical potentials of the pure components at the temperature and pressure of the solution. If we choose a different reference pressure, the activity coefficient will be a function of the pressure of the solution as well as the reference pressure.

Like the activity, the activity coefficient is a function of the temperature, pressure and the mole numbers of the solution. Because the pressure in the reference chemical potential of the pure component $\mu_i(T, P)$ is the solution pressure P , the activity coefficient is unity for a pure component

$$\lim_{n_j \rightarrow 0} \gamma_i(T, P, \mathbf{n}) = 1, \quad j \neq i \quad (121)$$

This activity coefficient is usually referred to as the symmetric activity coefficient.

According to eqn. (119) we can calculate the fugacity of component i in a mixture from the fugacity coefficient or from the pure component fugacity and the activity coefficient, that is

$$\hat{f}_i(T, P, n) = \hat{\varphi}_i(T, P, n) P x_i = f_i(T, P) \gamma_i(T, P, n) x_i \quad (122)$$

If we use an equation of state, we can calculate the fugacity coefficient according to eqn. (99), but in cases where the equation of state models fail we will resort to empirical activity coefficient models. This subject will be discussed in Section 12 and in Chapter 5.

The Gibbs energy of the mixture is

$$\begin{aligned} G(T, P, n) &= \sum_i n_i \mu_i(T, P, n) \\ &= \sum_i n_i \mu_i(T, P) + RT \sum_i n_i \ln \gamma_i(T, P, n) x_i \\ &= G^{id}(T, P, n) + RT \sum_i n_i \ln \gamma_i(T, P, n) \end{aligned} \quad (123)$$

In general, we define an excess property as the property of the mixture minus that of the equivalent ideal mixture at constant temperature and pressure, that is

$$\begin{aligned} M^E(T, P, n) &= M(T, P, n) - M^{id}(T, P, n) \\ &= M^r(T, P, n) + M^*(T, P, n) - \left(\sum_i M_i^r(T, P, n_i) + M^*(T, P, n) \right)^{id} \\ &= M^r(T, P, n) - \sum_i M_i^r(T, P, n_i) \end{aligned} \quad (124)$$

where $M^*(T, P, n)$ denotes the property of the hypothetical perfect gas mixture and $M_i^r(T, P, n_i)$ denotes the residual property of n_i moles of the pure substance. Of particular importance is the excess Gibbs energy

$$\begin{aligned} G^E(T, P, n) &= G(T, P, n) - G^{id}(T, P, n) = A^E(T, P, n) + PV^E \\ &= A^r(T, V, n) - \sum_i A_i^r(T, V_i, n_i) \\ &\quad + RT \sum_i n_i \ln \frac{V_i}{V} + P \left(V - \sum_i V_i \right) \end{aligned} \quad (125)$$

where V_i denotes the volume of n_i moles of the pure substance.

If we have an appropriate model for the $A(T, V, \mathbf{n})$ surface, we can by means of eqn. (125) derive the corresponding excess Gibbs energy model and in particular when $P = 0$, the equation can be used to incorporate activity coefficient models in an equation of state to improve the mixing rules.

According to the definition of an excess property, eqn. (124), and the equation for the Gibbs energy, eqn. (123), the excess Gibbs energy is calculable from the activity coefficients and vice versa

$$G^E(T, P, \mathbf{n}) = RT \sum_i n_i \ln \gamma_i \quad (126)$$

Therefore, we can calculate the activity coefficients as the partial molar excess Gibbs energies because

$$\begin{aligned} \left(\frac{\partial G^E}{\partial n_i} \right)_{T, P, n_j} &= \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j} - \left(\frac{\partial G^{id}}{\partial n_i} \right)_{T, P, n_j} = \mu_i - \mu_i^{id} \\ &= RT \ln \gamma_i \end{aligned} \quad (127)$$

but neither eqn. (126) nor eqn. (127) define the activity coefficient. The definition is shown in eqn. (119).

The reference state for the asymmetric activity coefficient in a single solvent

It may in some cases be convenient to replace the pure component chemical potential $\mu_i(T, P)$ in eqn. (120) by a reference state which includes the partial molar excess Gibbs energy at infinite dilution. Adding and subtracting this term gives

$$\mu_i(T, P, \mathbf{n}) = \mu_i(T, P) + RT \ln \gamma_i^\infty + RT \ln \frac{\gamma_i}{\gamma_i^\infty} x_i \quad (128)$$

where γ_i^∞ is the symmetric activity coefficient of component i at infinite dilution in a single solvent k . That is

$$\gamma_i^\infty(T, P, n_k) = \lim_{n_i \rightarrow 0} \gamma_i(T, P, \mathbf{n}), \quad i \neq k \quad (129)$$

It is convenient to take the ratio $\gamma_i / \gamma_i^\infty$ as the definition of the asymmetric activity coefficient, that is

$$\bar{\gamma}_i(T, P, \mathbf{n}) \equiv \frac{\gamma_i(T, P, \mathbf{n})}{\gamma_i^\infty(T, P, n_k)} = \frac{\hat{\varphi}_i(T, P, \mathbf{n})}{\hat{\varphi}_i^\infty(T, P, n_k)} \quad (130)$$

where $\hat{\varphi}_i^\infty(T, P, n_k)$ is the fugacity coefficient of component i in the mixture at infinite dilution in a single solvent k

$$\hat{\varphi}_i^\infty(T, P, n_k) = \lim_{n_i \rightarrow 0} \hat{\varphi}_i(T, P, \mathbf{n}), \quad i \neq k \quad (131)$$

As expected, eqn. (130) shows that the asymmetric activity coefficient $\tilde{\gamma}_i$ is unity in the limit of infinite dilution in a single solvent k , that is

$$\lim_{n_i \rightarrow 0} \tilde{\gamma}_i(T, P, n) = 1 , \quad i \neq k \quad (132)$$

but it would be completely mistaken to take this as an indication of ideal solution behaviour.

We insert the asymmetric activity coefficient $\tilde{\gamma}_i$ in eqn. (128) and write it in a form equivalent to eqn. (120)

$$\mu_i(T, P, n) = \tilde{\mu}_i(T, P, n_k) + RT \ln \tilde{\gamma}_i(T, P, n) x_i \quad (133)$$

where the reference state chemical potential is

$$\begin{aligned} \tilde{\mu}_i(T, P, n_k) &\equiv \mu_i(T, P) + RT \ln \gamma_i^\infty(T, P, n_k) \\ &= \mu_i(T, P) + \bar{G}_i^{E,\infty}(T, P, n_k) \end{aligned} \quad (134)$$

The equation shows that the reference state chemical potential $\tilde{\mu}_i(T, P, n_k)$ includes the partial molar Gibbs energy $\bar{G}_i^{E,\infty}$ of component i at infinite dilution in solvent k and it thus depends on the nature of the solute-solvent interaction. Eqn. (133) is not another definition of non-ideal solution behaviour, it is derived from eqn. (120), and it is exactly identical with eqn. (120). When the activity coefficient is asymmetric, we cannot use eqn. (122) to calculate the fugacity of component i in the solution. However, the equivalent expression can be obtained by making the substitution $\gamma_i = \gamma_i^\infty / \tilde{\gamma}_i$ in eqn. (122). The result is

$$\begin{aligned} \hat{f}_i(T, P, n) &= f_i(T, P) \gamma_i^\infty(T, P, n_k) \tilde{\gamma}_i(T, P, n) \\ &= h_i^\infty(T, P, n_k) \tilde{\gamma}_i(T, P, n) x_i \end{aligned} \quad (135)$$

where h_i^∞ is Henry's constant which by definition is

$$h_i^\infty(T, P, n_k) \equiv f_i(T, P) \gamma_i^\infty(T, P, n_k) = P \varphi_i^\infty(T, P, n_k) \quad (136)$$

Henry's constant is a function of the properties of the solute-solvent interaction in contrast to the reference fugacity $f_i(T, P)$ in eqn. (122) that is a pure component property.

Discussion

The introduction of the asymmetric activity coefficient and in particular eqn. (133) does not provide us with another or an equivalent definition of non-ideal

solution behaviour. Eqn. (133) has been derived from eqn. (120) by adding and subtracting the partial molar excess Gibbs energy at infinite dilution as shown in eqn. (128). To ensure a consistent framework only two equations are required to define the ideal and the non-ideal solution behaviour. Therefore, the symmetric and the asymmetric activity coefficients cannot be defined independently. *Once the reference state for and the behaviour of the ideal and the non-ideal solution are defined, it is mandatory that all other equations are derived from these definitions.* As mentioned in Section 10, it is most convenient that the definition of the ideal mixture, eqn. (111) conforms to the equation for the chemical potentials of a perfect gas mixture, eqn. (95). The definition of ideal solution behaviour must be independent of whether we deal with hydrocarbon mixtures, mixtures of commodity chemicals, polymer mixtures or electrolyte solutions. In the framework of the classical thermodynamics, the definitions of ideal and non-ideal solution behaviour cannot depend on the nature of the components in question. A further discussion of this subject is deferred to Section 13.

Although the asymmetric activity coefficient $\tilde{\gamma}_i$ is unity in the limit of infinite dilution this does not involve that the solution at infinite dilution is ideal in the sense of eqn. (111). In general, a highly diluted solute deviates much more from ideal solution behaviour than the solvent does. We should take cognizance of the fact that eqn. (120) has a pure component reference state whereas eqn. (133) has a reference state that includes the partial molar excess Gibbs energy of component i at infinite dilution in a single solvent k . This reference state depends on the nature of the solute-solvent interaction and asymmetric activity coefficients determined for solutes in one solvent cannot be applied for other solvents or mixed solvents. If the solvent is changed, the reference state will also change and so will Henry's constant because

$$\begin{aligned} \frac{h_i^\infty(\text{solvent } \alpha)}{\gamma_i^\infty(\text{solvent } \alpha)} &= \frac{h_i^\infty(\text{solvent } \beta)}{\gamma_i^\infty(\text{solvent } \beta)} \\ &= \frac{h_i^\infty(\text{mixed solvent})}{\gamma_i^\infty(\text{mixed solvent})} = f_i(T, P) \end{aligned} \quad (137)$$

The reference state for the asymmetric activity coefficient in mixed solvents

The application of asymmetric activity coefficients in mixed solvents is not straightforward because the reference state of a solute will inevitably depend on the solvent composition. The activity coefficient of a solute i at infinite dilution shall be defined as the limiting activity coefficient when all solute

concentrations approach zero while the mole numbers of solvent components are constant, that is

$$\gamma_i^\infty(T, P, \mathbf{n}_{solvents}) = \lim_{n_i \rightarrow 0} \gamma_i(T, P, \mathbf{n}), \quad i \neq solvents \quad (138)$$

and the reference state chemical potential is accordingly

$$\tilde{\mu}_i(T, P, \mathbf{n}_{solvents}) = \mu_i(T, P) + RT \ln \gamma_i^\infty(T, P, \mathbf{n}_{solvents}) \quad (139)$$

and Henry's constant

$$\begin{aligned} h_i^\infty(T, P, \mathbf{n}_{solvents}) &= f_i(T, P) \gamma_i^\infty(T, P, \mathbf{n}_{solvents}) \\ &= P \hat{\varphi}_i^\infty(T, P, \mathbf{n}_{solvents}) \end{aligned} \quad (140)$$

The equations show that the normalization of $\tilde{\gamma}$ depends on the solvent composition, and therefore the reference state and Henry's constant in mixed solvents shall depend on the solvent composition. Henry's constant in a mixed solvent cannot be calculated from Henry's constants in pure solvents. *There is no mixing rule for Henry's constants.* The variations of Henry's constant with solvent composition shall be obtained from a thermodynamic model for the fugacity coefficient in infinite dilution. It can also be obtained from the pure component fugacity and the symmetric activity coefficient at infinite dilution. In general, if these models were available, there would be no need for an asymmetric activity coefficient at all and therefore Henry's constant is often treated as an adjustable parameter.

In order to use the asymmetric normalization in mixed solvents one must therefore choose one of the solvents as the reference solvent and treat other components present as solutes.

Table 9: Activity coefficients, Henry's constants and their derivatives.

The symmetric activity coefficient

$$\begin{aligned} \gamma_i(T, P, \mathbf{n}) &\equiv \frac{a_i(T, P, \mathbf{n})}{x_i} = \frac{\hat{\varphi}_i(T, P, \mathbf{n})}{\varphi_i(T, P)} \\ &= \frac{\bar{G}_i^E}{RT} = \frac{1}{RT} \left(\frac{\partial G^E(T, P, \mathbf{n})}{\partial n_i} \right)_{T, P} \end{aligned} \quad (I)$$

continues

$$G^E = RT \sum_i n_i \ln \gamma_i \quad (\text{II})$$

$$H^E = -RT^2 \sum_i n_i \left(\frac{\partial \ln \gamma_i}{\partial T} \right)_{P,n} \quad (\text{III})$$

$$V^E = RT \sum_i n_i \left(\frac{\partial \ln \gamma_i}{\partial P} \right)_{T,n} \quad (\text{IV})$$

$$\left(\frac{\partial \ln \gamma_i}{\partial T} \right)_{P,n} = \left(\frac{\partial \ln \hat{\varphi}_i(T, P, n)}{\partial T} \right)_{P,n} - \left(\frac{\partial \ln \varphi_i(T, P)}{\partial T} \right)_P \quad (\text{V})$$

$$\left(\frac{\partial \ln \gamma_i}{\partial P} \right)_{T,n} = \frac{\bar{V}_i(T, P, n) - v_i(T, P)}{RT} \quad (\text{VI})$$

The asymmetric activity coefficient, k denotes a pure solvent

$$\tilde{\gamma}_i(T, P, n) \equiv \frac{\gamma_i(T, P, n)}{\gamma_i^\infty(T, P, n_k)} = \frac{\hat{\varphi}_i(T, P, n)}{\hat{\varphi}_i^\infty(T, P, n_k)} \quad (\text{VII})$$

$$\begin{aligned} \left(\frac{\partial \ln \tilde{\gamma}_i}{\partial T} \right)_{P,n} &= \left(\frac{\partial \ln \hat{\varphi}_i(T, P, n)}{\partial T} \right)_{P,n} \\ &\quad - \left(\frac{\partial \ln \hat{\varphi}_i^\infty(T, P, n_k)}{\partial T} \right)_{P,n} \end{aligned} \quad (\text{VIII})$$

$$\left(\frac{\partial \ln \tilde{\gamma}_i}{\partial P} \right)_{T,n} = \frac{\bar{V}_i(T, P, n) - V_i^\infty(T, P, n_k)}{RT} \quad (\text{IX})$$

Henry's constant

$$h_i^\infty(T, P, n_k) \equiv f_i(T, P) \gamma_i^\infty(T, P, n_k) = P \hat{\varphi}_i^\infty(T, P, n_k) \quad (\text{X})$$

$$\left(\frac{\partial \ln h_i^\infty}{\partial T} \right)_{P,n} = - \left(\frac{\partial \ln \hat{\varphi}_i^\infty(T, P, n_k)}{\partial T} \right)_{P,n} \quad (\text{XI})$$

$$\left(\frac{\partial \ln h_i^\infty}{\partial P} \right)_{T,n} = \frac{\bar{V}_i^\infty(T, P, n_k)}{RT} \quad (\text{XII})$$

continues

The ratio rule

$$\begin{aligned} \frac{h_i^\infty(\text{solvent } \alpha)}{\gamma_i^\infty(\text{solvent } \alpha)} &= \frac{h_i^\infty(\text{solvent } \beta)}{\gamma_i^\infty(\text{solvent } \beta)} \\ &= \frac{h_i^\infty(\text{mixed solvent})}{\gamma_i^\infty(\text{mixed solvent})} = f_i(T, P) \end{aligned} \quad (\text{XIII})$$

12 The equilibrium ratio

High pressure fluid phase equilibria

The equilibrium conditions for an isolated unconstrained multiphase system are shown in eqns. (51)-(53). These equations show that when an isolated unconstrained multiphase system is at equilibrium the temperature and pressure are uniform throughout the system and for any phase α or β

$$\mu_i^\beta = \mu_i^\alpha, \quad \beta \neq \alpha \quad \text{and} \quad i = 1, \dots, C \quad (141)$$

We can replace the chemical potentials by the corresponding fugacities if we use eqn. (96) to calculate the chemical potentials. Since the chemical potentials $\mu_i^*(T, P_0)$ are identical in all phases, the equivalent of eqn. (141) is

$$\hat{f}_i^\beta = \hat{f}_i^\alpha, \quad \beta \neq \alpha \quad \text{and} \quad i = 1, \dots, C \quad (142)$$

This equation is identical with eqn. (141) but more convenient to use because the fugacities are calculable from an equation of state.

When x_i and y_i denote the mole fractions of component i in an x -phase and a y -phase, respectively, we can write eqn. (142) as

$$\hat{\varphi}_i^x x_i = \hat{\varphi}_i^y y_i \quad (143)$$

The ratio of the y -phase mole fraction over the x -phase mole fraction is often denoted the equilibrium ratio K_i . In vapour-liquid equilibria y is usually a vapour phase mole fraction and x a liquid phase mole fraction. Using the definition $K = y/x$ an expression for the equilibrium ratio in terms of the fugacity coefficients of the component in the two phases is readily obtained from eqn. (143)

$$K_i = \frac{y_i}{x_i} = \frac{\hat{\varphi}_i^x}{\hat{\varphi}_i^y} \quad (144)$$

The fugacity coefficients are calculable from an appropriate equation of state using eqns. (99) and (100).

Low pressure vapour-liquid and gas-liquid equilibria

For many substances we do not have equations of state that with sufficient accuracy can correlate the properties of mixtures in the liquid state and we must therefore resort to activity coefficient models. Eqn. (122) shows that we can calculate the fugacity of component i in a mixture from the fugacity coefficient or from the pure component fugacity and the activity coefficient. If we use an equation of state to calculate the fugacity coefficient in the vapour phase v and the pure component fugacity and an activity coefficient in the liquid phase l , the result is

$$P y_i \hat{\phi}_i^v(T, P, n) = \hat{f}_i = f_i^l(T, P) \gamma_i(T, P, n) x_i \quad (145)$$

Usually, at low pressure we can assume that the vapour phase behaves almost like a perfect gas therefore the vapour phase fugacity coefficient $\hat{\phi}_i$ is approximately unity.

Furthermore, at low pressure the pure component fugacity is approximately equal to the pure component vapour pressure $P_i^{sat}(T)$. That is

$$P y_i = \hat{f}_i = P_i^{sat}(T) \gamma_i x_i \quad (146)$$

If we prefer to use the asymmetric activity coefficient, the equivalent of eqn. (146) is

$$P y_i = \hat{f}_i = h_i^\infty(T, P, n_k) \tilde{\gamma}_i(T, P, n) x_i \quad (147)$$

where k denotes the solvent. h_i^∞ is Henry's constant of component i in the solvent and it depends on the solvent composition and therefore this equation is not straightforward to apply for mixed solvents.

We have not mentioned Raoult's 'law' and Henry's 'law' because it is misleading to name an approximation a law. In thermodynamics we are concerned with two laws, the first and the second law, only. Raoult's 'law' and Henry's 'law' are neither consequences of nor indications of ideal solution behaviour. They are approximations valid in a certain range of composition solely to the fact that the activity coefficients may be considered constant. Raoult's 'law' applies to the solvent and Henry's 'law' to the solute. If x_1 is the solute concentration in a very dilute solution and x_2 the corresponding solvent concentration, then by combining eqns. (146) and (147) and noting that $\gamma_2 \approx 1$ the total pressure of the solution is

$$P \simeq P_1^{sat} \gamma_1^\infty x_1 + P_2^{sat} x_2 = h_1^\infty x_1 + P_2^{sat} x_2 \quad (148)$$

In an ideal solution all activity coefficients are unity at all concentrations and not just in a limited range of concentrations.

Low pressure liquid-liquid equilibria

When all the components are in the liquid state, we can use the right-hand side of eqn. (122) to calculate the fugacity of component i in the liquid phases. That is

$$f_i^\alpha(T, P) \gamma_i^\alpha(T, P, n) x_i^\alpha = f_i^\beta(T, P) \gamma_i^\beta(T, P, n) x_i^\beta \quad (149)$$

and because $f_i^\alpha(T, P) = f_i^\beta(T, P)$ the equation simplifies to

$$\gamma_i^\alpha x_i^\alpha = \gamma_i^\beta x_i^\beta \quad (150)$$

which shows that ideal mixtures are always fully miscible.

Solid solubility

If a pure solid is in equilibrium with a fluid phase, we can either use an equation of state or an activity coefficient model to calculate the fugacity \hat{f}_s of the solute. If we use an equation of state to calculate the fugacity coefficient $\hat{\varphi}_s$ of the solute s in the fluid phase. The equilibrium relation is

$$P x_s \hat{\varphi}_s = \hat{f}_s = f_s^{solid}(T, P) \quad (151)$$

where x_s is the mole fraction of the solid in the fluid phase.

However, if the fluid phase is a liquid phase, we may prefer to use an activity coefficient model. In this case the equilibrium relation is

$$f_s^{liq}(T, P) \gamma_s(T, P, n) x_s = \hat{f}_s = f_s^{solid}(T, P) \quad (152)$$

The reference state fugacities f_s^{liq} and f_s^{solid} are not identical but their mutual relation can be calculated. It depends on the change in enthalpy and heat capacity upon melting. If Δ denotes a property change upon a phase transition from liquid to solid and T_0 is a temperature where ΔH_0 has been measured, usually the triple point, then the fugacity of pure s in the liquid phase over that in the solid phase is calculable from the equation

$$\begin{aligned} \ln \frac{f_s^{liq}(T, P)}{f_s^{solid}(T, P)} &= \frac{\Delta G(T, P)}{RT} \\ &= \frac{\Delta H_0}{RT_0} \left(\frac{T_0}{T} - 1 \right) - \frac{\Delta C_p}{R} \left(\frac{T_0}{T} - 1 \right) + \frac{\Delta C_p}{R} \ln \frac{T_0}{T} \end{aligned} \quad (153)$$

ΔC_p is the difference in the heat capacity between s as a pure liquid and as a pure solid phase and it is assumed that this difference can be regarded as temperature independent. This equation neglects the effect of pressure on the properties of the solid and liquid phases.

13 Other reference states

Ideal solutions

Strictly speaking, no mixture is an ideal solution or an ideal mixture but the ideal mixture is a most convenient reference of normal behaviour of solutions and as mentioned in Section 10 there are no unique definition of an ideal solution, but it is most convenient that the definition of the ideal solution conforms to the equation of the chemical potential of a perfect gas mixture, eqn. (95). The definition of ideal mixture behaviour must of course be independent of the nature of the mixture. To ensure a consistent framework only two equations are required to define the ideal and the non-ideal solution behaviour. Once the reference state for and the behaviour of the ideal and the non-ideal solutions are defined, it is mandatory that all other equations are derived from these definitions. The definitions used throughout are eqns. (111) and (120). In various contexts, other definitions of 'ideal' solution behaviour are often encountered but the proper physical meaning of the reference potentials in these definitions must be deduced from eqns. (111) and (120). Two independent definitions of ideal mixture behaviour make little sense and besides it will disrupt the internal consistency of the framework.

We will investigate two equations of 'ideal' solution behaviour

$$\mu_i = \mu_{c_i}^0 + RT \ln c_i \quad (154)$$

and

$$\mu_i = \mu_{m_i}^0 + RT \ln m_i \quad (155)$$

where c_i is the molarity (moles of solute per litre of solution) and m_i the molality (moles of solute per kilogram of solvent, usually water). But in order to ensure a consistent framework these equations must comply with eqn. (111). Therefore the reference state chemical potentials $\mu_{c_i}^0$ and $\mu_{m_i}^0$ in eqns. (154) and (155), respectively, cannot arbitrarily be identified as the chemical potentials of the solute in a hypothetical one molar or one molal 'ideal' solution. The reference state chemical potential cannot depend on the measure of concentration nor the units employed. Since x_i , c_i , and m_i are interrelated, the reference state chemical potentials in the various equations must be interrelated because the chemical potentials on the left-hand side of the equations must be identical.

If we use the identity

$$c_i = \frac{n_i}{V} = \frac{n_i n}{n V} = x_i c \quad (156)$$

we can from eqn. (154) get the identity

$$\mu_i(T, P, c) = \mu_{c_i}^0 + RT \ln c_i = \mu_{c_i}^0 + RT \ln c + RT \ln x_i \quad (157)$$

To ensure a consistent framework, this equation must of course comply with the definition of ideal solution behaviour, eqn. (111). Therefore, if eqn. (154) provides the chemical potential of an ideal solution the reference chemical potential shall be

$$\mu_{c_i}^0 \equiv \mu_i(T, P) - RT \ln c \quad (158)$$

which demonstrates that the reference state $\mu_{c_i}^0$ in eqn. (154) depends on the molarity of the solution c . The reference chemical potential $\mu_{c_i}^0$ has little physical significance.

Ideal electrolyte solutions

In electrolyte solution thermodynamics molalities m_i are more often used than mole fractions. A laudable exception is Chapter XI 'Electrochemical systems' by Münster (1970). The reason for using molality is not obvious. The molality is defined as the number of moles of solute per kg of solvent, usually water. To convert from mole fractions to molality we make use of the identity

$$x_i = \frac{n_i}{n} = \frac{n_i}{\frac{n_w M_w}{1000}} \frac{n_w}{n} \frac{M_w}{1000} = \frac{m_i}{m_0} x_w \quad (159)$$

where n_i is the moles of solute, n the total number of moles in the solution, n_w is the moles of water, M_w is the molecular weight of water, m_i is the molality of the solute, x_w is the mole fraction of water, and finally m_0 is the molality of pure water, $m_0 = 55.5$. If we combine eqns. (155) and (156), we obtain the following identity

$$\mu_i(T, P, m) = \mu_{m_i}^0 + RT \ln m_i = \mu_{m_i}^0 + RT \ln \frac{m_0}{x_w} + RT \ln x_i \quad (160)$$

This equation must of course comply with the definition of ideal solution behaviour, eqn. (111). Therefore, if eqn. (156) indicates ideal solution behaviour, the reference chemical potential shall be

$$\mu_{m_i}^0 = \mu_i(T, P) - RT \ln \frac{m_0}{x_w} \quad (161)$$

which shows that the reference chemical potential $\mu_{m_i}^0$ in eqn. (156) depends on the mole fraction of solvent x_w . The reference chemical potential $\mu_{m_i}^0$ has little physical significance.

Non-ideal solutions

An asymmetric activity coefficient can be introduced in eqn. (154) to account for the deviation from 'ideality'. In this case the equation for the chemical

potential of component i is

$$\mu_i(T, P, \mathbf{c}) = \tilde{\mu}_{c_i}^0 + RT \ln c_i \tilde{\gamma}_i(T, P, \mathbf{c}) \quad (162)$$

The activity coefficient is defined in eqn. (120). The activity coefficient must of course be independent of the measure of concentration, i.e. whether we use mole fractions, molarity or molality, that is

$$\tilde{\gamma}_i(T, P, \mathbf{c}) \equiv \frac{\gamma_i(T, P, \mathbf{c})}{\gamma_i^\infty(T, P, c_k)} = \tilde{\gamma}_i(T, P, \mathbf{n}) \equiv \frac{\gamma_i(T, P, \mathbf{n})}{\gamma_i^\infty(T, P, n_k)} \quad (163)$$

otherwise it will have little physical significance. Partial derivatives with respect to molarity are not partial molar quantities. Like in eqn. (133) the reference state chemical potential in eqn. (162) depends on the activity coefficient at infinite dilution in solvent k . That is to ensure the consistency of the framework the reference chemical potentials shall be

$$\begin{aligned} \tilde{\mu}_{c_i}^0 &= \mu_{c_i}^0 + RT \ln \gamma_i^\infty(T, P, c_k) \\ &= \mu_i(T, P) - RT \ln c + RT \ln \gamma_i^\infty(T, P, c_k) \end{aligned} \quad (164)$$

where c_k is the molarity of the solvent.

Non-ideal electrolyte solutions

In electrolyte solutions an asymmetric activity coefficient is used to account for the deviation from ideality. In this case the equation for the chemical potential of component i becomes

$$\mu_i(T, P, \mathbf{m}) = \tilde{\mu}_{m_i}^0 + RT \ln m_i \tilde{\gamma}_i(T, P, \mathbf{m}) \quad (165)$$

As mentioned in the previous section, the activity coefficient is defined in eqn. (120) and the activity coefficient must of course be independent of the measure of concentration, i.e. whether we use mole fractions, molarity or molality, that is

$$\tilde{\gamma}_i(T, P, \mathbf{m}) \equiv \frac{\gamma_i(T, P, \mathbf{m})}{\gamma_i^\infty(T, P, m_k)} = \tilde{\gamma}_i(T, P, \mathbf{n}) \equiv \frac{\gamma_i(T, P, \mathbf{n})}{\gamma_i^\infty(T, P, n_k)} \quad (166)$$

otherwise it will phenomenology and expose little physical significance. This means that the activity coefficient on the molality scale and the mole fraction scale must be identical. Partial derivatives with respect to molality are not partial molar quantities and they have no particular physical significance.

Like in eqn. (133) the reference state chemical potential in eqn. (165) depends on the activity coefficient at infinite dilution in solvent k . That is

to ensure the consistency of the framework the reference chemical potential shall be

$$\begin{aligned}\tilde{\mu}_{m_i}^0 &= \mu_{m_i}^0 + RT \ln \gamma_i^\infty(T, P, m_k) \\ &= \mu_i(T, P) - RT \ln \frac{m_0}{x_w} + RT \ln \gamma_i^\infty(T, P, m_k)\end{aligned}\quad (167)$$

where m_k is the molality of the solvent.

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Chapter Appendix

Euler's theorem of homogeneous functions

Consider a homogeneous function M in the variables \mathbf{a} and \mathbf{b} . This function is by definition a homogeneous function of degree m in variables \mathbf{b} if when multiplying the variables \mathbf{b} by a factor of λ , the value of the function will increase by a factor of λ^m .

$$M(\mathbf{a}, \lambda\mathbf{b}) = \lambda^m M(\mathbf{a}, \mathbf{b}) \quad (\text{A1})$$

Theorem: Given the function $M(\mathbf{a}, \mathbf{b})$ which is homogeneous of degree m in variables \mathbf{b} then

$$m M(\mathbf{a}, \mathbf{b}) = \sum_i b_i \left(\frac{\partial M(\mathbf{a}, \mathbf{b})}{\partial b_i} \right)_{\mathbf{a}} \quad (\text{A2})$$

The proof is the following. The differential of eqn. (A1) with respect to the factor λ is

$$\begin{aligned} \left(\frac{\partial M(\mathbf{a}, \lambda\mathbf{b})}{\partial \lambda} \right)_{\mathbf{a}, \mathbf{b}} &= \left(\frac{\partial}{\partial \lambda} [\lambda^m M(\mathbf{a}, \mathbf{b})] \right)_{\mathbf{a}, \mathbf{b}} && \Leftrightarrow \\ \sum_i \left(\frac{\partial M(\mathbf{a}, \lambda\mathbf{b})}{\partial (\lambda b_i)} \right)_{\mathbf{a}} \left(\frac{\partial (\lambda b_i)}{\partial \lambda} \right)_{b_i} &= m \lambda^{m-1} M(\mathbf{a}, \mathbf{b}) && \Leftrightarrow \\ \sum_i b_i \left(\frac{\partial M(\mathbf{a}, \lambda\mathbf{b})}{\partial (\lambda b_i)} \right)_{\mathbf{a}} &= m \lambda^{m-1} M(\mathbf{a}, \mathbf{b}) && (\text{A3}) \end{aligned}$$

The differential of eqn. (A1) with respect to the variable b_i at constant λ is

$$\begin{aligned} \left(\frac{\partial M(\mathbf{a}, \lambda\mathbf{b})}{\partial b_i} \right)_{\mathbf{a}, \lambda} &= \left(\frac{\partial}{\partial b_i} [\lambda^m M(\mathbf{a}, \mathbf{b})] \right)_{\mathbf{a}, \lambda} && \Leftrightarrow \\ \left(\frac{\partial M(\mathbf{a}, \lambda\mathbf{b})}{\partial (\lambda b_i)} \right)_{\mathbf{a}} \left(\frac{\partial (\lambda b_i)}{\partial b_i} \right)_{\mathbf{a}, \lambda} &= \lambda^m \left(\frac{\partial M(\mathbf{a}, \mathbf{b})}{\partial b_i} \right)_{\mathbf{a}} && \Leftrightarrow \\ \left(\frac{\partial M(\mathbf{a}, \lambda\mathbf{b})}{\partial (\lambda b_i)} \right)_{\mathbf{a}} \lambda &= \lambda^m \left(\frac{\partial M(\mathbf{a}, \mathbf{b})}{\partial b_i} \right)_{\mathbf{a}} && \Leftrightarrow \\ \left(\frac{\partial M(\mathbf{a}, \lambda\mathbf{b})}{\partial (\lambda b_i)} \right)_{\mathbf{a}} &= \lambda^{m-1} \left(\frac{\partial M(\mathbf{a}, \mathbf{b})}{\partial b_i} \right)_{\mathbf{a}} && (\text{A4}) \end{aligned}$$

We combine the identities (A3) and (A4) into a new identity

$$\sum_i b_i \left[\lambda^{m-1} \left(\frac{\partial M(\mathbf{a}, \mathbf{b})}{\partial b_i} \right)_{\mathbf{a}} \right] = m \lambda^{m-1} M(\mathbf{a}, \mathbf{b}) \quad \Leftrightarrow$$

$$\sum_i b_i \left(\frac{\partial M(\mathbf{a}, \mathbf{b})}{\partial b_i} \right)_{\mathbf{a}} = m M(\mathbf{a}, \mathbf{b}) \quad (\text{A5})$$

which is identical with eqn. (A2): Euler's theorem of homogeneous functions of degree m in variables \mathbf{b} .

If $M(\mathbf{a}, \mathbf{b})$ is a homogeneous function of *degree one* in variables \mathbf{b} , then the first derivatives with respect to variables \mathbf{b} are themselves homogeneous functions of degree zero.

When m is unity, the derivative of eqn. (A2) with respect to b_k is

$$\begin{aligned} \left(\frac{\partial M(\mathbf{a}, \mathbf{b})}{\partial b_k} \right)_{\mathbf{a}} &= \left(\frac{\partial}{\partial b_k} \left[\sum_i b_i \left(\frac{\partial M(\mathbf{a}, \mathbf{b})}{\partial b_i} \right)_{\mathbf{a}} \right] \right)_{\mathbf{a}} \\ &= \left(\frac{\partial M(\mathbf{a}, \mathbf{b})}{\partial b_k} \right)_{\mathbf{a}} + \sum_i b_i \left(\frac{\partial^2 M(\mathbf{a}, \mathbf{b})}{\partial b_i \partial b_k} \right)_{\mathbf{a}} \end{aligned}$$

and in consequence of this

$$\sum_i b_i \left(\frac{\partial^2 M(\mathbf{a}, \mathbf{b})}{\partial b_i \partial b_k} \right)_{\mathbf{a}} = 0 \quad (\text{A6})$$

Eqn. (A5) can be applied to the function $M(\mathbf{a}, \mathbf{b})$ as well as to the derivatives of $M(\mathbf{a}, \mathbf{b})$. When we apply it to $\partial M(\mathbf{a}, \mathbf{b})/\partial b_k$, we can from eqn. (A6) conclude that m must be zero and therefore, the first derivatives of $M(\mathbf{a}, \mathbf{b})$ with respect to variables \mathbf{b} are themselves homogeneous functions of degree zero.

Similarly, we can prove that if $M(\mathbf{a}, \mathbf{b})$ is a homogeneous function of degree one in the variables \mathbf{b} , the second order derivatives are themselves homogeneous functions of degree -1 .

We calculate the derivative of eqn. (A6) with respect to b_i

$$\begin{aligned} &\left(\frac{\partial}{\partial b_i} \sum_j b_j \left(\frac{\partial^2 M(\mathbf{a}, \mathbf{b})}{\partial b_j \partial b_k} \right)_{\mathbf{a}} \right)_{\mathbf{a}} \\ &= \left(\frac{\partial^2 M(\mathbf{a}, \mathbf{b})}{\partial b_i \partial b_k} \right)_{\mathbf{a}} + \sum_j b_j \left(\frac{\partial^3 M(\mathbf{a}, \mathbf{b})}{\partial b_i \partial b_j \partial b_k} \right)_{\mathbf{a}} = 0 \quad (\text{A7}) \end{aligned}$$

This equation shows that

$$\sum_j b_j \left(\frac{\partial^3 M(\mathbf{a}, \mathbf{b})}{\partial a_i \partial b_j \partial b_k} \right)_{\mathbf{a}} = - \left(\frac{\partial^2 M(\mathbf{a}, \mathbf{b})}{\partial b_i \partial b_k} \right)_{\mathbf{a}} \quad (\text{A8})$$

Therefore we can conclude that, according to eqn. (A5) m must be -1 and thus the second order derivatives of a homogeneous function of degree one are themselves homogeneous functions of degree -1 .

The Gibbs-Duhem equation

The differential of $M(\mathbf{a}, \mathbf{b})$ is in general

$$dM(\mathbf{a}, \mathbf{b}) = \sum_i \left(\frac{\partial M}{\partial a_i} \right)_{\mathbf{b}} da_i + \sum_i \left(\frac{\partial M}{\partial b_i} \right)_{\mathbf{a}} db_i \quad (\text{A9})$$

When $m = 1$,

$$M(\mathbf{a}, \mathbf{b}) = \sum_i b_i \left(\frac{\partial M(\mathbf{a}, \mathbf{b})}{\partial b_i} \right)_{\mathbf{a}}$$

according to eqn. (A2). The differential of this homogeneous function of degree one is

$$dM(\mathbf{a}, \mathbf{b}) = \sum_i \left(\frac{\partial M}{\partial b_i} \right)_{\mathbf{a}} db_i + \sum_i b_i d \left(\frac{\partial M}{\partial b_i} \right)_{\mathbf{a}} \quad (\text{A10})$$

And simply by subtracting eqn. (A10) from eqn. (A9) we deduce the following constraint

$$\sum_i \left(\frac{\partial M}{\partial a_i} \right)_{\mathbf{b}} da_i - \sum_i b_i d \left(\frac{\partial M}{\partial b_i} \right)_{\mathbf{a}} = 0 \quad (\text{A11})$$

This equation is known as the Gibbs-Duhem equation.

The thermodynamic state functions

Consider a thermodynamic state function $M(\mathbf{a}, \mathbf{b})$ where \mathbf{a} is the vector of intensive variables, and \mathbf{b} is the vector of extensive variables. Thermodynamic functions are homogeneous functions of degree one in the extensive variables, that is when $m = 1$ eqn. (A2) shows that

$$M(\mathbf{a}, \mathbf{b}) = \sum_j b_j \left(\frac{\partial M(\mathbf{a}, \mathbf{b})}{\partial b_j} \right)_{\mathbf{a}} \quad (\text{A12})$$

$M(\mathbf{a}, \mathbf{b})$ can be any of the thermodynamic state functions U , A , H and G , and it also includes excess functions and residual functions.

If $M(\mathbf{a}, \mathbf{b}) = A(T, V, \mathbf{n})$, then $\mathbf{a} = T$ and $\mathbf{b} = (V, \mathbf{n})$. Application of eqn. (A12) shows that

$$A = -V P + \sum_j n_j \mu_j \quad (\text{A13})$$

If we apply eqn. (A12) to $G(T, P, \mathbf{n})$, then $\mathbf{a} = (T, P)$ and $\mathbf{b} = \mathbf{n}$ and the eventual result is well-known

$$G = \sum_j n_j \mu_j \quad (\text{A14})$$

Furthermore, the derivative of G with respect to the pressure is the volume V and the derivative with respect to the temperature is $-S$; therefore

$$\begin{aligned} \left(\frac{\partial G}{\partial P} \right)_{T, \mathbf{n}} &= V = \sum_j n_j \bar{V}_j && \text{and} \\ - \left(\frac{\partial G}{\partial T} \right)_{P, \mathbf{n}} &= S = \sum_j n_j \bar{S}_j \end{aligned} \quad (\text{A15})$$

If $M(\mathbf{a}, \mathbf{b})$ is a homogeneous function of degree one in \mathbf{b} , then the first derivatives with respect to variables \mathbf{b} are themselves homogeneous functions of degree zero as proved in eqn. (A6). This equation is essential when performing a consistency check of the first derivatives of the extensive variables. We show a few examples to illuminate the application of eqn. (A6).

If $M(\mathbf{a}, \mathbf{b}) = A(T, V, \mathbf{n})$, then $\mathbf{a} = T$ and $\mathbf{b} = (V, \mathbf{n})$. We have two choices, either $b_k = n_k$ or $b_k = V$.

First, we investigate the case where $b_k = n_k$. Application of eqn. (A6) shows that

$$\begin{aligned} \sum_j b_j \left(\frac{\partial^2 A(T, V, \mathbf{n})}{\partial b_j \partial b_k} \right)_{T, V} \\ = V \left(\frac{\partial^2 A(T, V, \mathbf{n})}{\partial V \partial n_k} \right)_T + \sum_j n_j \left(\frac{\partial^2 A(T, V, \mathbf{n})}{\partial n_j \partial n_k} \right)_{T, V} \\ = -V \left(\frac{\partial P}{\partial n_k} \right)_{T, V} + \sum_j n_j \left(\frac{\partial \mu_j(T, V, \mathbf{n})}{\partial n_k} \right)_{T, V} = 0 \end{aligned} \quad (\text{A16})$$

Now we investigate the case where $b_k = V$ and therefore according to eqn.

(A6)

$$\begin{aligned}
& \sum_j b_j \left(\frac{\partial^2 A(T, V, \mathbf{n})}{\partial b_j \partial b_k} \right)_{T,V} \\
&= V \left(\frac{\partial^2 A(T, V, \mathbf{n})}{\partial V^2} \right)_{T,\mathbf{n}} + \sum_j n_j \left(\frac{\partial^2 A(T, V, \mathbf{n})}{\partial n_j \partial V} \right)_T \\
&= -V \left(\frac{\partial P}{\partial V} \right)_{T,\mathbf{n}} + \sum_j n_j \left(\frac{\partial \mu_j(T, V, \mathbf{n})}{\partial V} \right)_{T,\mathbf{n}} = 0 \quad (\text{A17})
\end{aligned}$$

Eqns. (A16) and (A17) are useful when checking the derivatives of the Helmholtz function. But apart from that eqn. (A17) is just another way of showing that

$$\begin{aligned}
& \sum_j n_j \left(\frac{\partial \mu_j(T, V, \mathbf{n})}{\partial V} \right)_{T,\mathbf{n}} \left(\frac{\partial V}{\partial P} \right)_{T,\mathbf{n}} \\
&= \sum_j n_j \left(\frac{\partial \mu_j(T, V, \mathbf{n})}{\partial P} \right)_{T,\mathbf{n}} = \sum_j n_j \bar{V}_j = V \quad (\text{A18})
\end{aligned}$$

In the next example $M(\mathbf{a}, \mathbf{b}) = G(T, P, \mathbf{n})$, that is $\mathbf{a} = (T, P)$ and $\mathbf{b} = \mathbf{n}$ and therefore according to eqn. (A6) we get a very well-known relationship

$$\sum_j n_j \left(\frac{\partial^2 G(T, P, \mathbf{n})}{\partial n_j \partial n_k} \right)_{T,P} = \sum_j n_j \left(\frac{\partial \mu_j(T, P, \mathbf{n})}{\partial n_k} \right)_{T,P} = 0 \quad (\text{A19})$$

When G is replaced by the residual Gibbs energy, the result is

$$\begin{aligned}
& \sum_j n_j \left(\frac{\partial^2 G^r(T, P, \mathbf{n})}{\partial n_j \partial n_k} \right)_{T,P} \\
&= \sum_j n_j \left(\frac{\partial \ln \hat{\varphi}_j(T, P, \mathbf{n})}{\partial n_k} \right)_{T,P} = 0 \quad (\text{A20})
\end{aligned}$$

and similarly for the excess Gibbs energy

$$\begin{aligned}
& \sum_j n_j \left(\frac{\partial^2 G^E(T, P, \mathbf{n})}{\partial n_j \partial n_k} \right)_{T,P} \\
&= \sum_j n_j \left(\frac{\partial \ln \gamma_j(T, P, \mathbf{n})}{\partial n_k} \right)_{T,P} = 0 \quad (\text{A21})
\end{aligned}$$

When we apply the Gibbs-Duhem equation, (A11), to $A(T, V, \mathbf{n})$ or $G(T, P, \mathbf{n})$, the results are of course identical.

When $M(\mathbf{a}, \mathbf{b}) = A(T, V, \mathbf{n})$ where $\mathbf{a} = T$ and $\mathbf{b} = (V, \mathbf{n})$, then according to eqn. (A11)

$$-S dT + V dP - \sum_i n_i d\mu_i = 0 \quad (\text{A22})$$

And when $M(\mathbf{a}, \mathbf{b}) = G(T, P, \mathbf{n})$ where $\mathbf{a} = (T, P)$ and $\mathbf{b} = \mathbf{n}$, the result is identical with eqn. (A22).

Some relationships among partial derivatives

If the state of a system can be fully described by two of the three variables, x , y and z , related to each other by the functional form

$$F(x, y, z) = 0 \quad (\text{A23})$$

we may select any of the two variables as independent variables, thus $z(x, y)$. The exact differential of z is

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \quad (\text{A24})$$

If z is kept constant and provided dx and dy are different from zero, then

$$\left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_z + \left(\frac{\partial z}{\partial y} \right)_x = 0 \quad (\text{A25})$$

and

$$\left(\frac{\partial z}{\partial x} \right)_y + \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial y}{\partial x} \right)_z = 0 \quad (\text{A26})$$

By elimination of $(\partial z / \partial x)_y$ we have

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z = 1 \quad (\text{A27})$$

and hence from eqn. (A25) or (A26)

$$\left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x = -1 \quad (\text{A28})$$

Furthermore,

$$dF = \left(\frac{\partial F}{\partial x} \right)_{y,z} dx + \left(\frac{\partial F}{\partial y} \right)_{x,z} dy + \left(\frac{\partial F}{\partial z} \right)_{x,y} dz = 0 \quad (\text{A29})$$

When dz in eqn. (A24) is used to replace dz in eqn. (A29), the result is

$$\begin{aligned} & \left(\left(\frac{\partial F}{\partial x} \right)_{y,z} + \left(\frac{\partial F}{\partial z} \right)_{x,y} \left(\frac{\partial z}{\partial x} \right)_y \right) dx \\ & + \left(\left(\frac{\partial F}{\partial y} \right)_{x,z} + \left(\frac{\partial F}{\partial z} \right)_{x,y} \left(\frac{\partial z}{\partial y} \right)_x \right) dy = 0 \quad (\text{A30}) \end{aligned}$$

Inasmuch as x and y are regarded as independent variables and eqn. (A30) must hold for any value of dx and dy it follows that the coefficients in the brackets of dx and dy , must individually be zero. If $(\partial F / \partial z)$ has a non-zero value, then

$$\left(\frac{\partial z}{\partial x} \right)_y = - \frac{(\partial F / \partial x)_{y,z}}{(\partial F / \partial z)_{x,y}} \quad (\text{A31})$$

and .

$$\left(\frac{\partial z}{\partial y} \right)_x = - \frac{(\partial F / \partial y)_{x,z}}{(\partial F / \partial z)_{x,y}} \quad (\text{A32})$$

Furthermore, if the variable z itself is a function of the variables x and u , that is $z(x, u)$, then by straightforward differentiation

$$\left(\frac{\partial F}{\partial x} \right)_{u,y} = \left(\frac{\partial F}{\partial x} \right)_{y,z} + \left(\frac{\partial F}{\partial z} \right)_{x,y} \left(\frac{\partial z}{\partial x} \right)_u \quad (\text{A33})$$

and

$$\left(\frac{\partial F}{\partial u} \right)_{x,y} = \left(\frac{\partial F}{\partial z} \right)_{x,y} \left(\frac{\partial z}{\partial u} \right)_x \quad (\text{A34})$$

Some examples

Let F be a function where

$$F(P, V, T, n) = 0 \quad (\text{A35})$$

Application of eqns. (A27) and (A28) at constant n shows that

$$\left(\frac{\partial P}{\partial V} \right)_{T,n} \left(\frac{\partial V}{\partial T} \right)_{P,n} \left(\frac{\partial T}{\partial P} \right)_{V,n} = -1 \quad (\text{A36})$$

or

$$\left(\frac{\partial V}{\partial T} \right)_{P,n} = - \frac{\left(\frac{\partial P}{\partial T} \right)_{V,n}}{\left(\frac{\partial P}{\partial V} \right)_{T,n}} \quad (\text{A37})$$

Application of eqns. (A27) and (A28) at constant T shows that

$$\left(\frac{\partial P}{\partial V}\right)_{T,n} \left(\frac{\partial V}{\partial n_i}\right)_{P,T} \left(\frac{\partial n_i}{\partial P}\right)_{V,T} = -1 \quad (\text{A38})$$

or

$$\left(\frac{\partial V}{\partial n_i}\right)_{P,T} = -\frac{\left(\frac{\partial P}{\partial n_i}\right)_{V,T}}{\left(\frac{\partial P}{\partial V}\right)_{T,n}} \quad (\text{A39})$$

Application of eqns. (A27) and (A28) at constant V shows that

$$\left(\frac{\partial P}{\partial T}\right)_{V,n} \left(\frac{\partial T}{\partial n_i}\right)_{P,V} \left(\frac{\partial n_i}{\partial P}\right)_{V,T} = -1 \quad (\text{A40})$$

or

$$\left(\frac{\partial T}{\partial n_i}\right)_{P,V} = -\frac{\left(\frac{\partial P}{\partial n_i}\right)_{V,T}}{\left(\frac{\partial P}{\partial T}\right)_{V,n}} \quad (\text{A41})$$

Let us prove that

$$\left(\frac{\partial V}{\partial P}\right)_{S,n} = \frac{C_V}{C_P} \left(\frac{\partial V}{\partial P}\right)_{T,n} \quad (\text{A42})$$

F is now a function where

$$F(P, V, S, n) = 0 \quad (\text{A43})$$

Thus in eqn. (A36) we replace T by S and the result is

$$\left(\frac{\partial P}{\partial V}\right)_{S,n} \left(\frac{\partial V}{\partial S}\right)_{P,n} \left(\frac{\partial S}{\partial P}\right)_{V,n} = -1 \quad (\text{A44})$$

or

$$\left(\frac{\partial V}{\partial P}\right)_{S,n} = -\frac{\left(\frac{\partial S}{\partial P}\right)_{V,n}}{\left(\frac{\partial S}{\partial V}\right)_{P,n}} = -\frac{\left(\frac{\partial S}{\partial T}\right)_{V,n} \left(\frac{\partial T}{\partial P}\right)_{V,n}}{\left(\frac{\partial S}{\partial T}\right)_{P,n} \left(\frac{\partial T}{\partial V}\right)_{P,n}} \quad (\text{A45})$$

The ratio

$$\left(\frac{\partial T}{\partial P}\right)_{V,n} / \left(\frac{\partial T}{\partial V}\right)_{P,n}$$

is calculable from eqn. (A36)

$$\left(\frac{\partial V}{\partial P}\right)_{T,n} = - \frac{\left(\frac{\partial T}{\partial P}\right)_{V,n}}{\left(\frac{\partial T}{\partial V}\right)_{P,n}} \quad (\text{A46})$$

we insert eqn. (A46) in eqn. (A45) and finally

$$\left(\frac{\partial V}{\partial P}\right)_{S,n} = - \frac{\left(\frac{\partial S}{\partial T}\right)_{V,n}}{\left(\frac{\partial S}{\partial T}\right)_{P,n}} \left(\frac{\partial V}{\partial P}\right)_{T,n} = \frac{C_V}{C_P} \left(\frac{\partial V}{\partial P}\right)_{T,n} \quad (\text{A47})$$

The isentropic compression

$$\beta_S = - \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{S,n} \quad (\text{A48})$$

can be determined from measurements of sound speed data. The equations are shown in Chapter 2.

The Maxwell relationships

Let F be a thermodynamic state function

$$F(x_1, x_2, \dots, x_n) \quad (\text{A49})$$

the exact differential of F is then

$$dF = \sum_i \left(\frac{\partial F}{\partial x_i}\right)_{x_j} dx_i \quad (\text{A50})$$

where the order of differentiation is immaterial, that is

$$\frac{\partial^2 F}{\partial x_i \partial x_j} = \frac{\partial^2 F}{\partial x_j \partial x_i} \quad (\text{A51})$$

An example, let the function F be $G(T, P, n)$ then from eqn. (A50)

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \sum_i n_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P} dn_i \quad (\text{A52})$$

and from eqn. (26) in Section 2 we observe that

$$dG = -S dT + V dP + \sum_i \mu_i dn_i \quad (\text{A53})$$

wherefore the following identities exists

$$-S = \left(\frac{\partial G}{\partial T} \right)_{P,n} \quad (A54)$$

$$V = \left(\frac{\partial G}{\partial P} \right)_{T,n} \quad (A55)$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P} \quad (A56)$$

and furthermore from eqn. (A51)

$$\left(\frac{\partial^2 G}{\partial T \partial P} \right)_n = \left(\frac{\partial V}{\partial T} \right)_{P,n} = - \left(\frac{\partial S}{\partial P} \right)_{T,n} \quad (A57)$$

$$\left(\frac{\partial^2 G}{\partial T \partial n_i} \right)_P = \left(\frac{\partial \mu_i}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial n_i} \right)_{T,P} = -\bar{S}_i \quad (A58)$$

and

$$\left(\frac{\partial^2 G}{\partial P \partial n_i} \right)_T = \left(\frac{\partial \mu_i}{\partial P} \right)_T = \left(\frac{\partial V}{\partial n_i} \right)_{T,P} = \bar{V}_i \quad (A59)$$

An example: The partial derivatives of U at constant n

The four partial derivatives of U shown in Table 3 on page 13 can be derived as follows. Let $U(S, V, n)$ where the variables S and V are assumed to be functions of the variables x and y . The partial derivative of U with respect to the variable x at constant y is

$$\begin{aligned} \left(\frac{\partial U}{\partial x} \right)_y &= \left(\frac{\partial U}{\partial S} \right)_V \left(\frac{\partial S}{\partial x} \right)_y + \left(\frac{\partial U}{\partial V} \right)_S \left(\frac{\partial V}{\partial x} \right)_y \\ &= T \left(\frac{\partial S}{\partial x} \right)_y - P \left(\frac{\partial V}{\partial x} \right)_y \end{aligned} \quad (A60)$$

where x and y can be either T , P or V .

$$x = V, y = T$$

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - P \left(\frac{\partial V}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad (A61)$$

where we have used the Maxwell equation from Table 3 on page 13

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad (\text{XIX})$$

$x = P, y = T$

$$\left(\frac{\partial U}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T - P \left(\frac{\partial V}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T \quad (\text{A62})$$

where we have used the Maxwell equation from Table 3 on page 13

$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P \quad (\text{XX})$$

$x = T, y = V$

$$\left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V - P \left(\frac{\partial V}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V = C_V \quad (\text{A63})$$

$x = T, y = P$

$$\left(\frac{\partial U}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial T}\right)_P = C_P - P \left(\frac{\partial V}{\partial T}\right)_P \quad (\text{A64})$$

From $U(T, V)$ at constant n

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (\text{A65})$$

or

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad (\text{A66})$$

and inserting eqns. (A61) and (A63) the result is

$$\left(\frac{\partial U}{\partial T}\right)_P = C_V + \left(T \left(\frac{\partial P}{\partial T}\right)_V - P\right) \left(\frac{\partial V}{\partial T}\right)_P \quad (\text{A67})$$

Two derivatives that are not shown in Table 3 on page 13 can be derived from eqns. (A63) and (A64)

$$\left(\frac{\partial U}{\partial P}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V = C_V \left(\frac{\partial T}{\partial P}\right)_V \quad (\text{A68})$$

and

$$\left(\frac{\partial U}{\partial V}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P = C_P \left(\frac{\partial T}{\partial V}\right)_P - P \quad (\text{A69})$$

Finally, when subtracting eqn. (A67) from eqn. (A64) the result is

$$C_P - C_V = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = -T \frac{\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial V}{\partial T}\right)_P} \quad (\text{A70})$$

Chapter 2

Calculation of Thermodynamic Properties

Introduction

Calculation of thermodynamic properties from an equation of state may appear a trivial problem which only requires adherence to basic definitions as outlined in Chapter 1. The increasing complexity of thermodynamic models, however, calls for a systematic approach in order to avoid inefficient or even incorrect computer codes. In order to generate a fast and thermodynamically consistent computer code for calculation of the thermodynamic properties of mixtures, it is essential to use a modular approach which enables modification of single features of the model, e.g. a mixing rule for one of the model parameters without rewriting the entire code. This calls for a formalism, where the properties are calculated by combining partial derivatives of the Helmholtz function, which ensures a consistent set of relations and leads to an efficient code. This Chapter describes a procedure which ensures that the resulting thermodynamic model shall be fully consistent. Furthermore, tests for checking the calculated properties and their partial derivatives are shown to be straightforward.

1 The Helmholtz function

The pressure equation is often denoted an equation of state. Given a pressure equation

$$P = P(T, V, \mathbf{n}) \quad (1)$$

where V is the total volume and \mathbf{n} is the vector of mole numbers. The usual textbook approach to calculate mixture fugacity coefficients is by means of

an integral, i.e.

$$\begin{aligned} RT \ln \hat{\phi}_i &= \int_0^P \left(\bar{V}_i - \frac{RT}{P} \right) dP \\ &= - \int_{\infty}^V \left(\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right) dV - RT \ln Z \end{aligned} \quad (2)$$

where Z is the compressibility factor, $Z = PV/nRT$. However, interchange of the order of integration and differentiation in eqn. (2) leads to an equivalent, but much more convenient expression

$$\begin{aligned} RT \ln \hat{\phi}_i &= - \frac{\partial}{\partial n_i} \int_{\infty}^V \left(P - \frac{nRT}{V} \right) dV - RT \ln Z \\ &= \left(\frac{\partial A^r(T, V, \mathbf{n})}{\partial n_i} \right)_{T,V,n_j} - RT \ln Z \end{aligned} \quad (3)$$

where

$$A^r(T, V, \mathbf{n}) = - \int_{\infty}^V \left(P - \frac{nRT}{V} \right) dV \quad (4)$$

$A^r(T, V, \mathbf{n})$ is the residual Helmholtz function, i.e. the Helmholtz function of the mixture at the state variables (T, V, \mathbf{n}) minus that of the equivalent ideal gas mixture at the same state variables (T, V, \mathbf{n}) . The residual Helmholtz function is a homogeneous function of degree 1 in the extensive variables (V, \mathbf{n}) , and mixture parameters shall depend only on T , V , and \mathbf{n} to ensure that it remains a characteristic function, i.e., a function of state which contains every statement that the fundamental equation, eqn. (18) of Chapter 1, can make about the system. The expression for the residual Helmholtz energy is the key equation in equilibrium thermodynamics because other residual properties are calculable as partial derivatives in the independent variables T , V , and \mathbf{n} . In particular, it is important to recognise that mole numbers rather than mole fractions are the independent variables. Derivatives with respect to mole fractions are best avoided, as they require a definition of the 'dependent' mole fraction and in addition lead to more complex expressions missing many important symmetry properties.

The pressure equation itself, normally used to define the 'equation of state', is actually just one of these derivatives given by

$$P = - \left(\frac{\partial A^r(T, V, \mathbf{n})}{\partial V} \right)_{T,\mathbf{n}} + \frac{nRT}{V} \quad (5)$$

To modify a thermodynamic model, it is a must to introduce such modifications in the expression for $A^r(T, V, \mathbf{n})$ remembering that the characteristic

variables are T , V , and \mathbf{n} . This approach reduces the risk of errors, inconsistencies or misconceptions such as ‘pressure dependent interaction coefficients’.

In addition many model concepts relate directly to the Helmholtz function rather than to a pressure equation. This applies for example to a corresponding states model, to a ‘chemical’ model, and to a model where the Helmholtz function is calculable from the canonical partition function.

2 Thermodynamic properties and the derivatives of the reduced residual Helmholtz function

The thermodynamic properties are calculable as partial derivatives of the Helmholtz function $A^r(T, V, \mathbf{n})$ as shown in Table 6 in Chapter 1. However, it is in many cases more convenient to use the partial derivatives of the reduced residual Helmholtz function F

$$F = \frac{A^r(T, V, \mathbf{n})}{RT} \quad (6)$$

Therefore we provide expressions relating the thermodynamic properties to the partial derivatives of F . In the next section we summarise some useful identity checks to ensure a consistent computer code, and finally, in Section 4 we show the general expressions for the derivatives of a model for $F(n, T, V, B, D)$ where B and D are model parameters.

The pressure and its derivatives are

$$P = -RT \left(\frac{\partial F}{\partial V} \right)_{T, \mathbf{n}} + \frac{nRT}{V} \quad (7)$$

$$Z = \frac{PV}{nRT} \quad (8)$$

$$\left(\frac{\partial P}{\partial V} \right)_{T, \mathbf{n}} = -RT \left(\frac{\partial^2 F}{\partial V^2} \right)_{T, \mathbf{n}} - \frac{nRT}{V^2} \quad (9)$$

$$\left(\frac{\partial P}{\partial T} \right)_{V, \mathbf{n}} = -RT \left(\frac{\partial^2 F}{\partial T \partial V} \right)_{\mathbf{n}} + \frac{P}{T} \quad (10)$$

$$\left(\frac{\partial P}{\partial n_i} \right)_{T, V} = -RT \left(\frac{\partial^2 F}{\partial V \partial n_i} \right)_T + \frac{RT}{V} \quad (11)$$

$$\left(\frac{\partial V}{\partial n_i} \right)_{T, P} = \bar{V}_i = - \left(\frac{\partial P}{\partial n_i} \right)_{T, V} \Bigg/ \left(\frac{\partial P}{\partial V} \right)_{T, \mathbf{n}} \quad (12)$$

The fugacity coefficient and its derivatives are

$$\ln \hat{\varphi}_i = \left(\frac{\partial F}{\partial n_i} \right)_{T,V} - \ln Z \quad (13)$$

$$\left(\frac{\partial \ln \hat{\varphi}_i}{\partial T} \right)_{P,n} = \left(\frac{\partial^2 F}{\partial T \partial n_i} \right)_V + \frac{1}{T} - \frac{\bar{V}_i}{RT} \left(\frac{\partial P}{\partial T} \right)_{V,n} \quad (14)$$

$$\left(\frac{\partial \ln \hat{\varphi}_i}{\partial P} \right)_{T,n} = \frac{\bar{V}_i}{RT} - \frac{1}{P} \quad (15)$$

$$n \left(\frac{\partial \ln \hat{\varphi}_i}{\partial n_j} \right)_{T,P} = n \left(\frac{\partial \ln \hat{\varphi}_j}{\partial n_i} \right)_{T,P} = n \left(\frac{\partial^2 F}{\partial n_i \partial n_j} \right)_{T,V}$$

$$+ 1 + \frac{n}{RT} \frac{\left(\frac{\partial P}{\partial n_j} \right)_{T,V} \left(\frac{\partial P}{\partial n_i} \right)_{T,V}}{\left(\frac{\partial P}{\partial V} \right)_{T,n}} \quad (16)$$

The subscript n_j , which means that all except n_i are held constant, is omitted where no confusion can arise.

The residual bulk properties

$$\frac{S^r(T, V, n)}{R} = -T \left(\frac{\partial F}{\partial T} \right)_{V,n} - F \quad (17)$$

$$\frac{C_V^r(T, V, n)}{R} = -T^2 \left(\frac{\partial^2 F}{\partial T^2} \right)_{V,n} - 2T \left(\frac{\partial F}{\partial T} \right)_{V,n} \quad (18)$$

$$\frac{C_P^r - C_V^r}{R} = -\frac{T}{R} \frac{\left(\frac{\partial P}{\partial T} \right)_{V,n}^2}{\left(\frac{\partial P}{\partial V} \right)_{T,n}} - n \quad (19)$$

$$H^r(T, P, n) = A^r(T, V, n) + TS^r(T, V, n) + PV - nRT \quad (20)$$

$$G^r(T, P, n) = A^r(T, V, n) + PV - nRT - nRT \ln Z \quad (21)$$

$$\begin{aligned} S^r(T, P, n) &= S^r(T, V, n) + nR \ln Z \\ &= (H^r(T, P, n) - G^r(T, P, n))/T \end{aligned} \quad (22)$$

The sound speed

$$W^2 = \frac{V}{\beta_s M_W} \quad (23)$$

$$M_W = \sum_i n_i M_{W_i} \quad (24)$$

$$\beta_s = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_s = -\frac{1}{V} \frac{C_V}{C_P} \left/ \left(\frac{\partial P}{\partial V} \right)_{T,n} \right. \quad (25)$$

The Joule-Thomson coefficient

$$\eta = \left(\frac{\partial T}{\partial P} \right)_{H,n} = -\frac{1}{C_P} \left(V + T \left(\frac{\partial P}{\partial T} \right)_{V,n} \right/ \left(\frac{\partial P}{\partial V} \right)_{T,n} \right) \quad (26)$$

Some partial molar properties

$$\frac{\bar{H}_i^r(T, P, n)}{RT} = -T \left(\frac{\partial \ln \hat{\varphi}_i}{\partial T} \right)_{P,n} \quad (27)$$

$$\frac{\bar{G}_i^r(T, P, n)}{RT} = \ln \hat{\varphi}_i \quad (28)$$

$$\bar{S}_i^r(T, P, n) = (\bar{H}_i^r(T, P, n) - \bar{G}_i^r(T, P, n))/T \quad (29)$$

3 Test of calculated fugacity coefficients and partial derivatives

Unfortunately, even a systematic approach does not prevent coding errors, and it is necessary that computer codes are tested for internal consistency. We have found the identities listed below very useful. The analytical derivatives can always be tested by numerical evaluation of the derivatives, preferably carried out by means of central differences, i.e.

$$\frac{\partial f}{\partial n_i} = \frac{f(n_1, \dots, n_i + \varepsilon, \dots, n_c) - f(n_1, \dots, n_i - \varepsilon, \dots, n_c)}{2\varepsilon} \quad (30)$$

For composition derivatives ε should be chosen as about 10^{-5} times the sum of the mole numbers, which should yield results accurate to 8-10 digits. Note that the composition derivatives of $\ln \hat{\varphi}_i$ are homogeneous functions of degree -1 in the composition. When multiplied by n , these derivatives become homogeneous functions of degree zero. All tests should be performed with

$\sum n_i \neq 1$. The quantities in eqns. (13)-(16) are homogeneous functions of degree zero.

Algorithms for calculation of fugacity coefficients which, given temperature, pressure, and composition, return only fugacity coefficients and the compressibility factor Z , can be subjected to the following tests.

From the identity

$$\sum_i n_i \ln \hat{\varphi}_i = \frac{G^r(T, P, \mathbf{n})}{RT} \quad (31)$$

we can check the calculated fugacity coefficient because

$$\left(\frac{\partial}{\partial n_j} \sum_i n_i \ln \hat{\varphi}_i \right)_{T,P} = \frac{\bar{G}_j^r(T, P, \mathbf{n})}{RT} = \ln \hat{\varphi}_j \quad (32)$$

If this test is passed, it is likely that the first order compositional derivatives of the Helmholtz function are correct.

Further tests are:

$$\left(\frac{\partial \ln \hat{\varphi}_i}{\partial n_j} \right)_{T,P} = \left(\frac{\partial \ln \hat{\varphi}_j}{\partial n_i} \right)_{T,P} \quad (33)$$

and from the Gibbs-Duhem equation

$$\sum_i n_i \left(\frac{\partial \ln \hat{\varphi}_i}{\partial n_j} \right)_{T,P} = 0 \quad (34)$$

From the identity

$$\sum_i n_i \left(\frac{\partial \ln \hat{\varphi}_i}{\partial P} \right)_{T,\mathbf{n}} = \frac{(Z-1)n}{P} \quad (35)$$

we can check the pressure derivatives of the fugacity coefficients

$$\left(\frac{\partial}{\partial P} \sum_i n_i \ln \hat{\varphi}_i \right)_{T,\mathbf{n}} = \frac{(Z-1)n}{P} \quad (36)$$

If 'pressure dependent' binary interaction coefficients are used in the model, it will not pass the test.

To check the temperature derivatives of the fugacity coefficient we need access to the calculated residual enthalpy because

$$\sum_i n_i \left(\frac{\partial \ln \hat{\varphi}_i}{\partial T} \right)_{P,\mathbf{n}} = -\frac{H^r(T, P, \mathbf{n})}{RT^2} \quad (37)$$

4 Calculation of the partial derivatives of F

It is straightforward to calculate the appropriate partial derivatives of the reduced residual Helmholtz energy. Let the general form of eqn. (6) be

$$F = F(n, T, V, B, D) \quad (38)$$

where n is the total number of moles, T the temperature, and V the total volume. The parameters $B(T, V, n)$ and $D(T, V, n)$ are in this context explicit functions of the temperature, the total volume, and the mole numbers n .

First order derivatives

The derivatives of $F(\mathbf{u})$ with respect to y at constant \mathbf{x} are

$$\left(\frac{\partial F}{\partial y} \right)_x = \sum_k \left(\frac{\partial F}{\partial u_k} \right)_{u_m} \left(\frac{\partial u_k}{\partial y} \right)_x = \sum_k F_{u_k} \left(\frac{\partial u_k}{\partial y} \right)_x \quad (39)$$

where $u_k \neq u_m$. The vectors \mathbf{u} and \mathbf{x} may have some elements in common.

According to eqn. (38), $\mathbf{u} = (n, T, V, B, D)$ where

$$n = \sum_k n_k \quad (40)$$

Let $\mathbf{x} = (T, V, n_j)$ and $y = n_i$ then

$$\begin{aligned} \left(\frac{\partial F}{\partial n_i} \right)_{T,V} &= F_n \left(\frac{\partial n}{\partial n_i} \right)_{T,V} + F_B \left(\frac{\partial B}{\partial n_i} \right)_{T,V} + F_D \left(\frac{\partial D}{\partial n_i} \right)_{T,V} \\ &= F_n + F_B B_i + F_D D_i \end{aligned} \quad (41)$$

because

$$\left(\frac{\partial n}{\partial n_i} \right)_{T,V} = 1 \quad (42)$$

The subscript n_j , which means that all except n_i are held constant, is omitted where no confusion can arise. B_i and D_i are abbreviations for

$$B_i = \left(\frac{\partial B}{\partial n_i} \right)_{T,V} \quad (43)$$

$$D_i = \left(\frac{\partial D}{\partial n_i} \right)_{T,V} \quad (44)$$

Similarly, the derivative with respect to the temperature is

$$\left(\frac{\partial F}{\partial T} \right)_{V,n} = F_T + F_B B_T + F_D D_T \quad (45)$$

where

$$B_T = \left(\frac{\partial B}{\partial T} \right)_{V,n} \quad (46)$$

$$D_T = \left(\frac{\partial D}{\partial T} \right)_{V,n} \quad (47)$$

Finally, the derivative with respect to the volume is

$$\left(\frac{\partial F}{\partial V} \right)_{T,n} = F_V + F_B B_V + F_D D_V \quad (48)$$

where

$$B_V = \left(\frac{\partial B}{\partial V} \right)_{T,n} \quad (49)$$

$$D_V = \left(\frac{\partial D}{\partial V} \right)_{T,n} \quad (50)$$

The derivatives $(\partial F / \partial n_i)_{T,V}$ and $(\partial F / \partial V)_{T,n}$ are homogeneous functions of degree zero and $(\partial F / \partial T)_{T,n}$ is a homogeneous function of degree 1. Furthermore, to test that the derivatives are correct, Euler's theorem provides the identity for the homogeneous function $F(T, V, n)$ of degree 1.

$$F = V \left(\frac{\partial F}{\partial V} \right)_{T,n} + \sum_i n_i \left(\frac{\partial F}{\partial n_i} \right)_{T,V} \quad (51)$$

Second order derivatives

The general expression for the second order derivative of F with respect to y and z at constant x is

$$\begin{aligned} \left(\frac{\partial^2 F}{\partial y \partial z} \right)_x &= \sum_k \sum_l \left(\frac{\partial^2 F}{\partial u_k \partial u_l} \right)_{u_m} \left(\frac{\partial u_k}{\partial y} \right)_x \left(\frac{\partial u_l}{\partial z} \right)_x \\ &\quad + \sum_k \left(\frac{\partial F}{\partial u_k} \right)_{u_m} \left(\frac{\partial^2 u_k}{\partial y \partial z} \right)_x \\ &= \sum_k \sum_l F_{u_k u_l} \left(\frac{\partial u_k}{\partial y} \right)_x \left(\frac{\partial u_l}{\partial z} \right)_x + \sum_k F_{u_k} \left(\frac{\partial^2 u_k}{\partial y \partial z} \right)_x \end{aligned} \quad (52)$$

where $u_k, u_l \neq u_m$ and $\mathbf{u} = (n, T, V, B, D)$.

When $y = n_i$, $z = n_j$ and $\mathbf{x} = (T, V)$, we can obtain the second order derivative with respect to n_i and n_j . The subscript n_j , which means that all except n_i are held constant, is omitted where no confusion can arise.

$$\begin{aligned} \left(\frac{\partial^2 F}{\partial n_i \partial n_j} \right)_{T,V} &= F_{nn} + F_{nB} B_j + F_{nD} D_j \\ &\quad + (F_{Bn} + F_{BB} B_j + F_{BD} D_j) B_i + F_B B_{ij} \\ &\quad + (F_{Dn} + F_{DB} B_j + F_{DD} D_j) D_i + F_D D_{ij} \end{aligned} \quad (53)$$

In the first row $u_k = n$ and $u_l = n$, B and D , respectively. In the second row $u_k = B$ and again $u_l = n$, B and D , etc. According to eqn. (42)

$$\left(\frac{\partial^2 n}{\partial n_i \partial n_j} \right)_{T,V} = 0 \quad (54)$$

Similarly when $y = n_i$ and $z = T$ and $\mathbf{x} = (V, n_j)$.

$$\begin{aligned} \left(\frac{\partial^2 F}{\partial n_i \partial T} \right)_V &= F_{nT} + F_{nB} B_T + F_{nD} D_T \\ &\quad + (F_{BT} + F_{BB} B_T + F_{BD} D_T) B_i + F_B B_{iT} \\ &\quad + (F_{DT} + F_{DB} B_T + F_{DD} D_T) D_i + F_D D_{iT} \end{aligned} \quad (55)$$

The derivatives $\left(\frac{\partial^2 F}{\partial n_i \partial V} \right)_T$ are obtained from eqn. (55) by interchanging T and V .

$$\begin{aligned} \left(\frac{\partial^2 F}{\partial n_i \partial V} \right)_T &= F_{nV} + F_{nB} B_V + F_{nD} D_V \\ &\quad + (F_{BV} + F_{BB} B_V + F_{BD} D_V) B_i + F_B B_{iV} \\ &\quad + (F_{DV} + F_{DB} B_V + F_{DD} D_V) D_i + F_D D_{iV} \end{aligned} \quad (56)$$

Furthermore,

$$\begin{aligned} \left(\frac{\partial^2 F}{\partial T^2} \right)_{V,n} &= F_{TT} + F_{TB} B_T + F_{TD} D_T \\ &\quad + (F_{BT} + F_{BB} B_T + F_{BD} D_T) B_T + F_B B_{TT} \\ &\quad + (F_{DT} + F_{DB} B_T + F_{DD} D_T) D_T + F_D D_{TT} \end{aligned} \quad (57)$$

$$\begin{aligned} \left(\frac{\partial^2 F}{\partial T \partial V} \right)_n &= F_{VT} + F_{VB} B_T + F_{VD} D_T \\ &\quad + (F_{BT} + F_{BB} B_T + F_{BD} D_T) B_V + F_B B_{TV} \\ &\quad + (F_{DT} + F_{DB} B_T + F_{DD} D_T) D_V + F_D D_{TV} \end{aligned} \quad (58)$$

$$\begin{aligned} \left(\frac{\partial^2 F}{\partial V^2} \right)_{T,n} &= F_{VV} + F_{VB}B_V + F_{VD}D_V \\ &+ (F_{BV} + F_{BB}B_V + F_{BD}D_V) B_V + F_B B_{VV} \\ &+ (F_{DV} + F_{DB}B_V + F_{DD}D_V) D_V + F_D D_{VV} \end{aligned} \quad (59)$$

In order to test that the derivatives are correct, Euler's theorem provides two identities for the second derivatives of the homogeneous function $F(T, V, \mathbf{n})$

$$V \left(\frac{\partial^2 F}{\partial V \partial n_k} \right)_T + \sum_j n_j \left(\frac{\partial^2 F}{\partial n_j \partial n_k} \right)_{T,V} = 0 \quad \text{all } k = 1, \dots, C \quad (60)$$

and

$$V \left(\frac{\partial^2 F}{\partial V^2} \right)_{T,\mathbf{n}} + \sum_j n_j \left(\frac{\partial^2 F}{\partial n_j \partial V} \right)_T = 0 \quad (61)$$

In Section 2 we have shown how to evaluate the thermodynamic properties from the partial derivatives of F with respect to T , V and n_i . In this section we have shown that all partial derivatives of F with respect to T , V and n_i are readily obtained if we calculate the first and the second order partial derivatives of the model $F(n, T, V, B, D)$ with respect to n , T , V , B , and D , and the first and the second order partial derivatives of the mixture parameters $B(T, V, \mathbf{n})$ and $D(T, V, \mathbf{n})$ with respect to temperature, volume and the mole numbers \mathbf{n} . The mixture parameters shall be homogeneous functions of the composition but some of the derivatives of B and D with respect to temperature and volume may eventually be zero.

If we use the modular approach outlined in this section, modifications of the computer code is straightforward and very easy. If we change the expression for the mixture parameter D , the changes in the computer code involve the subroutines computing D , D_i , D_T , D_V , D_{ij} , D_{iT} , D_{iV} , D_{TT} , D_{VV} , and D_{TV} , only.

If the model is a classical equation of state, where the Helmholtz function consists of a repulsive and an attractive contribution, it may in some cases be advantageous to program the repulsive and the attractive contributions separately.

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Chapter 3

Thermodynamic Properties from a Cubic Equation of State

Introduction

In this chapter we discuss various aspects of the cubic equations of state because they have found widespread application in many process simulators due to their simplicity and robustness. We are aware of the theoretical flaws of the cubic equations of state, but nonetheless they may serve as examples to demonstrate how to calculate, in an efficient and straightforward way, the partial derivatives of the Helmholtz energy. The discussion is limited to the Redlich-Kwong-Soave-Peng-Robinson family because the Soave-Redlich-Kwong (SRK) and the Peng-Robinson (PR) equations of state are the two that have gained prevalent acceptance. Equations of state with more complex mixing rules like those based on activity coefficient models are treated similarly. Section 8 of Chapter 5 presents an example.

1 The cubic equation of state

More than a hundred different equations of state have been published since J.D. van der Waals proposed his equation of state in 1873. The van der Waals equation consists of a repulsive and a single attractive term

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

The van der Waals equation of state gives a qualitatively correct description of fluid properties and phase behaviour of fluids, but it has a critical compressibility factor of $3/8$ and thus gives a very poor correlation of densities in the critical region. Critical compressibility factors of pure fluids

range from 0.23 (water) to 0.30 (hydrogen). Polar substances have lower critical compressibility factors than hydrocarbons. Numerous modifications of the van der Waals equation have been proposed, but until now the most successful modification is the one by O. Redlich and J.N.S. Kwong in 1949. They modified the attractive term in van der Waals' equation of state and introduced a temperature dependent a -term

$$P = \frac{RT}{v - b} - \frac{a/\sqrt{T}}{v(v + b)} \quad (2)$$

This equation of state has a critical compressibility factor of $1/3$ and is thus an improvement over van der Waals' equation of state. The temperature dependence of the a -term introduced by Redlich and Kwong is not used any more and the equation is usually written in the form

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)} \quad (3)$$

The virial expansion of the compressibility factor Z in reduced density b/v of eqn. (3) is

$$\begin{aligned} Z = \frac{Pv}{RT} &= 1 + \left(1 - \frac{a}{RTb}\right) \frac{b}{v} + \left(1 + \frac{a}{RTb}\right) \left(\frac{b}{v}\right)^2 \\ &\quad + \left(1 - \frac{a}{RTb}\right) \left(\frac{b}{v}\right)^3 + \left(1 + \frac{a}{RTb}\right) \left(\frac{b}{v}\right)^4 + \dots \end{aligned} \quad (4)$$

In this Chapter we will use a more general expression for a cubic equation of state than the one in eqn. (3). The expression we use is

$$P = \frac{RT}{v - b} - \frac{a(T)}{(v + \delta_1 b)(v + \delta_2 b)} \quad (5)$$

or

$$Z \left(\frac{b}{v}, \frac{a(T)}{RTb} \right) = \frac{1}{1 - b/v} - \frac{a(T)}{RTb} \frac{b/v}{(1 + \delta_1 b/v)(1 + \delta_2 b/v)} \quad (6)$$

The expression for the residual Helmholtz function $A^r(T, v)$ is obtained from eqn. (5) by evaluating the integral as shown in eqn. (4) in Chapter 2. The result is

$$\begin{aligned} \frac{A^r(T, v)}{RT} &= F \left(\frac{b}{v}, \frac{a(T)}{RTb} \right) \\ &= -\ln(1 - b/v) - \frac{a(T)}{RTb(\delta_1 - \delta_2)} \ln \left(\frac{1 + \delta_1 b/v}{1 + \delta_2 b/v} \right) \end{aligned} \quad (7)$$

where the constants δ_1 and δ_2 determine the volumetric dependence of the attractive contribution which yields the Soave-Redlich-Kwong equation of state, eqn. (3), with $\delta_1 = 1$ and $\delta_2 = 0$ and the Peng-Robinson equation of state when $\delta_1 = 1 + \sqrt{2}$ and $\delta_2 = 1 - \sqrt{2}$. The latter is usually written as

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \quad (8)$$

The Peng-Robinson equation of state has a critical compressibility factor of 0.307. The major difference between the Soave-Redlich-Kwong and the Peng-Robinson equation is that the latter gives slightly better correlations for the volumetric properties but when applied to phase equilibrium correlations the differences are minor.

In the Redlich-Kwong-Peng-Robinson family the constants δ_1 and δ_2 can be replaced by a single parameter c where

$$\delta_1 + \delta_2 = 1 + c \quad \text{and} \quad \delta_1\delta_2 = -c \quad (9)$$

$c = 0$ yields the Redlich-Kwong equation of state and $c = 1$ yields the Peng-Robinson equation of state. When solving for δ_1 and δ_2 , the solution is

$$\delta_1 = \frac{1}{2} \left(c + 1 + \sqrt{(c+1)^2 + 4c} \right) \quad (10)$$

and

$$\delta_2 = \frac{1}{2} \left(c + 1 - \sqrt{(c+1)^2 + 4c} \right) \quad (11)$$

2 The pure component parameters

The critical point

Any classical equation of state must be subject to the following constraints at the critical point

$$\left(\frac{\partial P}{\partial v} \right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial v^2} \right)_T = 0$$

Moreover, we would like the equation of state to match the critical compressibility factor $Z_c(v_c, T_c, a_c, b_c)$. We have thus three equations but only two adjustable parameters a and b . Since the constraints must be fulfilled, the calculated critical compressibility factor will most likely not match the experimental figure. It is convenient to use the variables

$$Z_b = \left(\frac{Pb}{RT} \right)_c, \quad y = \left(\frac{v}{b} \right)_c \quad \text{and} \quad \Gamma_c = \left(\frac{a}{RTb} \right)_c$$

We introduce the variables in eqn. (5) and rearrange

$$Z_b(y-1)(y+\delta_1)(y+\delta_2) - (y+\delta_1)(y+\delta_2) + (y-1)\Gamma_c = 0 \quad (12)$$

and calculate the first and the second derivative of this equation with respect to y

$$\begin{aligned} Z_b [(y+\delta_1)(y+\delta_2) + (y-1)(2y+\delta_1+\delta_2)] \\ , - (2y+\delta_1+\delta_2) + \Gamma_c = 0 \end{aligned} \quad (13)$$

$$Z_b(3y+\delta_1+\delta_2-1)-1=0 \quad (14)$$

and finally we combine eqns. (12)-(14) to eliminate Z_b and Γ_c and after a little algebra the resulting equation is

$$y^3 - 3y^2 - 3y(d_1+d_2) - d_1(d_1+d_2) + d_2 = 0 \quad (15)$$

where $d_1 = \delta_1 + \delta_2$ and $d_2 = \delta_1\delta_2$. Eqn. (15) has the real root

$$y = 1 + A + B \quad (16)$$

where

$$A^3 = (1+\delta_1)^2(1+\delta_2) \quad (17)$$

and

$$B^3 = (1+\delta_1)(1+\delta_2)^2 \quad (18)$$

The critical compressibility factor is calculated from eqn. (14)

$$Z_c = y Z_b = \frac{y}{3y + d_1 - 1} \quad (19)$$

and Γ_c is calculated by eliminating Z_b from eqn. (13)

$$\left(\frac{a}{RTb}\right)_c = \frac{3y^2 + 3yd_1 + d_1^2 - d_2}{3y + d_1 - 1} \quad (20)$$

When the equation of state shall match the experimental temperature, T_c , and volume, v_c , at the critical point, the expressions for a_c and b_c are

$$a_c = \left(\frac{a}{RTb}\right)_c b_c RT_c = \frac{\Omega_a}{\Omega_b} b_c RT_c \quad (21)$$

$$b_c = Z_b \frac{RT_c}{P_c} = \Omega_b \frac{v_c}{Z_c} \quad (22)$$

Similarly, if the equation of state shall match the experimental pressure and temperature at the critical point, the expressions for a_c and b_c are

$$a_c = \left(\frac{a}{RTb} \right)_c b_c RT_c = \frac{\Omega_a}{\Omega_b} b_c RT_c = \Omega_a \frac{(RT_c)^2}{P_c} \quad (23)$$

$$b_c = Z_b \frac{RT_c}{P_c} = \Omega_b \frac{RT_c}{P_c} \quad (24)$$

The Redlich-Kwong equation of state, $c = 0$, has a critical compressibility factor of $1/3$ and the Peng-Robinson equation of state, $c = 1$, has a critical compressibility factor of 0.307. When the parameter c is increased, the critical compressibility factor decreases further. One could therefore be tempted to tune c to the critical compressibility factor, but this will be at the expense of the critical fugacity coefficient. The fugacity coefficient of a pure substance at the critical point is

$$\begin{aligned} \ln \varphi_c &= \frac{G^r(T_c, P_c)}{RT_c} = \frac{A^r(T_c, v_c)}{RT_c} + Z_c - 1 - \ln Z_c \\ &= -\ln(1 - 1/y) - \left(\frac{a}{RTb} \right)_c \frac{1}{\delta_1 - \delta_2} \ln \left(\frac{y + \delta_1}{y + \delta_2} \right) \\ &\quad + Z_c - 1 - \ln Z_c \end{aligned} \quad (25)$$

The critical fugacity coefficient decreases with increasing c . It is 0.6657 for the Redlich-Kwong equation of state and 0.6426 for the Peng-Robinson equation of state. Methane has a critical compressibility factor of 0.286 and a critical fugacity coefficient of 0.664. Figure 1 shows connected values of φ_c and Z_c calculated from the cubic equation of state and 'experimental' numbers obtained from the MBWR equation of state (Younglove, 1982; Younglove and Ely, 1987) and The Steam Tables (Haar et al., 1984).

The figure shows that when c is increased the critical compressibility factor decreases but the improvement of the calculated critical compressibility factor is at the expense of the fugacity coefficient. In ordinary vapour-liquid equilibrium calculations, where an equation of state model is used for all the phases, it does not pose a problem because the equilibrium ratio equals the ratio of the fugacity coefficients in the two phases and when the fugacity coefficients are scaled in the same proportion the equilibrium ratio will not be affected. But when different models are used for the different phases, as is the case in hydrate equilibrium calculations, it is important to get the fugacities right in order to predict the correct hydrate structure (Lundgaard and Mollerup, 1991).

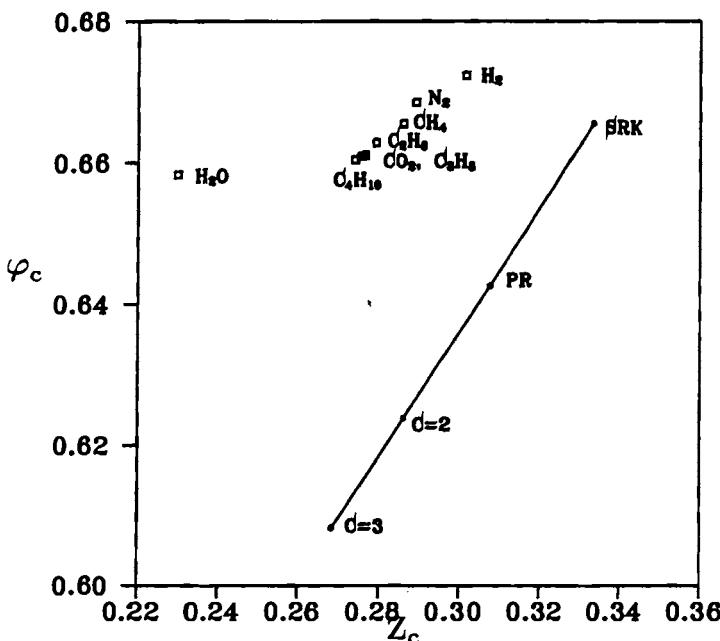


Figure 1: Critical fugacity coefficients versus critical compressibility factors. — eqn. (25), □ Younglove (1982); Younglove and Ely (1987), and Haar et al. (1984).

Tables 1 and 2 show a comparison of fugacity coefficients calculated at temperatures and pressures close to the hydrate-water-gas lines of methane and nitrogen hydrate. The abbreviations are: (PR) Peng-Robinson; (MBWR) the BWR equation of state by Younglove (1982), and Younglove and Ely (1987); (SRK) Soave-Redlich-Kwong. It is observed that the fugacity coefficients calculated from the SRK equation of state are in much better agreement with the figures from the MBWR equation of state than those of the PR equation of state.

Figure 2 shows the influence of the fugacity coefficient on the calculated dissociation pressure of nitrogen hydrate. The fugacity coefficients are calculated from the SRK, PR and MBWR equations of state. The parameters in the Kihara core model have been fitted to the four points at the gas-ice-hydrate line and the gas-water-hydrate lines are therefore predictions. The gas solubility of nitrogen in water has not been taken into account. The gas solubility influences the calculated dissociation pressures at the gas-water-

Table 1: Fugacity coefficients of methane from three equations of state

T (K)	P (MPa)	φ (PR)	φ (MBWR)	φ (SRK)
270.0	1.8	0.9453	0.9577	0.9553
280.0	5.6	0.8612	0.8874	0.8867
290.0	17.4	0.7116	0.7478	0.7634
300.0	53.6	0.6739	0.7395	0.7818
310.0	164.9	1.4885	1.9607	2.0559

Table 2: Fugacity coefficients of nitrogen from three equations of state

T (K)	P (MPa)	φ (PR)	φ (MBWR)	φ (SRK)
270.0	12.8	0.9359	0.9625	0.9820
280.0	32.3	0.9703	1.0258	1.0665
290.0	81.8	1.3207	1.5335	1.5789
300.0	207.0	3.7742	5.5238	5.3223

hydrates. This subject is discussed in Section 6 of Chapter 5 and some results are shown in Figures 3-6 of Chapter 5.

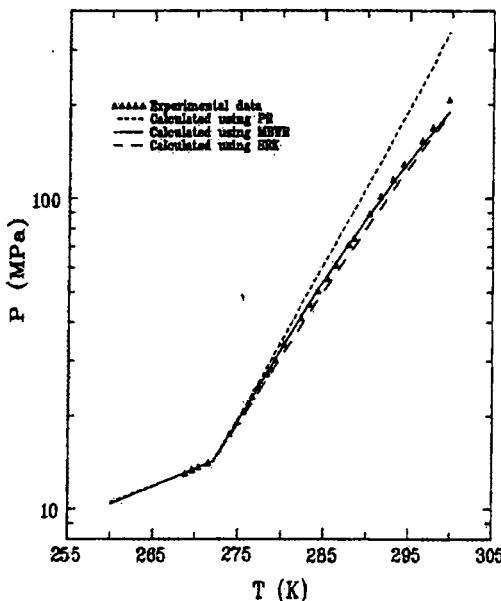


Figure 2: The figure shows the influence of the fugacity coefficient on the calculated dissociation pressure of nitrogen hydrate. The parameters in the Kihara core model have been fitted to the four points at the gas-ice-hydrate line and the gas-water-hydrate lines are extrapolations.

Subcritical temperatures

In the original van der Waals equation of state the parameters a and b are constant and retain their critical values. Redlich and Kwong, however, suggested that only b retains its critical value but that a is a function of the temperature.

$$a = a_c \sqrt{T_c/T} \quad (26)$$

This correlation is an improvement, but it is not satisfactory because the equation of state does not match saturation pressures of pure substances adequately.

To improve the correlation of pure component vapour pressures, the a -parameter must be determined by constraining the equation of state to fit the vapour pressures adequately. For a pure substance at a given saturation pressure $P(T)$ a single value of a exists which satisfies the saturation

condition:

$$\varphi^l(T, P(T), v_l, b, a(T)) = \varphi^v(T, P(T), v_v, b, a(T)) \quad (27)$$

where T is the saturation temperature and v_l and v_v are the saturated liquid and vapour volume, respectively.

The logarithm of the fugacity coefficient of a pure substance equals the reduced residual Gibbs energy $G^r(T, P)/RT$ for one mole of pure substance. The expression for the fugacity is

$$\ln \varphi_i = \frac{G^r(T, P)}{RT} = \frac{A^r(T, v)}{RT} + Z - 1 - \ln Z \quad (28)$$

where Z and $A^r(T, v)$ are calculated from eqns. (6) and (7), respectively.

Since b retains its critical value, the unknowns are a , v_l and v_v . The volumes at saturated are calculated by solving eqn. (5) for the liquid and the vapour roots, respectively, therefore a can be calculated by solving eqns. (5) and (27) simultaneously.

Several correlations of $a(T)$ at subcritical temperatures have been proposed. One of the first generalised correlations for the Redlich-Kwong equation of state was developed by G.M. Wilson in 1966. Wilson assumed that $a(T)$ is a linear function of the reduced temperature and estimated the constant m from the slope of the vapour pressure curve at the critical point using the correlation by Riedel

$$a(T) = a_c (1 + m(1 - T/T_c)) \quad (29)$$

where

$$m = 0.57 + 1.62\omega \quad (30)$$

Later, in 1972 G. Soave developed a similar correlation for the a -parameter in the Redlich-Kwong equation of state. Soave plotted the values of a/a_c obtained from vapour pressure data for a number of hydrocarbons against T/T_c and observed that the curves showed similar trends. By plotting $\sqrt{a/a_c}$ against $\sqrt{T/T_c}$, almost straight lines are obtained. As all lines must pass through $a = a_c$ at $T = T_c$, we can write

$$\sqrt{a(T)/a_c} = 1 + m_{SRK} \left(1 - \sqrt{T/T_c} \right)$$

or

$$a(T) = a_c \alpha(T_r, \omega) = a_c \left(1 + m_{SRK} \left(1 - \sqrt{T/T_c} \right) \right)^2 \quad (31)$$

where m_{SRK} can be connected directly with the acentric factor ω of the related compound because, as Soave observed, each value of ω defines a value

of the reduced vapour pressure at a reduced temperature of 0.7. Since, from the definition of the acentric factor

$$P_r = 10^{-1-\omega} \quad \text{at } T_r = 0.7 \quad (32)$$

we can for any value of ω calculate the reduced vapour pressure at a reduced temperature of 0.7 therefore we can determine a and thus $m_{SRK}(\omega)$ at a temperature of 0.7 times the critical temperature. No experimental data are involved. Soave correlated m_{SRK} against ω in the interval of ω from 0 to 0.5

$$m_{SRK} = 0.480 + 1.574\omega - 0.175\omega^2 \quad (33)$$

The procedure used by Soave can be used for any two constant equation of state.

When D.-Y. Peng and D.B. Robinson in 1976 developed their equation of state, eqn. (8), they used a correlation of $a(T)$ similar to Soave's but they estimated the three constants in the correlation of $m(\omega)$ by minimizing the residual sum of squares between calculated and experimental vapour pressures from the normal boiling point to the critical point. The resulting equation is

$$m_{PR} = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (34)$$

The generalised correlations by Soave and Peng-Robinson are fairly accurate at temperatures from the normal boiling point to the critical point although results obtained for polar substances and high boiling hydrocarbons are less accurate. The generalised correlations are less satisfactory at low reduced temperature. Although Soave developed his correlation of m_{SRK} at acentric factors ranging from 0 to 0.5 only, it extrapolates very well and shows a very good agreement with the values calculated from the equation of state at acentric factors from -0.5 to 2.0. Table 3 shows the ratio of correlated and calculated values.

A more rigorous temperature dependence of the attractive parameter a can be derived from the Clapeyron equation. Let P^s denote the vapour pressure and the subscripts v and l the saturated vapour and liquid phase, respectively. At the saturation line $\Delta G = G_v - G_l = 0$ and $dG_v - dG_l = 0$ therefore

$$\Delta G = \Delta U + P^s \Delta V - T \Delta S = 0 \quad \Rightarrow \quad \Delta U = -P^s \Delta V + T \Delta S$$

and

$$dG = -S dT + V dP^s \quad \Rightarrow \quad \Delta S = \Delta V \frac{dP^s}{dT}$$

Table 3: The ratio of m from the generalised correlation divided by m calculated from the equation of state at $T_r = 0.7$

ω	Soave	Peng-Robinson
-0.4	0.973	1.168
-0.2	1.009	0.747
0.0	1.000	0.989
0.4	1.000	1.000
0.8	0.998	0.976
1.2	0.991	0.940
1.6	0.977	0.895
2.0	0.959	0.842

ΔU is the heat of vaporization $U^{vap} = U_v - U_l$ and ΔV the difference in molar volumes $v_v - v_l$. When we eliminate ΔS , we get the Clapeyron equation

$$U^{vap} = -P^s (v_v - v_l) \left(1 - T \frac{d \ln P^s}{dT} \right) \quad (35)$$

The energy of vaporization is calculable from the residual energies U^r of the saturated phases using the formula

$$U^{vap} = U_v^r - U_l^r = \frac{\partial}{\partial(1/T)} \frac{A^r(T, v_v) - A^r(T, v_l)}{T} \quad (36)$$

where the derivative of the residual Helmholtz energy A^r is calculable from eqn. (7). If b is independent of the temperature and $a = a_c \alpha(T_r)$, the expression for the residual energy is

$$\begin{aligned} U^r &= \frac{\partial}{\partial(1/T)} \frac{A^r(T, v)}{T} = -\frac{\partial}{\partial(1/T)} \frac{\alpha}{T} f \\ &= \frac{\partial(\alpha/T_r)}{\partial T_r} T_r^2 f \end{aligned} \quad (37)$$

where T_r is the reduced temperature T/T_c and

$$f = \frac{a_c}{b(\delta_1 - \delta_2)} \ln \left(\frac{1 + \delta_1 b/v}{1 + \delta_2 b/v} \right) \quad (38)$$

Inserting eqn. (37) in eqn. (36) gives the expression for the energy of vaporization

$$U^{vap} = \frac{\partial(\alpha/T_r)}{\partial T_r} T_r^2 (f_v - f_l) \quad (39)$$

and when combining eqns. (35) and (39) we obtain the wanted expression for the temperature derivative of α along the saturation line

$$\begin{aligned}\frac{\partial(\alpha/T_r)}{\partial T_r} &= \frac{P^s(v_v - v_l)}{T_r^2(f_l - f_v)} \left(1 - T_r \frac{\partial \ln P_r^s}{\partial T_r}\right) \\ &= \frac{M}{T_r^2} \left(1 - T_r \frac{\partial \ln P_r^s}{\partial T_r}\right)\end{aligned}\quad (40)$$

where P_r^s is the reduced vapour pressure P^s/P_c . At the critical point we can show that

$$M_c = \frac{(Z_c + \delta_1 \Omega_b)(Z_c + \delta_2 \Omega_b)}{\Omega_a} \quad (41)$$

Furthermore, investigation of the PVT properties of several fluids show that M is approximately a linear function of the reduced temperature

$$M = \frac{P^s(v_v - v_l)}{f_l - f_v} = M_c + M_1(1 - T_r) \quad (42)$$

Finally, we assume that an appropriate vapour pressure equation is

$$\ln P_r^s = a_1(1 - 1/T_r) + a_2 \ln T_r \quad (43)$$

We insert eqns. (42) and (43) in eqn. (40) and integrate from $T_r = 1$ to T_r , and redefine the constants. At the lower limit of integration $\alpha(T_r) = \alpha(1) = 1$. The result is

$$\alpha(T_r) = 1 + \beta(1/T_r - 1) + \gamma T_r \ln T_r + \delta(T_r - 1) \quad (44)$$

where β , γ and δ are three parameters that can be estimated by a least square fit to figures for $a(T)$ determined from experimental vapour pressure data. The average deviation between calculated and experimental vapour pressures for polar substances or substances with a high normal boiling point is less than one tenth of the average deviation obtained when Soave's or Peng-Robinson's correlation is used.

Supercritical temperatures

There is no unique way to derive a correlation of $a(T)$ at supercritical temperatures. The natural extension of the vapour pressure curve is the critical isochore as the two curves have equal slopes at the critical point but experimental data along the critical isochore are difficult to utilise because cubic equations of state do not match the experimental critical point. We are therefore most likely left with no choice but to extrapolate the correlation developed at subcritical temperatures. Except for helium and hydrogen

$a(T)$ decreases when T increases therefore a correlation developed for $a(T)$ at subcritical temperatures could become negative when extrapolated to temperatures well above the critical temperature. Theoretically, $a(T)$ should go towards zero as the temperature goes towards infinity. In correlations like Soave's and Peng-Robinson's $a(T)$ decreases when T increases and they yield $a = 0$ at a reduced temperature of

$$T_r = (1 + 1/m)^2 \quad (45)$$

and as the temperature is increased further $a(T)$ goes towards infinity as T goes towards infinity.

A correlation like the one developed from the Clapeyron equation, eqn. (44), may give negative values for $\alpha(T_r)$ at temperatures above the critical temperature. In order to avoid this, we can extrapolate $\alpha(T_r)$ using the following expression when T_r is greater than one

$$\alpha_h(x) = \frac{1}{1 + c_1x + c_2x^2} \quad \text{where } x = T_r - 1 \quad (46)$$

where the constants c_1 and c_2 are estimated by matching the first and second derivatives of the two correlations at the critical point, i.e., $\alpha'(1) = \alpha'_h(0)$ and $\alpha''(1) = \alpha''_h(0)$.

The temperature dependence of b

In most of the cubic equations of state that have been developed it is assumed that b is independent of the temperature. This assumption is not only made out of convenience but also because a temperature dependence of the b -parameter shall most likely violate the condition of thermal stability, that is $T/C_V > 0$. At high density, where the volume v approaches b , the repulsive term outweighs the attractive term. In this case the residual isochoric heat capacity at constant volume predominates and therefore the condition of thermal stability requires that

$$\left(\frac{C_V}{T}\right)_{\text{repulsive}} = \frac{R}{v-b} \left(-2b_T - Tb_{TT} - \frac{Tb_T^2}{v-b}\right) + \frac{C_V^{id}}{T} > 0 \quad (47)$$

which is not likely to be fulfilled unless b is independent of the temperature because the last term in the parenthesis is always negative (Salim and Trebble, 1991).

3 Mixtures

The Helmholtz function

The thermodynamic properties of mixtures are calculable from an expression for the residual Helmholtz energy of a mixture. We postulate that this ex-

pression shall be obtained from eqn. (7) by replacing the pure component parameters a and b by appropriate expressions for the mixture parameters a_{mix} and b_{mix} . If we by B denotes nb_{mix} and by D denotes n^2a_{mix} , the expression for the Helmholtz energy for n moles of a mixture is

$$\frac{A^r(T, V, \mathbf{n})}{RT} = -n \ln(1 - B/V) - \frac{D(T)}{RTB(\delta_1 - \delta_2)} \ln \left(\frac{1 + \delta_1 B/V}{1 + \delta_2 B/V} \right) \quad (48)$$

where V is the total volume of the mixture. If it is assumed that a_{mix} and b_{mix} are quadratic sums of their pure component values, then

$$D = n^2 a_{mix} = \sum_i n_i \sum_j n_j a_{ij} \quad (49)$$

with

$$a_{ij} = a_{ji} = \sqrt{a_{ii} a_{jj}} (1 - k_{ij}) \quad (50)$$

and

$$nB = n^2 b_{mix} = \sum_i n_i \sum_j n_j b_{ij} \quad (51)$$

where

$$b_{ij} = b_{ji} = \frac{1}{2}(b_{ii} + b_{jj})(1 - l_{ij}) \quad (52)$$

It is often assumed that $l_{ij} = 0$ in which case eqn. (51) reduces to

$$B = \sum_i n_i b_{ii} \quad (53)$$

The binary interaction coefficients k_{ij} and l_{ij} are generally treated as constants most often with $l_{ij} = 0$. If desired they can be made functions of temperature, volume, and mole numbers only, but any modification should preserve the homogeneity of the Helmholtz function and ensure that it continues to be a characteristic function.

The Lorentz-Berthelot combining rules

For conformal intermolecular potentials like $u_{ij}(r) = \epsilon_{ij} F(\sigma_{ij}/r)$ it is common to write

$$\begin{aligned} \sigma_{ij} &= \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \\ \epsilon_{ij} &= \sqrt{\epsilon_{ii} \epsilon_{jj}} (1 - k_{ij}) \end{aligned} \quad (54)$$

where ϵ and σ are an energy and a distance and F denotes some function common to both species. The combining rule for σ is exact for mixtures of hard spheres and the assumption that this rule applied to $b^{1/3}$, the parameter in van der Waals' equation equivalent to σ , was made by Lorentz in 1881. The assumption that the combining rule for ϵ apply to the critical temperatures is built on the fact that at least for conformal fluids T_c is proportional to ϵ . In equations of state the Lorentz-Berthelot combining rules can be applied in several ways. If the parameters a and b are constants and retain their values determined at the critical point then a/b is proportional to the critical temperature. Combining eqns. (23) and (24) shows that

$$\frac{a_c}{b_c} = \frac{\Omega_a}{\Omega_b} RT_c \propto \epsilon$$

However, the parameter a does not retain its value at the critical point but is a weak function of temperature, but it is not prescribed that ϵ shall be a constant, therefore the Lorentz-Berthelot combining rules apply to the parameters a and b in a cubic equation of state in the following way

$$b_{ij}^{\frac{1}{3}} = \frac{1}{2} \left(b_{ii}^{\frac{1}{3}} + b_{jj}^{\frac{1}{3}} \right) \quad (55)$$

and

$$\frac{a_{ij}}{b_{ij}} = \sqrt{\frac{a_{ii}}{b_{ii}} \frac{a_{jj}}{b_{jj}}} (1 - k_{ij}) \quad (56)$$

These combining rules can replace the combining rules eqns. (50) and (52).

Applied to a generalised correlation like eqn. (31) we can calculate the unlike a term as

$$\frac{a_{ij}}{b_{ij}} = \frac{\Omega_a}{\Omega_b} RT_{c_{ij}} \alpha_{ij} \left(\omega_{ij}, \frac{T}{T_{c_{ij}}} \right) \quad (57)$$

where b_{ij} is calculated from eqn. (55) and since $T_c \propto \epsilon$

$$T_{c_{ij}} = \sqrt{T_{c_i} T_{c_j}} (1 - k_{ij}) \quad (58)$$

and

$$\omega_{ij} = \frac{1}{2} (\omega_{ii} + \omega_{jj}) \quad (59)$$

or one could fit ω_{ij} like k_{ij} if experimental data are available within a sufficiently large temperature interval.

4 Derivatives of the Helmholtz function

To calculate the thermodynamic properties we must calculate the partial derivatives as outlined in Chapter 2. The reduced residual Helmholtz function

of a generic equation of state including the Redlich-Kwong and the Peng-Robinson equations of state is

$$F = F(n, T, V, B, D) = -ng(V, B) - \frac{D(T)}{T} f(V, B) \quad (60)$$

where

$$g = \ln(1 - B/V) = \ln(V - B) - \ln V \quad (61)$$

$$f = \frac{1}{RB(\delta_1 - \delta_2)} \ln \frac{1 + \delta_1 B/V}{1 + \delta_2 B/V} = \frac{1}{RB(\delta_1 - \delta_2)} \ln \frac{V + \delta_1 B}{V + \delta_2 B} \quad (62)$$

$$n = \sum_i n_i \quad (63)$$

$$nB = \sum_i n_i \sum_j n_j b_{ij} \quad (64)$$

$$D(T) = \sum_i n_i \sum_j n_j a_{ij}(T) = \frac{1}{2} \sum_i n_i D_i \quad (65)$$

D_i is the compositional derivative of D , see eqn. (101).

The appropriate partial derivatives of the reduced residual Helmholtz energy are straight forward to calculate. First, F is differentiated twice with respect to its primary variables, i.e. n , T , V , B , and D , and second, the derivatives of the mixture parameters B and D are evaluated. This result in a set of ‘model derivatives’ independent of the chosen mixing rules and a set of ‘parameter derivatives’ which is not directly affected by the form of the equation of state. For the model in eqn. (60) B is a function of the composition and D depends on the composition and temperature and besides F_{nn} , F_{nT} , F_{nD} , and F_{DD} are zero. The partial derivatives of F needed for calculation of the thermodynamic properties are thus:

The first order partial derivatives

$$\left(\frac{\partial F}{\partial n_i} \right)_{T,V} = F_n + F_B B_i + F_D D_i \quad (66)$$

$$\left(\frac{\partial F}{\partial T} \right)_{V,n} = F_T + F_D D_T \quad (67)$$

$$\left(\frac{\partial F}{\partial V} \right)_{T,n} = F_V \quad (68)$$

The subscript n_j , which means that all except n_i are held constant, is omitted where no confusion can arise.

The second order partial derivatives

$$\left(\frac{\partial^2 F}{\partial n_i \partial n_j} \right)_{T,V} = F_{nB}(B_i + B_j) + F_{BD}(B_i D_j + B_j D_i) + F_B B_{ij} + F_{BB} B_i B_j + F_D D_{ij} \quad (69)$$

$$\left(\frac{\partial^2 F}{\partial n_i \partial T} \right)_V = (F_{BT} + F_{BD} D_T) B_i + F_{DT} D_i + F_D D_{iT} \quad (70)$$

$$\left(\frac{\partial^2 F}{\partial n_i \partial V} \right)_T = F_{nV} + F_{BV} B_i + F_{DV} D_i \quad (71)$$

$$\left(\frac{\partial^2 F}{\partial T^2} \right)_{V,n} = F_{TT} + 2F_{DT} D_T + F_D D_{TT} \quad (72)$$

$$\left(\frac{\partial^2 F}{\partial T \partial V} \right)_n = F_{TV} + F_{DV} D_T \quad (73)$$

$$\left(\frac{\partial^2 F}{\partial V^2} \right)_{T,n} = F_{VV} \quad (74)$$

The first order partial derivatives of F , g , and f

$$F_n = -g \quad (75)$$

$$F_T = \frac{D}{T^2} f \quad (76)$$

$$F_V = -n g_V - \frac{D}{T} f_V \quad (77)$$

$$F_B = -n g_B - \frac{D}{T} f_B \quad (78)$$

$$F_D = -\frac{f}{T} \quad (79)$$

$$g_V = \frac{1}{V-B} - \frac{1}{V} = \frac{B}{V(V-B)} \quad (80)$$

$$g_B = -\frac{V}{B} g_V = -\frac{1}{V-B} \quad (81)$$

$$\begin{aligned} f_V &= \frac{1}{RB(\delta_1 - \delta_2)} \left(\frac{1}{V + \delta_1 B} - \frac{1}{V + \delta_2 B} \right) \\ &= -\frac{1}{R(V + \delta_1 B)(V + \delta_2 B)} \end{aligned} \quad (82)$$

$$f_B = -\frac{f + Vf_V}{B} \quad (83)$$

The second order partial derivatives of F , g , and f

$$F_{nV} = -g_V \quad (84)$$

$$F_{nB} = -g_B \quad (85)$$

$$F_{TT} = -2 \frac{F_T}{T} \quad (86)$$

$$F_{BT} = \frac{Df_B}{T^2} \quad (87)$$

$$F_{DT} = \frac{f}{T^2} \quad (88)$$

$$F_{BV} = -n g_{BV} - \frac{D}{T} f_{BV} \quad (89)$$

$$F_{BB} = -n g_{BB} - \frac{D}{T} f_{BB} \quad (90)$$

$$F_{DV} = -\frac{f_V}{T} \quad (91)$$

$$F_{BD} = -\frac{f_B}{T} \quad (92)$$

$$F_{TV} = \frac{D}{T^2} f_V \quad (93)$$

$$F_{VV} = -n g_{VV} - \frac{D}{T} f_{VV} \quad (94)$$

$$g_{VV} = -\frac{1}{(V - B)^2} + \frac{1}{V^2} \quad (95)$$

$$g_{BV} = -\frac{g_V + Vg_{VV}}{B} = \frac{1}{(V - B)^2} \quad (96)$$

$$g_{BB} = -\frac{g_B + Vg_{BV}}{B} = \frac{1}{(V - B)^2} \quad (97)$$

$$f_{VV} = \frac{1}{RB(\delta_1 - \delta_2)} \left(-\frac{1}{(V + \delta_1 B)^2} + \frac{1}{(V + \delta_2 B)^2} \right) \quad (98)$$

$$f_{BV} = -\frac{2f_V + Vf_{VV}}{B} \quad (99)$$

$$f_{BB} = -\frac{2f_B + Vf_{BV}}{B} \quad (100)$$

The partial derivatives of D

$$D_i = 2 \sum_j n_j a_{ij} \quad (101)$$

$$D_{iT} = 2 \sum_j n_j \frac{\partial a_{ij}}{\partial T} \quad (102)$$

$$D_{ij} = 2a_{ij} \quad (103)$$

$$D_T = \frac{1}{2} \sum_i n_i D_{iT} \quad (104)$$

$$D_{TT} = \sum_i n_i \sum_j n_j \frac{\partial^2 a_{ij}}{\partial T^2} \quad (105)$$

By differentiation of eqn. (64) twice we get the derivatives of B

$$B + nB_i = 2 \sum_j n_j b_{ij} \quad (106)$$

$$B_j + B_i + nB_{ij} = 2b_{ij} \quad (107)$$

and solving for B_i and B_{ij}

$$B_i = \frac{2 \sum_j n_j b_{ij} - B}{n} \quad (108)$$

$$B_{ij} = \frac{2b_{ij} - B_i - B_j}{n} \quad (109)$$

It may look odd to split such a simple model and its derivatives into so many terms. However, adoption of the procedure prescribed here does not only lead to an easier and better structured approach for deriving thermodynamic properties, but it is also very likely to provide an efficient code in particular when derivatives of fugacity coefficients are required. It is also much easier to modify the model using this modular approach, because changes in g , f , B , or D are easy to implement because the general structure of the

computer program as such is not affected. Even in the case where say D is made volume dependent, this can be handled in a few additional subroutines, and it is not necessary to rewrite the entire computer code.

The derivatives of $g(\beta)$ and $f(\beta)$

Someone may find it more convenient to calculate the derivatives of g and f using the equations

$$g(\beta) = \ln(1 - B/V) = \ln(1 - \beta) \quad (110)$$

$$\begin{aligned} f(B, \beta) &= \frac{1}{RB(\delta_1 - \delta_2)} \ln \frac{1 + \delta_1 B/V}{1 + \delta_2 B/V} \\ &= \frac{1}{RB(\delta_1 - \delta_2)} \ln \frac{1 + \delta_1 \beta}{1 + \delta_2 \beta} \end{aligned} \quad (111)$$

where

$$\beta = \frac{B}{V} \quad (112)$$

The derivatives of β are

$$\beta_B = \frac{\beta}{B} \quad \text{and} \quad \beta_{BB} = 0 \quad (113)$$

$$\beta_V = -\frac{\beta}{V} = -\beta\beta_V \quad \text{and} \quad \beta_{VV} = -2\frac{\beta_V}{V} \quad (114)$$

$$\beta_{BV} = \frac{\beta_V}{B} \quad (115)$$

Therefore we can write eqns. (80)-(83) in the following way

$$g_V = g_\beta \beta_V \quad (116)$$

$$g_B = g_\beta \beta_B = -\frac{g_V}{\beta} \quad (117)$$

$$f_V = f_\beta f_V \quad (118)$$

$$f_B = f_\beta \beta_B - \frac{f}{B} = -\frac{f_V}{\beta} - \frac{f}{B} \quad (119)$$

and similarly for eqns. (95)-(100)

$$g_{VV} = g_{\beta\beta} (\beta_V)^2 + g_\beta \beta_{VV} \quad (120)$$

$$g_{BV} = g_{\beta\beta} \beta_B \beta_V + g_\beta \beta_{BV} \quad (121)$$

$$g_{BB} = g_{\beta\beta} (\beta_B)^2 + g_\beta \beta_{BB} \quad (122)$$

$$f_{VV} = f_{\beta\beta} (\beta_V)^2 + f_\beta \beta_{VV} \quad (123)$$

$$f_{BV} = f_{\beta\beta} \beta_B \beta_V + f_\beta \beta_{BV} - \frac{f_\beta}{B} \beta_V = -\frac{f_{VV}}{\beta} - 2 \frac{f_V}{B} \quad (124)$$

$$f_{BB} = f_{\beta\beta} (\beta_B)^2 + f_\beta \beta_{BB} - 2 \frac{f_B}{B} = -\frac{f_{BV}}{\beta} - 2 \frac{f_B}{B} \quad (125)$$

The derivatives of g and f are

$$g_\beta = -\frac{1}{1-\beta} \quad (126)$$

$$g_{\beta\beta} = -\frac{1}{(1-\beta)^2} = \frac{g_\beta}{1-\beta} \quad (127)$$

$$f_\beta = \frac{1}{RB(\delta_1 - \delta_2)} \left(\frac{\delta_1}{1 + \delta_1 \beta} - \frac{\delta_2}{1 + \delta_2 \beta} \right) \quad (128)$$

$$f_{\beta\beta} = \frac{1}{RB(\delta_1 - \delta_2)} \left(-\frac{\delta_1^2}{(1 + \delta_1 \beta)^2} + \frac{\delta_2^2}{(1 + \delta_2 \beta)^2} \right) \quad (129)$$

5 Calculation of the volume

If the equation of state is cubic, it may be solved analytically with respect to the molar volume or the compressibility factor. However, use of a general Newton-Raphson method does not limit one to a cubic equation of state and besides not all two-parameter equations of state are necessarily cubic.

Suppose we are searching for the roots in the function $h(x) = 0$ and that x_0 is an approximate value of one of the roots, then an improved value of the root is given by

$$x - x_0 = \Delta = -\frac{h(x_0)}{h_x(x_0)} \quad (130)$$

where h_x is the first derivative of h with respect to x .

An improved value can also be calculated from a second order approximation

$$h(x) = h(x_0) + h_x(x_0)(x - x_0) + \frac{1}{2} h_{xx}(x_0)(x - x_0)^2 = 0 \quad (131)$$

where h_{xx} is the second derivative of h with respect to x .

We now replace $x - x_0$ in the last term of eqn. (131) by Δ from eqn. (130) and solve for $x - x_0$

$$x - x_0 = \Delta \left(1 + \frac{1}{2} \frac{\Delta}{\Delta_1} \right) \quad (132)$$

where

$$\Delta_1 = -\frac{h_x(x_0)}{h_{xx}(x_0)} \quad (133)$$

An improved value of the root can be calculated from eqn. (132) whenever $|\Delta/\Delta_1| \leq 1$. If $\Delta/\Delta_1 < -1$, a value of -1 is used in eqn. (132). In the case where $\Delta > \Delta_1$ the calculation may be diverging or approaching a stationary point. A new value of the root is then supposed to be

$$x - x_0 = \Delta_1 \quad (134)$$

and an extrapolated value of h is calculated as

$$h_{ex} = h(x_0) + \Delta_1 h_x(x_0) \quad (135)$$

If $|h_{ex}| > |h(x_0)|$, it is likely that the search for a root in $h(x)$ near x_0 is diverging and a new value of x_0 must be estimated. If there is more than one root, the stable root is the one with the lowest Gibbs energy.

Calculation of the volume in a two-parameter equation of state

The total volume V ranges from B to infinity whereas B/V is always between 0 and 1 which makes it a bit easier to perform a Newton-Raphson iteration in B/V instead of in V . The volume corresponding to the specified pressure, temperature, and composition is calculated from the pressure equation

$$P = \frac{nRT}{V} - RT \left(\frac{\partial F}{\partial V} \right)_{T,n} = \frac{nRT}{V} + RT \left(n g_V + \frac{D}{T} f_V \right) \quad (136)$$

We now transform eqn. (136) to an equation where the variable $\beta = B/V$ replaces the total volume V . To do so we multiply by B/nRT

$$\frac{PB}{nRT} = \frac{B}{V} + B \left(g_V + \frac{D}{nT} f_V \right) \quad (137)$$

The function $h(\beta) = h(B/V)$ is thus

$$h(\beta) = \frac{B}{V} + B \left(g_V + \frac{D}{nT} f_V \right) - \frac{PB}{nRT} = 0 \quad (138)$$

where the range of the real root $\beta = B/V$ is $0 < \beta < 1$. Furthermore, as

$$V_\beta = \frac{\partial V}{\partial \beta} = \frac{\partial}{\partial \beta} \left(\frac{B}{\beta} \right) = -\frac{B}{\beta^2} \quad (139)$$

the first derivative of $h(\beta)$ is

$$h_\beta = 1 + B \left(g_{VV} + \frac{D}{nT} f_{VV} \right) V_\beta = 1 - \frac{B^2}{\beta^2} \left(g_{VV} + \frac{D}{nT} f_{VV} \right) \quad (140)$$

and similarly the second derivative is

$$\begin{aligned} h_{\beta\beta} &= 2 \frac{B^2}{\beta^3} \left(g_{VV} + \frac{D}{nT} f_{VV} \right) + \frac{B^3}{\beta^4} \left(g_{VVV} + \frac{D}{nT} f_{VVV} \right) \\ &= \frac{2}{\beta} (1 - h_\beta) + \frac{B^3}{\beta^4} \left(g_{VVV} + \frac{D}{nT} f_{VVV} \right) \end{aligned} \quad (141)$$

where

$$g_{VVV} = \frac{2}{(V - B)^3} - \frac{2}{V^3} \quad (142)$$

and

$$f_{VVV} = \frac{1}{RB(\delta_1 - \delta_2)} \left(\frac{2}{(V + \delta_1 B)^3} - \frac{2}{(V + \delta_2 B)^3} \right) \quad (143)$$

For any of the real roots of $h(\beta)$ it is required that $h_\beta > 0$.

Good initial estimates of β is either $\beta = PB/nRT$ or $\beta = 2/(2 + T_R)$ where T_R is a pseudocritical reduced temperature of the mixture

$$T_R = \frac{nT}{\sum_i n_i T_{c_i}} \quad (144)$$

6 Elimination of the gas constant

It is often convenient to eliminate the gas constant in the residual Helmholtz function, eqn. (48), because this gives flexibility regarding the units used for T_c and P_c and reduces the risk of making an error regards the consistency of the units used. Moreover, in many cases the pressure, temperature and the composition vector \mathbf{n} are specified and the output is the compressibility factor, the fugacity coefficients and its derivatives, therefore we can consider the total volume as an internal variable. To eliminate the gas constant we define the pure component parameters \tilde{a}_{ii} and \tilde{b}_{ii}

$$\tilde{a}_{ii}(T) = \frac{a_{ii}}{R^2} = \Omega_a \frac{T_{c_{ii}}^2}{P_{c_{ii}}} \alpha(T) \quad (145)$$

and

$$\tilde{b}_{ii} = \frac{b_{ii}}{R} = \Omega_b \frac{T_{c_{ii}}}{P_{c_{ii}}} \quad (146)$$

The new mixture parameters are

$$n\tilde{B} = \sum_i n_i \sum_j n_j \tilde{b}_{ij} \quad (147)$$

and

$$\tilde{D}(T) = \sum_i n_i \sum_j n_j \tilde{a}_{ij}(T) \quad (148)$$

Furthermore let

$$\tilde{V} = \frac{V}{R} \quad (149)$$

The reduced residual Helmholtz function, eqn. (48), in terms of these variables, is

$$\frac{A^r(T, V, n)}{RT} = -n \ln(1 - \tilde{B}/\tilde{V}) - \frac{\tilde{D}(T)}{T \tilde{B} (\delta_1 - \delta_2)} \ln \left(\frac{1 + \delta_1 \tilde{B}/\tilde{V}}{1 + \delta_2 \tilde{B}/\tilde{V}} \right) \quad (150)$$

The derivatives shown in Section 4 can be used with a few minor modifications.

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Chapter 4

The Ultimate Two-Parameter Equation of State

Introduction

Over the years, numerous attempts have been made to improve an inherent deficiency in the two-parameter equation of state, i.e. its lack of ability to correlate volumetric properties with sufficient accuracy. None of them have gained widespread acceptance, because the overall improvements are often minor. As shown in Chapter 3 we can improve the compressibility factor at the critical point but this will be at the expense of the critical fugacity coefficient. If we tune the two-parameter equation of state to improve the correlation of densities, correlation of other properties like fugacities, enthalpies, heat capacities or Henry's constants may become less accurate. One must realise that the cubic equation of state is a very crude approximation to the description of real fluid behaviour. It requires at least three parameters to match the experimental critical compressibility factor.

Equations of state that can correlate the behaviour of pure fluids have been developed, but it requires a lot of parameters. An equation like the Modified Benedict-Webb-Rubin (MBWR) equation of state can be used

$$Z = 1 + A\rho + B\rho^2 + C\rho^3 + D\rho^4 + E\rho^5 + F\rho^6 + G\rho^7 + H\rho^8 + \exp(\gamma\rho^2)(I\rho^2 + J\rho^4 + K\rho^6 + L\rho^8 + M\rho^{10} + N\rho^{12}) \quad (1)$$

where parameters A through N are temperature dependent, γ is a constant, and ρ is the molar density. The analytical expression for the residual Helmholtz energy is calculable from eqn. (1) using the formula

$$\frac{A^r(T, v)}{RT} = - \int_{\infty}^v \frac{Z(T, v) - 1}{v} dv = \int_0^{\rho} \frac{Z(T, \rho) - 1}{\rho} d\rho \quad (2)$$

An equation of state of this type is excellent for pure fluids, Younglove and Ely (1987), but not suitable for correlation of properties of fluid mixtures because mixing rules for the parameters A through N are not easily derived. Thus other model concepts are wanted. More recently Span and Wagner (2003a,b,c) have developed similar equations of state for a variety of fluids.

1 Model concepts

The model concept used in many equations of state is as follows. Given a pure component equation of state

$$\frac{A^r(T, v)}{RT} = F(T, v, \mathbf{q}) \quad (3)$$

where F is a function common to all fluids and \mathbf{q} is a parameter vector. In the cubic equation of state $\mathbf{q} = (a, b)$ and F could be the Redlich-Kwong-Soave or the Peng-Robinson equation of state or some other cubic equation of state model. In order to apply the equation of state F to mixtures we have to develop mixing rules for the parameter vector \mathbf{q} , that is, to develop a prescription that tell us how to calculate the elements of \mathbf{q} for the mixture knowing the composition and the \mathbf{q} vectors for the pure components. We can write this concept in the following way

$$\frac{A^r(T, V, \mathbf{n})}{RT} = F(T, V, \mathbf{Q}) \quad (4)$$

where \mathbf{Q} is the parameter vector for the mixture calculable from the \mathbf{q} vectors of the pure substances. In the cubic equation of state $\mathbf{Q} = (D/n, B)$ where

$$D = \sum_i n_i \sum_j n_j a_{ij} \quad (5)$$

and

$$nB = \sum_i n_i \sum_j n_j b_{ij} \quad (6)$$

but for an equation like the MBWR shown above it is not feasible to derive mixing rules for fourteen parameters and therefore we have to look for other model concepts.

Let $F(T, V, \mathbf{q})$ be an equation of state for a pure substance. If we know F for this particular fluid, is it then possible to derive a model concept that allow us to calculate F of other pure fluids or of a mixture of fluids from $F(T_0, v_0, \mathbf{q})$? The answer is yes. Actually, that is exactly the concept we apply when we use a cubic equation of state model although usually, we do

not state it that way. The proof will be given in the next section. If it works for a cubic equation of state model, it will also work for a model like the one we can derive from eqn. (1).

We make the following assumption. The residual Helmholtz energy of a mixture is calculable from the model

$$\frac{A^r(T, V, \mathbf{n})}{nRT} = \frac{A_0^r(T_0, v_0)}{RT_0} = F_0(T_0, v_0, \mathbf{q}) \quad (7)$$

where $F_0(T_0, v_0, \mathbf{q})$ is an equation of state for a pure substance and \mathbf{q} the corresponding parameter vector. We denote this substance a reference substance by adding the subscript 0. If $F_0(T_0, v_0, \mathbf{q})$ is an equation of state like the MBWR, then \mathbf{q} is the parameters A through N . The temperature T_0 and the volume v_0 are the temperature and the molar volume of the reference substance that must be calculable from the specified temperature T , volume V , and composition \mathbf{n} of the mixture. Instead of deriving mixing rules for the fourteen parameters we have a much easier task, we must prescribe how to calculate T_0 and v_0 from (T, V, \mathbf{n}) and some characteristic parameters of the pure substances; a prescription that must be independent of the particular form of $F_0(T_0, v_0, \mathbf{q})$. The characteristic parameters are usually critical constants, ascentric factors, etc. If we can derive correlations that enable us to calculate the ratio of volumes V/v_0 and temperatures T/T_0 , we will be able to calculate the properties of the fluid mixture knowing the properties of the reference fluid $F_0(T_0, v_0, \mathbf{q})$. No mixing rules are required for the \mathbf{q} -parameters. As will be shown in the subsequent section we can, from any two-parameter cubic equations of state, derive simple correlations for two scale factors \hat{H} and \hat{F} that will enable us to calculate the ratio of the volumes and the temperatures

$$\hat{H} = \frac{V}{v_0} \quad (8)$$

and

$$\frac{\hat{F}}{n} = \frac{T}{T_0} \quad (9)$$

The scale factors \hat{H} and \hat{F} are composition dependent homogeneous functions of degree one in the variables \mathbf{n} . That is the reason why \hat{F} in eqn. (9) is divided by the total number of moles n . The scale factors of a pure substance are by definition

$$h = \frac{v}{v_0} \quad (10)$$

and

$$f = \frac{T}{T_0} \quad (11)$$

In the next section we will show that for a two-parameter cubic equation of state, the modelling principles of eqns. (4) and (7) are in fact equivalent.

2 The scale factors in a two-parameter cubic equation of state

The cubic equation of state model is analysed in Chapter 3. The residual Helmholtz energy of a pure substance is, see eqn. (7) of Chapter 3

$$\frac{A^r(T, v)}{RT} = -\ln(1 - b/v) - \frac{a(T)}{RTb} \frac{1}{\delta_1 - \delta_2} \ln \left(\frac{1 + \delta_1 b/v}{1 + \delta_2 b/v} \right) \quad (12)$$

We define two parameters

$$\Gamma \equiv \frac{a(T)}{bRT} \quad \text{and} \quad \beta \equiv \frac{b}{v} \quad (13)$$

and insert them in eqn. (12). The result is

$$\begin{aligned} \frac{A^r(T, v)}{RT} &= -\ln(1 - \beta) - \frac{\Gamma}{\delta_1 - \delta_2} \ln \left(\frac{1 + \delta_1 \beta}{1 + \delta_2 \beta} \right) \\ &= F(\beta, \Gamma) \end{aligned} \quad (14)$$

where F is a function common to all fluids which depends the generic form of the two-parameter equation of state. Eqn. (14) shows that the reduced residual Helmholtz energy is a function of two parameters β and Γ , only.

Pure substances

Since F is a function common to all fluids, let us denote them 1 and 0. They shall have identical reduced residual Helmholtz energies, i.e.

$$\frac{A_1^r(T_1, v_1)}{RT_1} = \frac{A_0^r(T_0, v_0)}{RT_0} \Leftrightarrow F(\beta_1, \Gamma_1) = F(\beta_0, \Gamma_0) \quad (15)$$

when $\Gamma_1 = \Gamma_0$ and $\beta_1 = \beta_0$ or when

$$\frac{a_1(T_1)}{b_1 RT_1} = \frac{a_0(T_0)}{b_0 RT_0} \quad (16)$$

and

$$\frac{b_1}{v_1} = \frac{b_0}{v_0} \quad (17)$$

From these equations we calculate the corresponding ratios of volumes v_1/v_0 and temperatures T_1/T_0 . These ratios define the two scale factors h and f for fluid 1 relative to fluid 0.

The scale factor for volumes is

$$h_1 = \frac{v_1}{v_0} = \frac{b_1}{b_0} = \frac{T_{c_1} P_{c_0}}{T_{c_0} P_{c_1}} \quad (18)$$

The scale factor for temperatures is

$$f_1 = \frac{T_1}{T_0} = \frac{a_1(T_1) b_0}{a_0(T_0) b_1} = \frac{T_{c_1}}{T_{c_0}} \frac{\alpha(T_{r_1})}{\alpha(T_{r_0})} \quad (19)$$

The corresponding ratio of reduced temperatures is thus

$$\frac{T_{r_1}}{T_{r_0}} = \theta_1 = \frac{\alpha(T_{r_1})}{\alpha(T_{r_0})} \quad (20)$$

where, in eqn. (20), we have utilised that $a(T) = a_c \alpha(T_r)$. We note that h is independent of the particular choice of cubic equation of state. The a -parameter must be a function of the temperature in order to correlate the vapour pressures of pure substances adequately, but f is not particularly dependent on the choice of cubic equation of state because the ratio of the α -parameters of any two fluids 1 and 0 is almost identical for a range of cubic equations of state. Calculations using different equations of state like Soave's (Soave, 1972) or Peng-Robinson's (Peng and Robinson, 1976) and others confirm that the correlations for f are alike (Mollerup, 1980). In general eqn. (20) gives no explicit formula for the scale factor f because T_{r_0} depends on f . Combining eqns. (18) and (20) shows that

$$f_1 h_1 = \frac{a_1(T_1)}{a_0(T_0)} = \frac{a_1(T_1)}{a_0(T_1/f_1)} \quad (21)$$

and therefore no explicit expression for f_1 can be obtained.

If we take the derivative of eqn. (15) with respect to v_1 at constant temperature, the result is

$$\begin{aligned} \left(\frac{\partial}{\partial v_1} \frac{A_1^r(T_1, v_1)}{RT_1} \right)_{T_1} &= \left(\frac{\partial}{\partial v_0} \frac{A_0^r(T_0, v_0)}{RT_0} \right)_{T_0} \left(\frac{\partial v_0}{\partial v_1} \right)_{T_1} \\ &\quad + \left(\frac{\partial}{\partial T_0} \frac{A_0^r(T_0, v_0)}{RT_0} \right)_{v_0} \left(\frac{\partial T_0}{\partial v_1} \right)_{T_1} \end{aligned} \quad (22)$$

The last term is zero because T_0 is volume independent according to eqn. (20). The partial derivative of v_0 with respect to v_1 is calculable from eqn. (18), the result is

$$\frac{\partial v_0}{\partial v_1} = \frac{1}{h_1} = \frac{v_0}{v_1} \quad (23)$$

and consequently from eqn. (22).

$$-\frac{P_1}{RT_1} + \frac{1}{v_1} = \left(-\frac{P_0}{RT_0} + \frac{1}{v_0} \right) \frac{\partial v_0}{\partial v_1} = \left(-\frac{P_0}{RT_0} + \frac{1}{v_0} \right) \frac{v_0}{v_1} \quad (24)$$

or when multiplying by v_1

$$Z_1(T_1, v_1) = Z_0(T_0, v_0) = Z_0 \left(\frac{T_1}{f_1}, \frac{v_1}{h_1} \right) \quad (25)$$

Eqns. (15) and (25) establish the principles for calculating temperature dependent scale factors from any class of equation of state. The correlations for the scale factors f and h derived from a cubic equation of state are in fact very accurate.

We will now compare f calculated from a MBWR equation of state with f calculated from Soave's Redlich-Kwong equation of state. Table 1 shows an example where the ratio of reduced temperatures θ , calculated from Soave's

Table 1: Comparison of the shape factors $\theta = T_r/T_{r_0}$ for helium and hydrogen calculated with methane as reference fluid and θ calculated from Soave's correlation.

T_r	Helium		Hydrogen	
	calculated	Soave's correlation	calculated	Soave's correlation
0.42			0.806	0.833
0.58	0.790	0.800	0.877	0.867
0.70	0.859	0.861	0.919	0.921
1	1	1	1	1
4	1.86	2.07	1.45	1.56
8	2.95	3.25	2.08	2.11
12	4.01	4.33	2.70	2.59
16	5.07	5.37	3.31	3.04
20	6.12	6.37		
25	7.43	7.60		
30	8.74	8.79		
35	10.1	9.97		
40	11.4	11.1		
45	12.7	12.3		
50	14.0	13.4		

correlation, are compared with the exact numbers calculated for helium and hydrogen when methane is the reference fluid. The exact numbers are calculated from a MBWR equation of state along the saturation line and its extension, the critical isochore, using eqn. (18) for h . When the ratio of reduced temperatures is calculated from Soave's correlation, the result is

$$\theta_1 = \frac{T_{r_1}}{T_{r_0}} = \frac{\alpha_1(T_{r_1})}{\alpha_0(T_{r_0})} = \left(\frac{1 + m_1 - m_1 \sqrt{T_{r_1}}}{1 + m_0 - m_0 \sqrt{T_{r_0}}} \right)^2 \quad (26)$$

Since, in this case, $T_{r_0} = T_{r_1}/\theta_1$, we can eliminate T_{r_1} from eqn. (26) and thus get an explicit expression for θ_1 . The result is

$$\theta_1 = \left(\frac{1 + m_1}{1 + m_0} - \frac{m_1 - m_0}{1 + m_0} \sqrt{T_{r_1}} \right)^2 \quad (27)$$

The calculations in Table 1 demonstrate that we can calculate the properties of helium and hydrogen from the properties of methane if we use Soave's correlation of $\alpha(T_r)$ to calculate the scale factor f . The scale factor h is the ratio of critical constants and thus independent of the choice of the correlation of f . The reason why we have chosen to apply the principles to helium and hydrogen and not to some hydrocarbons is firstly, that the range of reduced temperatures is very large and secondly, that these fluids have properties that are very dissimilar to the properties of a hydrocarbon like methane. A list of possible reference fluids are given in Table 2.

Mixtures

When we use a cubic equation of state, the thermodynamic properties of a mixture is calculable from an expression for the residual Helmholtz energy of a mixture that shall be obtained from eqn. (12) by replacing the pure component parameters a and b by appropriate expressions for the mixture parameters a_{mix} and b_{mix} . If $B = nb_{mix}$ and $D = n^2a_{mix}$, the expression for the Helmholtz energy for n moles of a mixture is

$$\begin{aligned} \frac{A^r(T, V, \mathbf{n})}{nRT} &= -\ln(1 - B/V) - \frac{D}{nRTB} \frac{1}{\delta_1 - \delta_2} \ln \left(\frac{1 + \delta_1 B/V}{1 + \delta_2 B/V} \right) \\ &= F(\beta_{mix}, \Gamma_{mix}) \end{aligned} \quad (28)$$

where the mixture parameters

$$\Gamma_{mix} \equiv \frac{D}{nBRT} \quad \text{and} \quad \beta_{mix} \equiv \frac{B}{V} \quad (29)$$

Table 2: Critical compressibility factors, temperature and pressure limits of some pure fluids. The temperature and pressure limits are the limits on T_0 and P_0 . The references are: [1] Younglove (1982), [2] Younglove and Ely (1987), and [3] Span and Wagner (2003c).

Fluid	Z_c	T_{min} (K)	T_{max} (K)	P_{max} (MPa)	Ref.
Redlich-Kwong	0.333				
Peng-Robinson	0.307				
<i>p</i> -Hydrogen	0.301	14	400	120	[1]
Nitrogen	0.289	63	1900	120	[1]
Methane	0.286	90	673	1500	[2]
Ethane	0.279	90	623	80	[2]
Propane	0.276	85	623	1000	[2]
Butane	0.274	134	700	70	[2]
Carbon dioxide	0.275	215	1100	300	[1]
Methanol	0.226	176	673	70	[3]

The mixing rules adopted for B and D are optional as long as they provide a consistent model.

Since F is a function that apply to mixtures as well as to pure fluids we can calculate the reduced residual Helmholtz energy of a mixture from the reduced residual Helmholtz energy of a reference substance 0 because the following equality shall apply

$$F(\beta_{mix}, \Gamma_{mix}) = F(\beta_0, \Gamma_0) \quad (30)$$

and consequently $\Gamma_{mix} = \Gamma_0$ and $\beta_{mix} = \beta_0$ and therefore

$$\frac{D}{nRTB} = \frac{a_0(T_0)}{RT_0 b_0} \quad (31)$$

and

$$\frac{B}{V} = \frac{b_0}{v_0} \quad (32)$$

From eqns. (31) and (32) we can calculate the corresponding ratios of volume and temperatures that define the two mixture scale factors \hat{H} and \hat{F}

$$\hat{H} = \frac{V}{v_0} = \frac{B}{b_0} \quad (33)$$

and

$$\hat{F} = \frac{nT}{T_0} = \frac{D}{B} \frac{b_0}{a_0(T_0)} \quad (34)$$

Note that \hat{H} and \hat{F} are first order homogeneous functions in the mole numbers like B and D/n .

The derivation demonstrates the equivalence between the model concepts of eqns. (4) and (7) for a cubic equation of state. So far we have not made any assumptions as regards the mixing rules for B and D . Any mixing rules that provide a consistent model can be used. The mixing rules for the scale factors \hat{H} and \hat{F} are derived from the mixing rules for D and B .

3 Mixing rules for scale factors

The conventional mixing rules

For computation of \hat{H} and \hat{F} it is expedient but not a necessity to adopt the conventional mixing rules for B and D from the cubic equation of state. If we do this, the result is

$$\hat{H}nb_0 = nB = \sum_i n_i \sum_j n_j b_{ij} \quad (35)$$

and

$$\hat{F}\hat{H}a_0(T_0) = \hat{F}\hat{H}a_0(nT/\hat{F}) = D = \sum_i n_i \sum_j n_j a_{ij}(T) \quad (36)$$

Eqn. (36) shows that in general no explicit expression for \hat{F} can be obtained. The derivatives of \hat{H} are similar to the derivatives of B but the derivatives of \hat{F} are slightly more complex than the derivatives of D because of the implicit concentration dependence. The combining rules for b_{ij} and a_{ij} are optional, but it is expedient to use the Lorentz-Berthelot combining rules discussed in Chapter 3 because formally they correspond to the combining rules usually adopted for h_{ij} and f_{ij} (Mollerup and Rowlinson, 1974)

$$\begin{aligned} b_{ij}^{\frac{1}{2}} &= \frac{1}{2} \left(b_{ii}^{\frac{1}{2}} + b_{jj}^{\frac{1}{2}} \right) \quad \Leftrightarrow \quad h_{ij}^{\frac{1}{2}} = \frac{1}{2} \left(h_{ii}^{\frac{1}{2}} + h_{jj}^{\frac{1}{2}} \right) \\ \frac{a_{ij}}{b_{ij}} &= \sqrt{\frac{a_{ii}}{b_{ii}} \frac{a_{jj}}{b_{jj}}} (1 - k_{ij}) \quad \Leftrightarrow \quad f_{ij} = \sqrt{f_{ii} f_{jj}} (1 - k_{ij}) \end{aligned} \quad (37)$$

Non-quadratic mixing rules

As mentioned previously, it is not necessary to make assumptions as regards the composition dependence of the mixture parameters B and D except

that they provide a consistent model. In case we want to make use of non-quadratic mixing rules for the scale factor f , it is straightforward to do so. For mixtures of polar substances mixing rules derived from excess Gibbs energy models are advantageous to use. Mollerup (1986) and Michelsen (1990) derived the following mixing rule for the D -parameter

$$\frac{D}{RTB} = \sum_i n_i \frac{a_{ii}(T)}{RTb_{ii}} + \frac{1}{q} \left(\frac{G^E}{RT} + \sum_i n_i \ln \frac{B}{nb_{ii}} \right) \quad (38)$$

where the numerical value of q depends on the particular two-parameter equation of state. Combining eqns. (34) and (38) and multiplication with RTb_0 yield the desired expression

$$\begin{aligned} \hat{F}a_0(T_0) &= \hat{F}a_0(nT/\hat{F}) \\ &= b_0 \sum_i n_i \frac{a_{ii}(T)}{b_{ii}} + \frac{RTb_0}{q} \left(\frac{G^E}{RT} + \sum_i n_i \ln \frac{B}{nb_{ii}} \right) \end{aligned} \quad (39)$$

where B may be quadratic or non-quadratic in the composition dependence. Application of a non-quadratic mixing rule in equations of state is discussed in Chapter 5.

4 The new model concept

There is no need to make an attempt to ‘improve’ the two-parameter cubic equation of state itself. It is much more straightforward to improve the modelling concept. In the new modelling concept we utilise the correlations for the cubic equation of state parameters a and b to calculate correlations for the scale factors for temperature f and volume h . When we have the correlations of f and h , we can use them to scale any suitable reference equation of state. A suitable equation of state could be the MBWR equation of state or an equation of state by Span and Wagner. The choice of reference substance depends on the particular application. It could be hydrogen, a hydrocarbon, a refrigerant, methanol, water or any other fluid whose properties are accurately correlated. Application of scale factors is not limited to a particular class of fluids and we are not limited as regards pressure because correlations of pure component properties are available at pressures to 1000 MPa and above where most cubic equations of state fail. Table 2 shows some possible reference fluids.

The equation that defines the modelling principle is

$$A^r(T, V, \mathbf{n}) = \hat{F}M(T_0, v_0) \quad (40)$$

where M is the residual molar Helmholtz function of the reference substance at the temperature T_0 and molar volume v_0 calculable as

$$v_0 = \frac{V}{\hat{H}} \quad (41)$$

and

$$T_0 = \frac{nT}{\hat{F}} \quad (42)$$

where \hat{F} and \hat{H} are calculated from the cubic equation of state parameters $B = nb_{mix}$ and $D = n^2a_{mix}$ and the corresponding parameters for the reference fluid a_0 and b_0

$$\hat{H} = \frac{B}{b_0} \quad (43)$$

and

$$\hat{F} = \frac{D}{B} \frac{b_0}{a_0(T_0)} \quad (44)$$

Mixing rules for \hat{F} and \hat{H} are analysed in Section 3. The mixing rules for the scale factors are derived from the mixing rules adopted for B and D in the cubic equation of state, quadratic or non-quadratic. We have thus developed a two-parameter model that retains the simplicity of the classical two-parameter equation of state as regards computational speed and robustness but improves the correlation and prediction of thermodynamic properties due to the choice of an accurate reference equation of state. The advantages of deriving scale factor correlations from a cubic two-parameter equation of state are several. First, correlations and mixing rules for the two parameters are readily available; second, one can improve the correlated properties simply by replacing the cubic two-parameter equation of state by an accurate pure-component equation of state; third, it is very easy to use a characterization procedure, developed for a cubic two-parameter equation of state and thus extend computations of PVT properties of reservoir fluids to very high pressures because correlations of pure component properties by the MBWR and the Span-Wagner equations of state are available at pressures to 1000 MPa and above.

5 Associating fluids

If one can combine an association term and a cubic equation of state as it is done in the CPA model (Kontogeorgis et al., 1996), one can also include a term accounting for association in the new model eqn. (40). That is

$$A^r(T, V, \mathbf{n}) = \hat{F} M(T_0, v_0) + A^{asc}(T, V, \mathbf{n}, \mathbf{n}^\mathbf{B}) \quad (45)$$

where \mathbf{n}^B is the composition vector of molecules not bonded at sites B . The choice of radial distribution function in the association term is a matter of convenience and not of principles. It can either be a hard sphere-radial distribution function or the radial distribution function from the CPA model.

6 Application of Soave's and Peng-Robinson's correlations

When we apply Soave's (Soave, 1972) or Peng-Robinson's (Peng and Robinson, 1976) correlation for the a -parameter and the mixing rule, eqn. (36), the scale factor \hat{F} is calculable from the equation

$$\hat{H}\hat{F}a_{c_0} \left(1 + m_0 - m_0 \sqrt{\frac{Tn}{T_{c_0}\hat{F}}} \right)^2 = D = \sum_i n_i \sum_j n_j a_{ij}(T) \quad (46)$$

If we take the square root of the left- and right-hand side, we can solve for $\sqrt{\hat{F}}$

$$\sqrt{\hat{F}} = \frac{m_0 \sqrt{\frac{Tn}{T_{c_0}}} + \sqrt{\frac{D}{\hat{H}a_{c_0}}}}{1 + m_0} \quad (47)$$

\hat{H} is calculated from eqn. (43).

In the examples the reference fluid equation of state is the MBWR (Younglove and Ely, 1987). The combining rule for a_{ij} is the conventional one, i.e. $a_{ij} = \sqrt{a_{ii}a_{jj}}(1 - k_{ij})$ and standard interaction coefficients k_{ij} have been used, that is hydrocarbon-hydrocarbon interaction coefficients are zero, hydrocarbon interaction coefficients with nitrogen range from 0.02 to 0.05, and hydrocarbon interaction coefficients with carbon dioxide range from 0.12 to 0.15. Except for Figure 4 methane is used as reference fluid.

A comparison of experimental and calculated LNG densities is given in Table 3. The experimental data are by Hiza and Haynes (1980); the molar composition of the mixture is: nitrogen 4.25, methane 81.30, ethane 4.75, propane 4.87, isobutane 2.41, and butane 2.42.

The abbreviations used in the Table and the Figures are, PR: Peng-Robinson's equation of state; MPR: the MBWR model with Peng-Robinson's scale factor for f ; MSRK: the MBWR model with Soave's scale factor for f .

Table 3: Comparison of experimental and calculated LNG densities (mole/litre).

P (MPa)	T (K)	exp.	PR	MPR	MSRK
0.183	105	24.850	27.471	24.387	24.383
0.252	110	24.516	27.125	24.070	24.067
0.338	115	23.178	26.765	23.749	23.746
0.443	120	23.858	26.390	23.424	23.422

Figure 1 shows a comparison of experimental and calculated compressibility factors of a natural gas mixture. The experimental data are some unpublished Burnett measurements. The dotted line is the Peng-Robinson equation of state, the dashed line is the Soave-Redlich-Kwong equation of state, and the full line is the MSRK and the MPR models. The MSRK and the MPR models give identical results.

Figure 2 shows a comparison of calculated phase envelopes; the dotted line is the Peng-Robinson equation of state, the dashed line is the Soave-Redlich-Kwong equation of state, and the full line is the MSRK and the MPR models. The MSRK and the MPR models give identical results.

Figure 3 shows another comparison of calculated phase envelopes; the dashed line is the Soave-Redlich-Kwong equation of state and the full line is the MSRK model. The Redlich-Kwong-Soave equation of state predicts an unstable liquid region.

Figure 4 shows a comparison of calculated and experimental compressibility factors at saturation pressures of the phase envelope of a 0.147 propane and 0.853 pentane mixture; the dashed line is the Soave-Redlich-Kwong equation of state and the full line is the MSRK model with butane as the reference fluid. A propane reference fluid gives similar results (Mollerup, 1998).

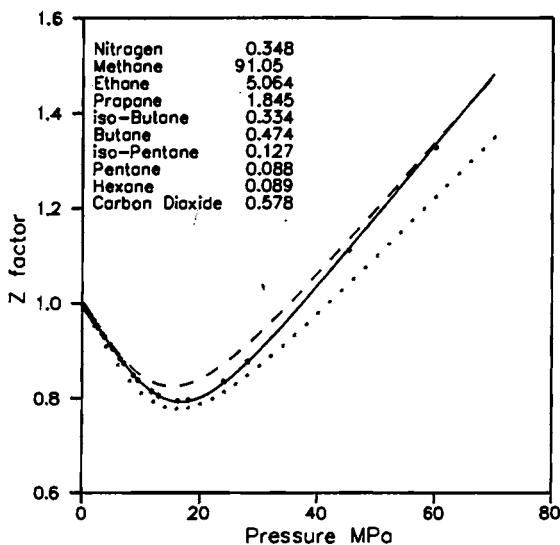


Figure 1: Calculated and experimental Z factors of a natural gas mixture at 310 K. Dashed line: The SRK EoS; dotted line: The PR EoS; full line: The MSRK and MPR models. The experimental data are Burnett measurements.

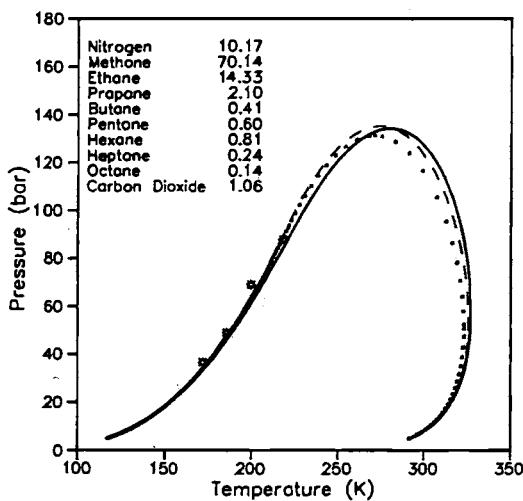


Figure 2: Calculated and experimental phase envelopes. Dashed line: The SRK EoS; dotted line: The PR EoS; full line: The MSRK and MPR models. The experimental data are by Cunningham et al. (1980).

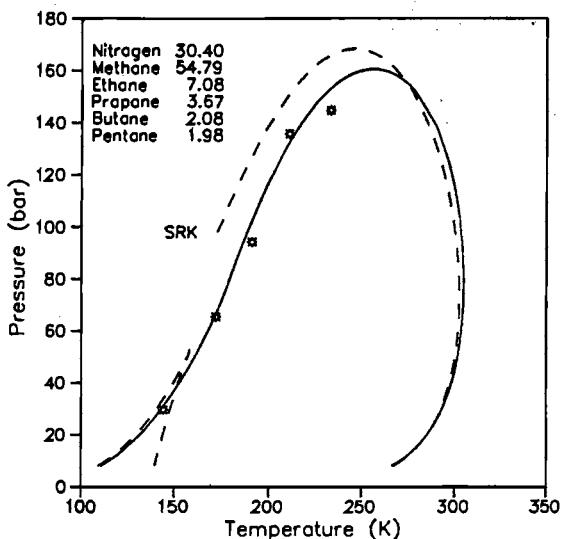


Figure 3: Calculated and experimental phase envelopes. Dashed line: The SRK EoS; full line: The MSRK model. The experimental data are by Cunningham et al. (1980).

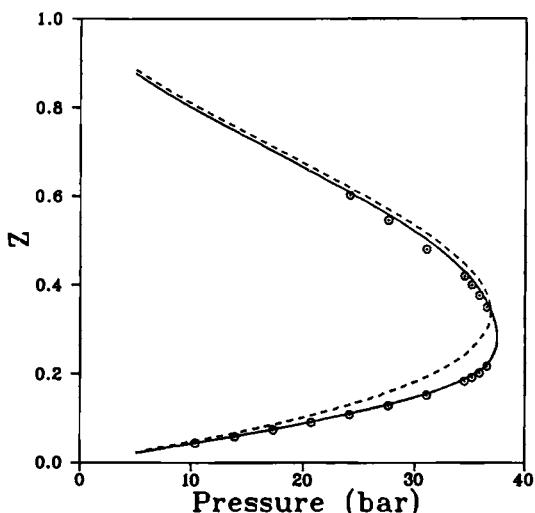


Figure 4: Calculated and experimental compressibility factors as function of pressure along the phase envelope of a 0.147 propane and 0.853 pentane mixture. Dashed line: The SRK EoS; full line: The MSRK model with butane as the reference fluid. The experimental data are by Kay (1970).

Figure 5 present the (P, T) , (P, x) , (ρ, T) , and (T, x) projections of the gas-liquid critical locus of the CO_2 and n -decane system. The solid lines are the calculated results. The scale factor f are from Soave's correlation, $k_{ij} = 0.14$ and CO_2 is the reference fluid (Cismonti, 2003). Experimental data by Reamer and Sage (1963).

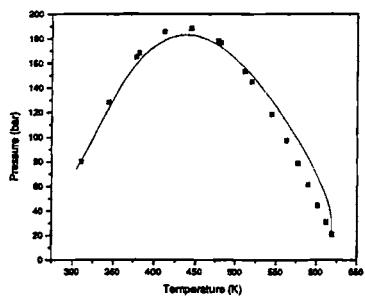
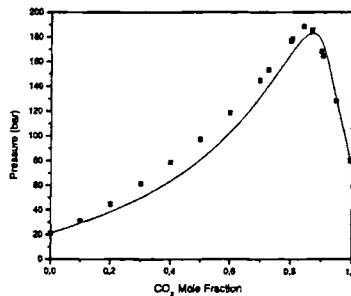
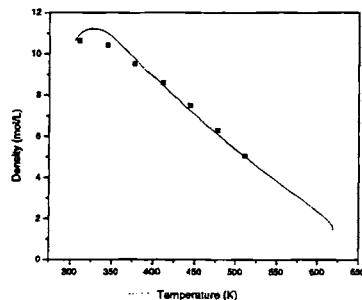
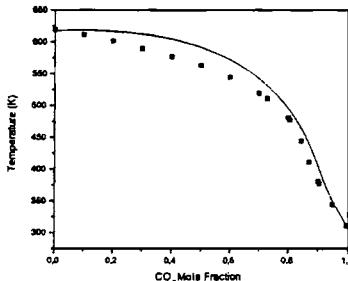
(a) (P, T) -projection of the critical locus.(b) (P, x) -projection of the critical locus.(c) (ρ, T) -projection of the critical locus.(d) (T, x) -projection of the critical locus.

Figure 5: The (P, T) , (P, x) , (ρ, T) , and (T, x) projections of the gas-liquid critical line of the carbon dioxide and n -decane system. The solid lines are the results calculated with the MSRK model.

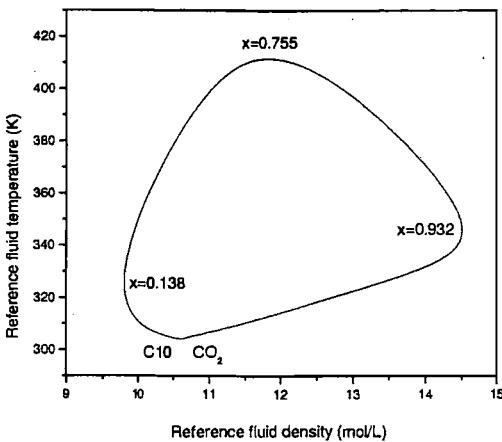


Figure 6: The reference fluid temperature T_0 and reference fluid density ρ_0 along the critical line calculated with the corresponding state method. The mole fractions of CO_2 are indicated at the maximum and minimum in density, and maximum in temperature. (Cismondi, 2003).

7 The partial derivatives

The reference equation of state model, eqn. (40), differs from the two-parameter cubic equation of state in having two mixture scale factors that in general have implicit concentration dependence. In the present model only the \hat{F} parameter has implicit concentration dependence due to the temperature dependence of f because the scale factors are derived from cubic equations of state where b is temperature independent.

To calculate the thermodynamic properties we adopt the modular approach developed in Chapter 2. Tables of the thermodynamic and the derived properties are shown in Tables 3 and 8 in Chapter 1. The steps are as follows:

First, we calculate the first and second order partial derivatives of the residual Helmholtz function A^r , eqn. (40), with respect to T , V , and n_i in terms of the partial derivatives of \hat{F} and M with respect to T , V , and n_i .

from eqn. (40).

$$\left(\frac{\partial A^r}{\partial T} \right)_{V,n} = \hat{F}_T M + \hat{F} M_T \quad (48)$$

$$\left(\frac{\partial A^r}{\partial V} \right)_{T,n} = \hat{F} M_V \quad (49)$$

$$\left(\frac{\partial A^r}{\partial n_i} \right)_{T,V} = \hat{F}_i M + \hat{F} M_i \quad (50)$$

$$\left(\frac{\partial^2 A^r}{\partial T^2} \right)_{V,n} = \hat{F}_{TT} M + 2\hat{F}_T M_T + \hat{F} M_{TT} \quad (51)$$

$$\left(\frac{\partial^2 A^r}{\partial V^2} \right)_{T,n} = \hat{F} M_{VV} \quad (52)$$

$$\left(\frac{\partial^2 A^r}{\partial n_i \partial n_j} \right)_{T,V} = \hat{F}_{ij} M + \hat{F}_j M_i + \hat{F}_i M_j + \hat{F} M_{ij} \quad (53)$$

$$\left(\frac{\partial^2 A^r}{\partial T \partial V} \right)_n = \hat{F}_T M_V + \hat{F} M_{TV} \quad (54)$$

$$\left(\frac{\partial^2 A^r}{\partial T \partial n_i} \right)_V = \hat{F}_{Ti} M + \hat{F}_T M_i + \hat{F}_i M_T + \hat{F} M_{Ti} \quad (55)$$

$$\left(\frac{\partial^2 A^r}{\partial V \partial n_i} \right)_T = \hat{F}_i M_V + \hat{F} M_{Vi} \quad (56)$$

Next, calculate the first and second order partial derivatives of M with respect to T , V , and n_i in terms of the partial derivatives of M with respect to T_0 and v_0 and the derivatives of T_0 and v_0 with respect to T , V , and n_i .

$$M_T = M_{T_0} T_{0,T} \quad (57)$$

$$M_V = M_{v_0} v_{0,V} \quad (58)$$

$$M_i = M_{T_0} T_{0,i} + M_{v_0} v_{0,i} \quad (59)$$

$$M_{TT} = M_{T_0} T_0 (T_{0,T})^2 + M_{T_0} T_{0,TT} \quad (60)$$

$$M_{VV} = M_{v_0} v_0 (v_{0,V})^2 + M_{v_0} v_{0,VV} \quad (61)$$

$$\begin{aligned} M_{ij} = & M_{T_0} T_0 T_{0,i} T_{0,j} + M_{T_0} T_0 T_{0,ij} + M_{v_0} v_0 v_{0,i} v_{0,j} \\ & + M_{v_0} v_{0,ij} + M_{T_0} v_0 (T_{0,i} v_{0,j} + T_{0,j} v_{0,i}) \end{aligned} \quad (62)$$

$$M_{TV} = M_{T_0 v_0} T_{0,T} v_{0,V} \quad (63)$$

$$M_{Ti} = M_{T_0 T_0} T_{0,T} T_{0,i} + M_{T_0 v_0} T_{0,T} v_{0,i} + M_{T_0} T_{0,Ti} \quad (64)$$

$$M_{Vi} = M_{v_0 v_0} v_{0,V} v_{0,i} + M_{T_0 v_0} T_{0,i} v_{0,V} + M_{v_0} v_{0,Vi} \quad (65)$$

The first and second order partial derivatives of v_0 with respect to V and n_i are calculated from eqn. (41), that is from

$$\hat{H}v_0 = V \quad (66)$$

Like B , \hat{H} does not depend on T and V but only on the composition. The first and second order partial derivatives of the scale factor \hat{H} with respect to the mole number n_i are obtained from eqn. (35), the results are

$$\hat{H}_i = \frac{B_i}{b_0} = \frac{2 \sum_j n_j b_{ij} - B}{nb_0} \quad (67)$$

and

$$\hat{H}_{ij} = \frac{B_{ij}}{b_0} = \frac{2b_{ij} - B_i - B_j}{nb_0} \quad (68)$$

The parameters b_0 and B and the derivatives B_i and B_{ij} are obtained from the two-parameter equation of state.

To calculate the derivatives with respect to composition we differentiate eqn. (66) twice, that is

$$\hat{H}_i v_0 + \hat{H} v_{0,i} = 0$$

and

$$\hat{H}_{ij} v_0 + \hat{H}_i v_{0,j} + \hat{H}_j v_{0,i} + \hat{H} v_{0,ij} = 0$$

and similarly we calculate the derivatives with respect to V . We divide by $\hat{H}v_0$. The first order derivatives are

$$\frac{v_{0,i}}{v_0} = -\frac{\hat{H}_i}{\hat{H}} = -\frac{B_i}{B} \quad (69)$$

and

$$v_{0,V} = \frac{1}{\hat{H}} = \frac{b_0}{B} \quad (70)$$

The second order compositional derivative is

$$\frac{v_{0,ij}}{v_0} = -\frac{\hat{H}_{ij}}{\hat{H}} - \frac{\hat{H}_i}{\hat{H}} \frac{v_{0,j}}{v_0} - \frac{\hat{H}_j}{\hat{H}} \frac{v_{0,i}}{v_0} \quad (71)$$

When we use eqn. (69) to eliminate $v_{0,i}$ and $v_{0,j}$, the result is

$$\frac{v_{0,ij}}{v_0} = -\frac{\hat{H}_{ij}}{\hat{H}} + 2 \frac{\hat{H}_i}{\hat{H}} \frac{\hat{H}_j}{\hat{H}} = -\frac{B_{ij}}{B} + 2 \frac{B_i}{B} \frac{B_j}{B} \quad (72)$$

The other second order derivatives are

$$v_{0,Vi} = -\frac{\hat{H}_i}{\hat{H}^2} = -\frac{B_i b_0}{B^2} \quad (73)$$

and

$$v_{0,VV} = 0 \quad (74)$$

The first and second order partial derivatives of T_0 with respect to T and n_i are calculated from eqn. (42) ,

$$\hat{F}T_0 = nT \quad (75)$$

Since the parameter a in the cubic equation of state is temperature dependent, \hat{F} is a function of composition and temperature as well. To calculate the derivatives with respect to composition we differentiate twice, that is

$$\hat{F}_iT_0 + \hat{F}T_{0,i} = T$$

and

$$\hat{F}_{ij}T_0 + \hat{F}_iT_{0,j} + \hat{F}_jT_{0,i} + \hat{F}T_{0,ij} = 0$$

and similarly we calculate the derivatives with respect to T . We divide by $\hat{F}T_0$. The first order derivatives are

$$\frac{T_{0,i}}{T_0} = \frac{1}{n} - \frac{\hat{F}_i}{\hat{F}} \quad (76)$$

and

$$\frac{T_{0,T}}{T_0} = \frac{1}{T} - \frac{\hat{F}_T}{\hat{F}} \quad (77)$$

The second order derivatives are

$$\frac{T_{0,ij}}{T_0} = -\frac{\hat{F}_{ij}}{\hat{F}} - \frac{\hat{F}_i}{\hat{F}} \frac{T_{0,j}}{T_0} - \frac{\hat{F}_j}{\hat{F}} \frac{T_{0,i}}{T_0} \quad (78)$$

$$\frac{T_{0,Ti}}{T_0} = -\frac{\hat{F}_{Ti}}{\hat{F}} - \frac{\hat{F}_T}{\hat{F}} \frac{T_{0,i}}{T_0} - \frac{\hat{F}_i}{\hat{F}} \frac{T_{0,T}}{T_0} \quad (79)$$

$$\frac{T_{0,TT}}{T_0} = -\frac{\hat{F}_{TT}}{\hat{F}} - 2 \frac{\hat{F}_T}{\hat{F}} \frac{T_{0,T}}{T_0} \quad (80)$$

To calculate the partial derivative of \hat{F} with respect to composition we differentiate eqn. (36) with respect to n_i

$$\hat{F}_i \hat{H} a_0 + \hat{F} \hat{H}_i a_0 + \hat{F} \hat{H} a_{0,T_0} T_{0,i} = D_i = 2 \sum_j n_j a_{ij}$$

and when dividing by $D = \hat{F} \hat{H} a_0$, the result is

$$\frac{\hat{F}_i}{\hat{F}} + \frac{\hat{H}_i}{\hat{H}} + \frac{a_{0,T_0}}{a_0} T_{0,i} = \frac{D_i}{D} \quad (81)$$

We now use eqn. (76) to eliminate $T_{0,i}$ and get

$$\frac{\hat{F}_i}{\hat{F}} = \frac{\frac{D_i}{D} - \frac{\hat{H}_i}{\hat{H}} - \frac{a_{0,T_0}}{a_0} \frac{T_0}{n}}{1 - \frac{a_{0,T_0}}{a_0} \frac{T_0}{n}} = \frac{\frac{D_i}{D} - \frac{B_i}{B} - \frac{a_{0,T_0}}{a_0} \frac{T_0}{n}}{1 - \frac{a_{0,T_0}}{a_0} \frac{T_0}{n}} \quad (82)$$

The first order partial derivative of \hat{F} with respect to T is derived similarly

$$\frac{\hat{F}_T}{\hat{F}} = \frac{\frac{D_T}{D} - \frac{a_{0,T_0}}{a_0} \frac{T_0}{T}}{1 - \frac{a_{0,T_0}}{a_0} \frac{T_0}{n}} \quad (83)$$

The expression for the derivatives of D , D_i and D_T , are shown in Section 4 in Chapter 3.

To derive the second order partial derivative of \hat{F} with respect to the mole numbers n_i and n_j we differentiate eqn. (36) twice

$$\begin{aligned} & \hat{F}_{ij} \hat{H} a_0 + \hat{F}_i \hat{H}_j a_0 + \hat{F}_i \hat{H} a_{0,T_0} T_{0,j} + \hat{F}_j \hat{H}_i a_0 + \hat{F} \hat{H}_{ij} a_0 \\ & + \hat{F} \hat{H}_i a_{0,T_0} T_{0,j} + \hat{F}_j \hat{H} a_{0,T_0} T_{0,i} + \hat{F} \hat{H}_j a_{0,T_0} T_{0,i} \\ & + \hat{F} \hat{H} a_{0,T_0} T_{0,i} T_{0,j} + \hat{F} \hat{H} a_{0,T_0} T_{0,ij} = D_{ij} = 2a_{ij} \end{aligned}$$

and divide by $D = \hat{F} \hat{H} a_0$ to get a neater expression

$$\begin{aligned} & \frac{\hat{F}_{ij}}{\hat{F}} + \frac{\hat{F}_i}{\hat{F}} \frac{\hat{H}_j}{\hat{H}} + \frac{\hat{F}_i}{\hat{F}} \frac{a_{0,T_0}}{a_0} T_{0,j} + \frac{\hat{F}_j}{\hat{F}} \frac{\hat{H}_i}{\hat{H}} + \frac{\hat{H}_{ij}}{\hat{H}} \\ & + \frac{\hat{H}_i}{\hat{H}} \frac{a_{0,T_0}}{a_0} T_{0,j} + \frac{\hat{F}_j}{\hat{F}} \frac{a_{0,T_0}}{a_0} T_{0,i} + \frac{\hat{H}_j}{\hat{H}} \frac{a_{0,T_0}}{a_0} T_{0,i} \\ & + \frac{a_{0,T_0}}{a_0} T_{0,i} T_{0,j} + \frac{a_{0,T_0}}{a_0} T_{0,ij} = \frac{D_{ij}}{D} \quad (84) \end{aligned}$$

The other second order partial derivatives are derived similarly. The results are

$$\begin{aligned} & \frac{\hat{F}_{Ti}}{\hat{F}} + \frac{\hat{F}_i}{\hat{F}} \frac{a_{0,T_0}}{a_0} T_{0,T} + \frac{\hat{F}_T}{\hat{F}} \frac{\hat{H}_i}{\hat{H}} + \frac{\hat{H}_i}{\hat{H}} \frac{a_{0,T_0}}{a_0} T_{0,T} \\ & + \frac{\hat{F}_T}{\hat{F}} \frac{a_{0,T_0}}{a_0} T_{0,i} + \frac{a_{0,T_0}}{a_0} T_{0,T} T_{0,i} + \frac{a_{0,T_0}}{a_0} T_{0,Ti} = \frac{D_{Ti}}{D} \quad (85) \end{aligned}$$

and

$$\frac{\hat{F}_{TT}}{\hat{F}} + \frac{2\hat{F}_T}{\hat{F}} \frac{a_{0,T_0}}{a_0} T_{0,T} + \frac{a_{0,T_0} T_0}{a_0} (T_{0,T})^2 + \frac{a_{0,T_0}}{a_0} T_{0,TT} = \frac{D_{TT}}{D} \quad (86)$$

We use eqns. (78)-(80) to eliminate the second order partial derivatives of T_0 from eqns. (84)-(86) and solve for the second order derivatives of \hat{F} . The results are

The compositional derivative

$$\begin{aligned} \frac{\hat{F}_{ij}}{\hat{F}} &= \frac{\frac{D_{ij}}{D} - \frac{\hat{F}_i}{\hat{F}} \frac{\hat{H}_j}{\hat{H}} - \frac{\hat{F}_j}{\hat{F}} \frac{\hat{H}_i}{\hat{H}} - \frac{\hat{H}_{ij}}{\hat{H}}}{1 - \frac{a_{0,T_0}}{a_0} T_0} \\ &\quad + \frac{-\frac{\hat{H}_i}{\hat{H}} \frac{a_{0,T_0}}{a_0} T_{0,j} - \frac{\hat{H}_j}{\hat{H}} \frac{a_{0,T_0}}{a_0} T_{0,i} - \frac{a_{0,T_0} T_0}{a_0} T_{0,i} T_{0,j}}{1 - \frac{a_{0,T_0}}{a_0} T_0} \end{aligned} \quad (87)$$

The temperature-composition derivative

$$\frac{\hat{F}_{Ti}}{\hat{F}} = \frac{\frac{D_{Ti}}{D} - \frac{\hat{F}_T}{\hat{F}} \frac{\hat{H}_i}{\hat{H}} - \frac{\hat{H}_i}{\hat{H}} \frac{a_{0,T}}{a_0} T_{0,T} - \frac{a_{0,T_0} T_0}{a_0} T_{0,T} T_{0,i}}{1 - \frac{a_{0,T_0}}{a_0} T_0} \quad (88)$$

The temperature derivative

$$\frac{\hat{F}_{TT}}{\hat{F}} = \frac{\frac{D_{TT}}{D} - \frac{a_{0,T_0} T_0}{a_0} (T_{0,T})^2}{1 - \frac{a_{0,T_0}}{a_0} T_0} \quad (89)$$

The expression for the derivatives of D are shown in Section 4 in Chapter 3. This completes the derivations.

8 Derivatives of non-quadratic mixing rules

The derivatives of \hat{F} are calculated from eqn. (39), that is

$$\hat{F} a_0(T_0) = b_0 \sum_i n_i \frac{a_{ii}(T)}{b_{ii}} + \frac{RTb_0}{q} \left(\frac{G^E}{RT} + \sum_i n_i \ln \frac{B}{nb_{ii}} \right) = D^G \quad (90)$$

Since the left-hand side of the equation does not contain \hat{H} , the equations for the derivatives are less complex than the derivatives in the previous section.

The compositional derivative is

$$\frac{\hat{F}_i}{\hat{F}} = \frac{\frac{D_i^G}{D^G} - \frac{a_{0,T_0}}{a_0} \frac{T_0}{n}}{1 - \frac{a_{0,T_0}}{a_0} T_0} \quad (91)$$

where

$$D_i^G = b_0 \left(\frac{a_{ii}(T)}{b_{ii}} + \frac{RT}{q} \left(\ln \gamma_i + \ln \frac{B}{nb_{ii}} + \frac{nB_i}{B} - 1 \right) \right) \quad (92)$$

The first order partial derivative of \hat{F} with respect to T is derived similarly, that is

$$\frac{\hat{F}_T}{\hat{F}} = \frac{\frac{D_T^G}{D^G} - \frac{a_{0,T_0}}{a_0} \frac{T_0}{T}}{1 - \frac{a_{0,T_0}}{a_0} T_0} \quad (93)$$

The second order compositional derivative is

$$\frac{\hat{F}_{ij}}{\hat{F}} = \frac{\frac{D_{ij}^G}{D^G} - \frac{a_{0,T_0 T_0}}{a_0} T_{0,i} T_{0,j}}{1 - \frac{a_{0,T_0}}{a_0} T_0} \quad (94)$$

The other second order partial derivatives are

$$\frac{\hat{F}_{Ti}}{\hat{F}} = \frac{\frac{D_{Ti}^G}{D^G} - \frac{a_{0,T_0 T_0}}{a_0} T_{0,T} T_{0,i}}{1 - \frac{a_{0,T_0}}{a_0} T_0} \quad (95)$$

and

$$\frac{\hat{F}_{TT}}{\hat{F}} = \frac{\frac{D_{TT}^G}{D^G} - \frac{a_{0,T_0 T_0}}{a_0} (T_{0,T})^2}{1 - \frac{a_{0,T_0}}{a_0} T_0} \quad (96)$$

The derivatives $T_{0,i}$ and $T_{0,T}$ are calculated as shown in eqns. (76) and (77).

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Chapter 5

Excess Gibbs Energy Models

Introduction

Activity coefficients are usually calculated from models of the excess properties that are functions of temperature and composition, only. However, if an expression for the Helmholtz energy is used as a frame of reference in deriving excess Gibbs energy models, it becomes easier to comprehend the physical significance of the various terms in the model. In fact, van Laar did so when in 1910 he derived his equation for the excess Gibbs energy from van der Waals' equation of state. Later, Scatchard and Hildebrand also derived their equation from van der Waals' model and the Flory-Huggins equation can be derived in a similar manner. The local composition activity coefficient models were derived from the two-fluid theory and the Boltzmann distribution law and have proven to be most powerful excess Gibbs energy models. But when excess Gibbs energy models can be derived from an equation of state, we can also incorporate the Boltzmann distribution law or an excess Gibbs energy model in an equation of state in order to improve the conventional mixing rules. Two approaches are discussed; the limit at infinite pressure by Huron and Vidal and the limit at zero pressure by Mollerup. Finally, in Section 6, it is shown how a density dependent local composition model can be derived and incorporated in a two-parameter equation of state to improve the correlation of gas solubilities in water.

1 The van der Waals model

In order to calculate the molar excess Gibbs energy from an equation of state we take advantage of the fact that

$$G^E(T, P, \mathbf{x}) = A^E(T, P, \mathbf{x}) + Pv^E \quad (1)$$

where, as shown in Chapter 1, the molar excess Helmholtz energy is calculable as the residual Helmholtz energy of the mixture minus the pure component contributions. That is

$$\begin{aligned} A^E(T, P, \mathbf{x}) &= A^r(T, P, \mathbf{x}) - \sum_i x_i A_i^r(T, P) \\ &= A^r(T, v, \mathbf{x}) - \sum_i x_i A_i^r(T, v_i) + RT \sum_i x_i \ln(v_i/v) \end{aligned} \quad (2)$$

where v_i is the pure component molar volume. The term $RT \sum_i x_i \ln(v_i/v)$ in the equation is due to the fact that we have changed the variables in the residual Helmholtz energy from (T, v) to (T, P) . The Helmholtz function is calculable from the pressure equation of state $P(T, V, \mathbf{n})$ because

$$A^r(T, V, \mathbf{n}) = - \int_{\infty}^V (P - nRT/V) dV$$

Despite its simplicity, the van der Waals equation of state gives a qualitatively correct description of fluid behaviour. It is therefore often used as a model to investigate the properties of fluid mixtures. All other two-parameter equations of state, where the repulsive term from the van der Waals equation of state is preserved, are variations of the van der Waals theme. They may be slightly more accurate but the qualitative behaviour is the same. From the van der Waals equation

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \quad (3)$$

we can calculate the residual Helmholtz energy of one mole of mixture. The result is

$$\frac{A^r(T, v, \mathbf{x})}{RT} = - \frac{S^r(T, v, \mathbf{x})}{R} + \frac{U^r(T, v, \mathbf{x})}{RT} = - \ln(1 - b/v) - \frac{a}{RTv} \quad (4)$$

Here the first term on the right-hand side is due to the repulsive forces and the second term is due to the attractive forces. In order to model the mixture properties some appropriate mixing rules for the mixture parameters a and b must be adopted. We choose the conventional mixing rules where only binary interactions are considered therefore the mixture parameter a is approximated by van der Waals' expression

$$a = \sum_i x_i \sum_j x_j a_{ji} \quad (5)$$

where for the present purpose it is sufficient to assume that

$$a_{ji} = \sqrt{a_{ii} a_{jj}} \quad (6)$$

For the mixture parameter b it is common practice to assume that

$$b = \sum_i x_i b_i \quad (7)$$

but generally there is no obvious reason for not using a double summation on the b -parameter as well. a_{ii} and b_i are pure component parameters.

The molar residual Helmholtz energy of pure species are calculable from eqn. (4) when the mixture parameters a and b are replaced by the pure component parameters a_{ii} and b_i , that is

$$\frac{A_i^r(T, v_i)}{RT} = -\frac{S_i^r(T, v_i)}{R} + \frac{U_i^r(T, v_i)}{RT} = -\ln(1 - b_i/v_i) - \frac{a_{ii}}{RTv_i} \quad (8)$$

When inserting the van der Waals model, eqns. (4) and (8), in eqn. (2) the result is

$$\frac{A^E(T, P, x)}{RT} = \sum_i x_i \ln \frac{1 - b_i/v_i}{1 - b/v} - \frac{a}{RTv} + \sum_i x_i \frac{a_{ii}}{RTv_i} + \sum_i x_i \ln \frac{v_i}{v} \quad (9)$$

where, as mentioned, the last term in this equation is due to the fact that we have changed the variables from (T, v) to (T, P) .

If the a - and b -parameters in van der Waals' model are temperature independent, we can obtain some simple expressions for the excess energy and the excess entropy, since

$$U^E = \left(\frac{\partial(A^E/T)}{\partial(1/T)} \right)_{V,n}$$

and

$$\frac{A^E}{RT} = \frac{U^E}{RT} - \frac{S^E}{R}$$

and consequently

$$\frac{U^E(T, P, x)}{RT} = -\frac{a}{RTv} + \sum_i x_i \frac{a_{ii}}{RTv_i} \quad (10)$$

and

$$\frac{S^E(T, P, x)}{R} = -\sum_i x_i \ln \frac{1 - b_i/v_i}{1 - b/v} - \sum_i x_i \ln \frac{v_i}{v} \quad (11)$$

According to the simplified van der Waals model the excess energy is the result of the attractive forces. The first excess entropy term in eqn. (11), the so-called free-volume term, is due to the repulsive forces and the second term in eqn. (11) is identical with the last term in eqn. (9) and does not depend on the equation of state model.

2 Classical excess Gibbs energy models

Since the variables of the excess models presented in Sections 2 and 3 are P , T and x only, we will omit the arguments. Molarities and molalities are best avoided as discussed in Chapter 1. Excess Gibbs energy models are first order homogeneous functions in the mole numbers and shall be independent of the assignment of the components. Any excess Gibbs energy model must satisfy the consistency tests shown in Section 4. In the classical excess Gibbs energy models it is usually assumed that the excess volume is zero, that is $v = \sum x_i v_i$, and therefore $G^E = A^E$. This assumption makes the excess energy model pressure independent because

$$\left(\frac{\partial G^E}{\partial P} \right)_{T,n} = V^E$$

The van Laar equation (van Laar, 1910)

Van Laar derived his excess model from van der Waals' equation of state. He assumed that $v = b$ and $v_i = b_i$ and consequently $S^E = 0$ therefore the excess Gibbs energy equals the excess enthalpy which becomes equal to the excess energy because the excess volume is assumed to be zero. The general form of his model is

$$\frac{G^E}{RT} = \frac{H^E}{RT} - \frac{S^E}{R} \approx \frac{U^E}{RT} = -\frac{a}{RTb} + \sum_i x_i \frac{a_{ii}}{RTb_i} \quad (12)$$

Van Laar used the mixing and combining rules, eqns. (5)-(7) and showed that for a binary mixture

$$\begin{aligned} x_1 \frac{a_{11}}{b_1} + x_2 \frac{a_{22}}{b_2} - \frac{x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22}}{x_1 b_1 + x_2 b_2} \\ = \frac{x_1 x_2 b_1 b_2}{b} \left(\frac{\sqrt{a_{11}}}{b_1} - \frac{\sqrt{a_{22}}}{b_2} \right)^2 \end{aligned} \quad (13)$$

and when inserted in eqn. (12), we get the van Laar equation

$$\frac{G^E}{RT} = \frac{x_1 x_2 b_1 b_2}{b RT} \left(\frac{\sqrt{a_{11}}}{b_1} - \frac{\sqrt{a_{22}}}{b_2} \right)^2 \quad (14)$$

This equation applies to binary mixtures only.

The Scatchard-Hildebrand equation (Hildebrand and Scott, 1964)

Scatchard and Hildebrand independently modified the van Laar theory by introducing the solubility parameter δ which is defined as

$$\delta_i^2 = \frac{\Delta U^{vap}}{v_i} = -\frac{U_i^r}{v_i} \quad (15)$$

At low pressure the energy of vaporization is numerically equal to the residual energy because the vapour phase can be considered a perfect gas. Energies or heats of vaporization and molar liquid volumes of pure species can be determined experimentally and one can therefore estimate solubility parameters independent of the solution properties. Solubility parameters have been determined for many solvents, Hansen (2000). For a van der Waals fluid the relationship between the solubility parameter and the a -parameter is

$$\delta_i^2 = \frac{a_{ii}}{v_i^2} \quad \text{or} \quad a_{ii} = v_i^2 \delta_i^2 \quad (16)$$

This value of the pure component a -parameter may be different from the pure component a -parameter in van der Waals' equation of state which is determined by the critical properties of the fluid and not the energy of vaporization. For the mixture parameter we utilise the simple relationships from eqns. (5) and (6)

$$a = \left(\sum_i x_i \sqrt{a_{ii}} \right)^2 = \left(\sum_i x_i v_i \delta_i \right)^2 = v^2 \delta^2 \quad (17)$$

whereby the mixture solubility parameter becomes the volume fraction average of the pure component solubility parameters

$$\delta = \sum_i w_i \delta_i \quad (18)$$

where w_i is the volume fraction defined by

$$w_i = \frac{x_i v_i}{v} = \frac{x_i v_i}{\sum_j x_j v_j} \quad (19)$$

Substitution of eqns. (16), (17) and (19) into eqn. (10) leads to the following model for the excess energy

$$\frac{U^E}{RT} = \frac{\sum_i x_i v_i}{RT} \left(\sum_j w_j \delta_j^2 - \delta^2 \right) \quad (20)$$

For the excess entropy term Scatchard and Hildebrand used the isotropic term, which is the last term in eqn. (11)

$$\frac{S^E}{R} = - \sum_i x_i \ln \frac{v_i}{v} = - \sum_i x_i \ln \frac{w_i}{x_i} \quad (21)$$

Subtracting the excess entropy term from eqn. (20) gives the final expression for the excess Gibbs energy since the excess volume is assumed to be zero.

$$\frac{G^E}{RT} = \frac{\sum_i x_i v_i}{RT} \left(\sum_j w_j \delta_j^2 - \delta^2 \right) + \sum_i x_i \ln \frac{w_i}{x_i} \quad (22)$$

The first term is usually named a residual term and the last term is named a combinatorial term. If tabulated values of solubility parameters and molar volumes are used, see Hansen (2000), the Scatchard-Hildebrand model becomes a purely predictive model. The model can be improved if an adjustable binary interaction parameter χ_{ij} is introduced in order to modify the unlike interaction in the a -parameter to account for the deviation from the geometric mean, that is $a_{ij} = v_i v_j \delta_i \delta_j \chi_{ij}$. The result is

$$\begin{aligned}\delta^2 &= \frac{1}{v^2} \sum_i x_i \sum_j x_j a_{ij} = \frac{1}{v^2} \sum_i x_i \sum_j x_j v_i \delta_i v_j \delta_j \chi_{ij} \\ &= \sum_i w_i \delta_i \sum_j w_j \delta_j \chi_{ij}\end{aligned}\quad (23)$$

The Flory-Huggins equation (Flory, 1941; Huggins, 1941)

Polymer molecules are often treated as segmented molecules having r_i number of segments, where each segment has a volume v_0 . The volume v_i of a segmented molecule with r_i segments is then $v_0 r_i$. The Flory-Huggins equation is an excess Gibbs energy model for segmented molecules but otherwise similar to the Scatchard-Hildebrand equation. Because the molecules are segmented, the volume fraction w_i is equal to the segment fraction ϕ_i

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad (24)$$

therefore the excess entropy in the Flory-Huggins model for segmented molecules becomes

$$\frac{S^E}{R} = - \sum_i x_i \ln \frac{\phi_i}{x_i} \quad (25)$$

and the excess Gibbs energy for segmented molecules is thus

$$\frac{G^E}{RT} = \frac{v_0 \sum_i x_i r_i}{RT} \left(\sum_j \phi_j \delta_j^2 - \delta^2 \right) + \sum_i x_i \ln \frac{\phi_i}{x_i} \quad (26)$$

where

$$\delta = \sum_i \phi_i \delta_i \quad (27)$$

As in the Scatchard-Hildebrand equation, the first term in eqn. (26) is named a residual term and the last term is named a combinatorial term. For a binary mixture this equation reduces to the familiar expression

$$\frac{G^E}{RT} = \frac{v_0}{RT} (\delta_1 - \delta_2)^2 \phi_1 \phi_2 (x_1 r_1 + x_2 r_2) + x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} \quad (28)$$

The excess entropy terms

The excess entropy term in the simplified van der Waals model, eqn. (11), is composed of two terms the so called free-volume term and the isotropic term. If we adopt the linear mixing rule $b = \sum_i x_i b_i$ and assume that the excess volume is negligible, that is $v = \sum_i x_i v_i$, the excess entropy term in van der Waals' model eqn. (11) becomes

$$\frac{S^E}{R} = - \sum_i x_i \ln \frac{v_i - b_i}{v - b} = - \sum_i x_i \ln \frac{v_i - b_i}{\sum_j x_j (v_j - b_j)} \quad (29)$$

The excess entropy term in the Scatchard-Hildebrand equation, eqn. (21), is

$$\frac{S^E}{R} = - \sum_i x_i \ln \frac{w_i}{x_i} = - \sum_i x_i \ln \frac{v_i}{\sum_j x_j v_j}$$

and the excess entropy term in the Flory-Huggins equation, eqn. (25), is

$$\frac{S^E}{R} = - \sum_i x_i \ln \frac{\phi_i}{x_i} = - \sum_i x_i \ln \frac{r_i}{\sum_j x_j r_j}$$

We observe that the composition dependence of the three excess entropy terms, eqns. (21), (25) and (29) is alike, and if the parameters v_i , b_i and r_i are treated as adjustable parameters the results will be similar.

3 The local composition excess Gibbs energy models

The two-fluid local composition excess energy model

Wilson's equation from 1964 was the first local composition excess model and it had a tremendous influence on the development of a series of new activity coefficient models. The innovation was due to the application of the Boltzmann distribution law. Shortly after in 1968 Renon and Prausnitz developed their NRTL (Non-Random Two-Liquid) model, and finally in 1975 Abrams and Prausnitz derived the UNIQUAC (UNIversal QUAsi-Chemical) model.

In this outline we do not follow the historical development nor do we report the original derivations but present a formal derivation of a model for the excess energy U^E which, when integrated with respect to $1/T$, gives the wanted expression for the excess Helmholtz energy. The excess energy is in general calculable as

$$U^E = U^r - \sum_i x_i U_i^r = U - \sum_i x_i U_i \quad (30)$$

where superscript r denotes a residual property. First, we postulate that the energy of the mixture is equal to the mole fraction average of an energy U_i^m of species i in the mixture

$$U = \sum_i x_i U_i^m \quad (31)$$

The energy U_i^m is a hypothetical energy of species i in the mixture and not a partial molar energy. This fluid mixture concept, eqn. (31), is denoted the two-fluid theory because originally it was applied to a binary liquid mixture. Scott (1956) applied it to a corresponding states treatment of non-electrolyte solutions. To proceed we need a model for the energy U_i^m . This model is provided by assuming that the energy U_i^m is calculable from the Boltzmann distribution law

$$U_i^m = \frac{\sum_j \psi_j E_{ji} U_{ji}}{\sum_j \psi_j E_{ji}} \quad (32)$$

where ψ_j is a statistical weight and U_{ji} the energy of the interaction of the molecules i and j . The exponential term E_{ji} is by definition

$$E_{ji} = \exp\left(-\frac{U_{ji}}{RT}\right) \quad (33)$$

Finally, combining eqns. (30)-(32) provide us with an expression for the excess energy of the mixture

$$\begin{aligned} U^E &= \sum_i x_i \left(\frac{\sum_j \psi_j E_{ji} U_{ji}}{\sum_j \psi_j E_{ji}} - U_i \right) \\ &= \sum_i x_i \frac{\sum_j \psi_j \exp\left(-\frac{U_{ji} - U_{ii}}{RT}\right) (U_{ji} - U_{ii})}{\sum_j \psi_j \exp\left(-\frac{U_{ji} - U_{ii}}{RT}\right)} \end{aligned} \quad (34)$$

where of course $U_{ii} = U_i$.

The excess Helmholtz energy

To derive an expression for the excess Helmholtz energy from the excess energy we integrate the excess energy with respect to $1/T$ from T_0 to T

$$\frac{A^E}{RT} - \frac{A^E}{RT_0} = \int_{\frac{1}{T_0}}^{\frac{1}{T}} \frac{U^E}{R} d\left(\frac{1}{T}\right) = F(T) - F(T_0) \quad (35)$$

Provided U_{ji} in eqn. (34) is independent of temperature and $T_0 \rightarrow \infty$ the result is

$$\frac{A^E}{RT} = - \sum_i x_i \ln \sum_j \frac{\psi_j}{\sum_k \psi_k} \exp\left(-\frac{U_{ji} - U_{ii}}{RT}\right) + \lim_{T_0 \rightarrow \infty} \left(\frac{A^E}{RT_0} \right) \quad (36)$$

Since it is assumed that U_{ji} is independent of the temperature, eqn. (34) shows that the excess energy over RT is zero in the limit of infinite temperature therefore the high temperature limit of the excess Helmholtz energy over RT is equal to minus the excess entropy at infinite temperature over R . That is

$$\lim_{T_0 \rightarrow \infty} \left(\frac{A^E}{RT_0} \right) = \lim_{T_0 \rightarrow \infty} \left(\frac{U^E}{RT_0} - \frac{S^E}{R} \right) = -\frac{S^E(T \rightarrow \infty)}{R} \quad (37)$$

The Wilson equation (Wilson, 1964)

Wilson derived the first local composition model. To derive Wilson's equation we make the assumption $G^E = A^E$, and for the statistical weight we assign $\psi_j = x_j v_j$ where v_j is a pure component liquid volume. As the high-temperature limit of the excess Helmholtz energy we use the isotropic term from eqn. (21). The Wilson formula for G^E is thus

$$\begin{aligned} \frac{G^E}{RT} &= - \sum_i x_i \ln \sum_j \frac{x_j v_j}{\sum_k x_k v_k} \exp \left(-\frac{\Delta U_{ji}}{RT} \right) + \sum_i x_i \ln \frac{w_i}{x_i} \\ &= - \sum_i x_i \ln \sum_j \frac{v_j}{v_i} x_j \exp \left(-\frac{\Delta U_{ji}}{RT} \right) \end{aligned} \quad (38)$$

The two parameters $\Delta U_{ji} = U_{ji} - U_{ii}$ and $\Delta U_{ij} = U_{ij} - U_{jj}$ are adjustable parameters, but the liquid volumes are usually the saturated liquid volumes at room temperature. Wilson's equation cannot show phase instability and therefore it cannot correlate liquid-liquid equilibria. A combinatorial term like for instance eqn. (29) could just as well be used in Wilson's equation.

The NRTL equation (Renon and Prausnitz, 1968)

Essentially, the NRTL equation is, like the van Laar equation, an equation for the excess energy, therefore, to derive an excess Gibbs energy model, we shall make the assumption that $G^E = U^E$. Renon and Prausnitz introduced a parameter $\alpha_{ij} = \alpha_{ji}$ in eqn. (34) characterizing the non-randomness of the mixture. This parameter damps the influence of the exponential term. For the statistical weight they assigned $\psi_j = x_j$. The result is

$$G^E = U^E = \sum_i x_i \frac{\sum_j x_j \exp \left(-\alpha_{ji} \frac{\Delta U_{ji}}{RT} \right) \Delta U_{ji}}{\sum_j x_j \exp \left(-\alpha_{ji} \frac{\Delta U_{ji}}{RT} \right)} \quad (39)$$

The two parameters $\Delta U_{ji} = U_{ji} - U_{ii}$ and $\Delta U_{ij} = U_{ij} - U_{jj}$ are adjustable parameters. The non-randomness parameter is in the order of one third.

The UNIQUAC equation (Abrams and Prausnitz, 1975)

The UNIQUAC equation is derived by integration of a slightly different excess energy model using surface area energies instead of the usual molar energies. The expression for the excess energy of the mixture in the UNIQUAC model is

$$U^E = \sum_i x_i q_i (\tilde{U}_i^m - \tilde{U}_{ii}) = \sum_i x_i q_i \left(\frac{\sum_j \psi_j \tilde{E}_{ji} \tilde{U}_{ji}}{\sum_j \psi_j \tilde{E}_{ji}} - \tilde{U}_{ii} \right) \quad (40)$$

where q_i is the relative surface area of molecule i , ψ_j is a statistical weight, \tilde{U}_{ji} is the surface area energy of the interaction between the molecules i and j and \tilde{E}_{ji} is by definition

$$\tilde{E}_{ji} = \exp \left(- \frac{\tilde{U}_{ji}}{RT} \right) \quad (41)$$

Furthermore, we assume that $G^E = A^E$, and for the statistical weight we assign $\psi_j = x_j q_j$. We perform the integration as shown in eqn. (35) and the combinatorial term is taken from an equation of Guggenheim (1952) for athermal polymer mixtures of molecules of different size and shape. Guggenheim derived it for a binary mixture of a monomer and an open-chain polymer with r segments. In the UNIQUAC equation the combinatorial term is

$$\lim_{T_0 \rightarrow \infty} \left(\frac{A^E}{RT_0} \right) = \sum_i x_i \ln \frac{\phi_i}{x_i} + \frac{z}{2} \sum_i x_i q_i \ln \frac{\theta_i}{\phi_i} \quad (42)$$

The coordination number z is normally assumed to be 10 and ϕ_i is the segment fraction defined in eqn. (24), and θ_i is the surface-area fraction

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (43)$$

The first term in eqn. (42) is similar to the combinatorial term from the Flory-Huggins equation, eqn. (25). When performing the integration and adding the high temperature limit, the UNIQUAC equation is

$$\begin{aligned} \frac{G^E}{RT} = & - \sum_i x_i q_i \ln \sum_j \theta_j \exp \left(- \frac{\Delta \tilde{U}_{ji}}{RT} \right) \\ & + \sum_i x_i \ln \frac{\phi_i}{x_i} + \frac{z}{2} \sum_i x_i q_i \ln \frac{\theta_i}{\phi_i} \end{aligned} \quad (44)$$

where $\Delta \tilde{U}_{ji} = \tilde{U}_{ji} - \tilde{U}_{ii}$ and $\Delta \tilde{U}_{ij} = \tilde{U}_{ij} - \tilde{U}_{jj}$ are two adjustable parameters.

A comment on the local composition models

In the Boltzmann distribution the absolute size of the statistical weight is immaterial because the distribution is normalised. In all the models, we have derived, the statistical weight ψ_j is either equal to or proportional to the mole fraction. In the Wilson equation the constant of proportionality is the molar liquid volume. The apparent lack of a combinatorial term in Wilson's equation is due to the fact that the normalised statistical weight equals the weight fraction in the isotropic term. One could choose another constant of proportionality in the statistical weight or more likely choose a different combinatorial term like eqn. (29) for example. In the NRTL equation the statistical weight is equal to the mole fraction and a non-randomness parameter is introduced. Another possibility would be to use eqn. (34), choose a statistical weight ψ_j proportional to the mole fraction, i.e. $\psi_j = x_j s_j$, and fit the constant of proportionality s_j .

The UNIQUAC equation poses a problem, because the energy parameter $\Delta\tilde{U}_{ij}$ and the second term, $\frac{z}{2} \sum_i x_i q_i \ln \frac{\theta_i}{\phi_i}$, in the combinatorial term depend on the absolute size of the surface parameter q . Besides, the second term in the combinatorial term is proportional to the coordination number. Thus, a change of the coordination number z or a new normalization of the surface parameter q require a new parameter table, and parameter tables using different normalizations are not compatible. In contrast, if we double all liquid volumes in Wilson's equation, it would not change the energy parameters.

Group contribution models

In a group contribution model the pure species are treated as a mixture of groups and it is assumed that the energy of a mixture of groups can be calculated from an equation similar to eqn. (40) when applied to a mixture of different groups instead of a mixture of different molecules.

If we divide a pure fluid i into NG different groups and the number of each group k is v_k^i where $k = 1, \dots, NG$, we assert that the energy of the pure fluid i is calculable from a local composition contribution group model

$$U_i = \sum_k^{NG} v_k^i Q_k \Upsilon_k^i = \sum_k^{NG} v_k^i Q_k - \frac{\sum_j^{NG} \Theta_j^i \tilde{E}_{jk} \tilde{U}_{jk}}{\sum_j^{NG} \Theta_j^i \tilde{E}_{jk}} \quad (45)$$

where Υ_k^i is the energy per unit surface area of group k in the pure substance i , Q_j is the group surface area of group j and Θ_j^i is the group surface-area

fraction of group j in the pure substance i which is

$$\Theta_j^i = \frac{Q_j v_j^i}{\sum_k v_k^i Q_k} \quad (46)$$

\tilde{U}_{jk} is the interaction energy per unit surface area of the j - k group interaction, \tilde{E}_{jk} is by definition

$$\tilde{E}_{jk} = \exp \left(- \frac{\tilde{U}_{jk}}{RT} \right) \quad (47)$$

In a fluid mixture the energy is calculated as the sum of the energies of the various groups in the mixture. The molar energy of a mixture whose molecules consist of a number of groups v_k^i , $k = 1, \dots, NG$, and a number of components $i = 1, \dots, NC$ is

$$U = \sum_i^{NC} x_i \sum_k^{NG} v_k^i Q_k \Upsilon_k = \sum_i^{NC} x_i \sum_k^{NG} v_k^i Q_k \frac{\sum_j^{NG} \Theta_j \tilde{E}_{jk} \tilde{U}_{jk}}{\sum_j^{NG} \Theta_j \tilde{E}_{jk}} \quad (48)$$

where Υ_k is the energy per unit surface area of group k in the mixture and Θ_j is the group surface-area fraction of group j in the mixture. That is, the surface area of all j groups divided by the total surface area.

$$\Theta_j = \frac{Q_j \sum_l^{NC} n_l v_j^l}{\sum_l^{NC} n_l \sum_m^{NG} v_m^l Q_m} \quad (49)$$

where n_l is the number of moles of species l .

The group contribution model for the molar excess energy is according to the model calculable as

$$U^E = \sum_i^{NC} x_i \sum_k^{NG} v_k^i Q_k (\Upsilon_k - \Upsilon_k^i) \quad (50)$$

The UNIFAC equation (Fredenslund et al., 1975)

A group contribution version of the UNIQUAC equation, the UNIFAC equation, can be derived by integrating the expression for U^E , eqn. (50), with

respect to $1/T$ in the same manner as we did for the UNIQUAC equation. The high-temperature limit of the excess Helmholtz energy is the combinatorial term from the UNIQUAC equation, eqn. (42). As usual it is assumed that $G^E = A^E$. The residual term is

$$\begin{aligned} \frac{A^E}{RT} - \frac{A^E}{RT_0} &= \int_{\frac{1}{T_0}}^{\frac{1}{T}} \sum_i^{NC} x_i \sum_k^{NG} v_k^i Q_k (\Upsilon_k - \Upsilon_k^i) d\left(\frac{1}{RT}\right) \\ &= - \sum_i^{NC} x_i \sum_k^{NG} v_k^i Q_k (\Lambda_k - \Lambda_k^i) \end{aligned} \quad (51)$$

where Λ_k is the reduced residual Helmholtz energy per unit surface area of group k in the mixture

$$\Lambda_k = \ln \sum_j^{NG} \Theta_j \tilde{E}_{jk} \quad (52)$$

\tilde{E}_{jk} is defined in eqn. (47) and Λ_k^i the reduced residual Helmholtz energy per unit surface area of group k in a solution containing only molecules of type i , i.e. the pure substance i

$$\Lambda_k^i = \ln \sum_j^{NG} \Theta_j^i \tilde{E}_{jk} \quad (53)$$

If we calculate the compositional derivative of eqn. (51) we get an expression for the residual contribution to the activity coefficient of species α

$$\ln \gamma_\alpha^R = - \sum_k^{NG} v_k^\alpha Q_k (\Lambda_k - \Lambda_k^i) - \sum_i^{NC} n_i \sum_k^{NG} v_k^i Q_k \frac{\partial \Lambda_k}{\partial n_\alpha} \quad (54)$$

To calculate the derivative of Λ_k we write this term as

$$\Lambda_k = \ln \sum_j^{NG} \Theta_j \tilde{E}_{jk} = \ln \sum_l^{NC} n_l \sum_j^{NG} v_j^l Q_j E_{jk} - \ln \sum_l^{NC} n_l \sum_j^{NG} v_j^l Q_j \quad (55)$$

and carry out the differentiation. The last term in eqn. (54) becomes

$$\begin{aligned}
 & \sum_i^{NC} n_i \sum_k^{NG} v_k^i Q_k \left(\frac{\sum_j^{NG} \nu_j^\alpha Q_j E_{jk}}{\sum_l^{NC} \sum_j^{NG} \nu_j^l Q_j E_{jk}} - \frac{\sum_j^{NG} \nu_j^\alpha Q_j}{\sum_l^{NC} \sum_j^{NG} \nu_j^l Q_j} \right) \\
 &= \sum_j^{NG} \nu_j^\alpha Q_j \left(\sum_k^{NG} \frac{Q_k \left(\sum_i^{NC} n_i v_k^i \right) E_{jk}}{\sum_j^{NG} Q_j \left(\sum_l^{NC} n_l \nu_j^l \right) E_{jk}} - \frac{\sum_i^{NC} n_i \sum_k^{NG} v_k^i Q_k}{\sum_l^{NC} \sum_j^{NG} \nu_j^l Q_j} \right) \\
 &= \sum_j^{NG} \nu_j^\alpha Q_j \left(\sum_k^{NG} \frac{\Theta_k E_{jk}}{\sum_j^{NG} \Theta_j E_{jk}} - 1 \right)
 \end{aligned} \tag{56}$$

The activity coefficient of species α is

$$\ln \gamma_\alpha = \ln \gamma_\alpha^R + \ln \gamma_\alpha^C \tag{57}$$

where $\ln \gamma_\alpha^C$ is the combinatorial contribution calculable from eqn. (42) and $\ln \gamma_\alpha^R$ the residual contribution from eqn. (54).

4 Consistency tests of excess Gibbs energy models

Algorithms for calculation of activity coefficients which, given temperature and composition, return only the activity coefficients can be subjected to the following tests.

From the identity

$$\sum_i n_i \ln \gamma_i = \frac{G^E(T, P, \mathbf{n})}{RT} \tag{58}$$

we can check the calculated activity coefficient because

$$\frac{\partial}{\partial n_j} \sum_i n_i \ln \gamma_i = \frac{\bar{G}_j^E(T, P, \mathbf{n})}{RT} = \ln \gamma_j \tag{59}$$

If this test is passed, it is likely that the first order compositional derivative of the excess Gibbs energy model is correct.

Further tests are:

$$\begin{aligned} \frac{\partial}{\partial n_j} \left(\frac{\partial G^E}{\partial n_i} \right)_{T,P} &= \frac{\partial}{\partial n_i} \left(\frac{\partial G^E}{\partial n_j} \right)_{T,P} \Leftrightarrow \\ \left(\frac{\partial \ln \gamma_i}{\partial n_j} \right)_{T,P} &= \left(\frac{\partial \ln \gamma_j}{\partial n_i} \right)_{T,P} \end{aligned} \quad (60)$$

Furthermore, from the Gibbs-Duhem equation, see the appendix to Chapter 1, page 50

$$\sum_i n_i \left(\frac{\partial \ln \gamma_i}{\partial n_j} \right)_{T,P} = 0 \quad (61)$$

5 The infinite and the zero pressure limits of the excess functions

When we calculate excess functions from an equation of state, two limits are of particular interest, the infinite and the zero pressure limits. We will investigate these limits using the residual Helmholtz function outlined in Section 4. The residual Helmholtz function is

$$\frac{A^r(T, v, x)}{RT} = -\ln(1 - \beta) - \Gamma h(\beta) \quad (62)$$

where

$$\Gamma = \frac{a}{RTb} \quad \text{and} \quad \beta = \frac{b}{v} \quad (63)$$

and

$$h(\beta) = \frac{1}{\delta_1 - \delta_2} \ln \frac{1 + \delta_1 \beta}{1 + \delta_2 \beta} \quad (64)$$

The corresponding pressure equation is

$$P = \frac{RT}{v - b} - \frac{a}{(v + \delta_1 b)(v + \delta_2 b)} \quad (65)$$

The excess Helmholtz function derived from eqn. (62) is, see eqn. (2),

$$\begin{aligned} \frac{A^E(T, P, x)}{RT} &= \sum_i x_i \ln \frac{1 - \beta_i}{1 - \beta} - \Gamma h(\beta) \\ &\quad + \sum_i x_i \Gamma_{ii} h(\beta_i) + \sum_i x_i \ln \frac{v_i}{v} \end{aligned} \quad (66)$$

Subscript i denotes pure species. The excess Gibbs energy can be calculated from eqn. (1). Two pressure limits of eqn. (66) will be investigated, the infinite pressure and the zero pressure limit.

The infinite pressure limit (Huron and Vidal, 1979)

Huron and Vidal derived an expression for the excess Gibbs energy at infinite pressure from the equation of state and showed that this expression can be utilised to derive new mixing rules for the α -parameter in the equation of state. We write the pressure equation, eqn. (65), as

$$\frac{P(v-b)}{RT} = 1 - \frac{\Gamma\beta(1-\beta)}{(1+\beta\delta_1)(1+\beta\delta_2)} \quad (67)$$

which shows that

$$\lim_{v \rightarrow b} \frac{P(v-b)}{RT} = 1 \quad (68)$$

If we adopt the linear mixing rule, eqn. (7), for b it follows immediately that Pv^E vanishes in the limit when $v \rightarrow b$, i.e. when $\beta \rightarrow 1$ because

$$\lim_{\beta \rightarrow 1} \frac{Pv^E}{RT} = \lim_{v \rightarrow b} \frac{P(v-b)}{RT} - \lim_{v_i \rightarrow b_i} \frac{\sum_i x_i P(v_i - b_i)}{RT} = 0 \quad (69)$$

and furthermore in view of eqn. (68)

$$\begin{aligned} & \lim_{v \rightarrow b} \left(\sum_i x_i \ln \frac{1-\beta_i}{1-\beta} + \sum_i x_i \ln \frac{v_i}{v} \right) \\ &= \lim_{v \rightarrow b} \sum_i x_i \ln \frac{v_i - b_i}{v - b} = \ln \frac{P}{RT} - \ln \frac{P}{RT} = 0 \end{aligned} \quad (70)$$

and consequently from eqns. (1) and (66)

$$\lim_{v \rightarrow b} \frac{G^E(P, T, \mathbf{x})}{RT} = \frac{G^{E,\infty}}{RT} = h(1) \sum_i x_i (\Gamma_{ii} - \Gamma) \quad (71)$$

Thus any mixing rule for Γ gives a model for the excess Gibbs energy at infinite pressure and the other way round, any model for the excess Gibbs energy at infinite pressure gives a mixing rule for the Γ -parameter when we solve the equation for the mixture parameter Γ

$$\Gamma = \sum_i x_i \Gamma_{ii} - \frac{1}{h(1)} \frac{G^{E,\infty}}{RT} \quad (72)$$

When we insert an activity coefficient model $G^E(\gamma, \mathbf{x})$ in eqn. (72) and insert this Γ in eqn. (62), the new model for the residual Helmholtz function is

$$\frac{A^r(T, V, \mathbf{x})}{RT} = -\ln(1-\beta) - \left(\sum_i x_i \Gamma_{ii} - \frac{1}{h(1)} \frac{G^E(\gamma, \mathbf{x})}{RT} \right) h(\beta) \quad (73)$$

Because the limit derived in eqn. (71) does not apply to normal pressure, we cannot use available activity coefficient parameters in eqn. (73) therefore we have to refit the activity coefficient parameters. At normal pressure $\beta \approx 0.7 - 0.8$ for liquids and consequently the limit calculated in eqn. (68) does not apply.

Any reasonable model can be used in eqn. (73). Huron and Vidal showed that if we choose an NRTL model it is convenient to use the following modification

$$\frac{a}{b} = \sum_i x_i \frac{a_{ii}}{b_i} - \frac{1}{h(1)} \sum_i x_i \frac{\sum_j x_j b_j \exp\left(-\alpha_{ji} \frac{\Delta U_{ji}}{RT}\right) \Delta U_{ji}}{\sum_j x_j b_j \exp\left(-\alpha_{ji} \frac{\Delta U_{ji}}{RT}\right)} \quad (74)$$

because it transforms to the $a = \sum_i x_i \sum_j x_j a_{ij}$, traditionally used for hydrocarbon mixtures, when

$$\alpha_{ij} = \alpha_{ji} = 0, \quad U_{ii} = -\frac{a_{ii}}{b_i} h(1) \quad \text{and} \quad U_{ij} = -\frac{2a_{ij}}{b_i + b_j} h(1)$$

In eqn. (74) we can treat ΔU_{ji} and ΔU_{ij} as two adjustable parameters per binary interaction.

The zero pressure limit (Mollerup, 1986)

The zero pressure limit is in many cases appropriate because activity coefficient model parameters are usually determined by fitting the model to low pressure vapour-liquid equilibrium data. Furthermore, liquid phase properties are readily calculated at zero pressure and hardly distinguishable from the fluid properties at low pressure because liquids are not very compressible and finally, at zero pressure $G^E = A^E$ because $P = 0$ and v^E is finite. It is thus at zero pressure possible to incorporate an excess Gibbs energy activity coefficient model in an equation of state and use existing model parameters and *a priori* predict vapour-liquid equilibria at elevated pressures where no experimental data are available.

At zero pressure we take advantage of the rather simple relationship between Γ and β obtained from eqn. (65)

$$1 - \beta = \frac{(1 + \delta_1 \beta)(1 + \delta_2 \beta)}{\Gamma \beta} \quad (75)$$

This equation is a quadratic equation in β and for a Redlich-Kwong fluid where $\delta_1 = 1$ and $\delta_2 = 0$ it has a real high density root when Γ is larger than 5.8. The reduced liquid density $\beta = b/v$ at zero pressure and the

reduced density at the saturation pressure are similar at temperatures close to and below the normal boiling point. In Figure 1 we compare the reduced densities of a Redlich-Kwong fluid. The dashed line is the reduced density at the saturation pressure and the black dots are the reduced density at zero pressure. The figure shows that the difference between the reduced liquid density at zero pressure and the reduced saturation density is negligible at temperatures below the normal boiling point which often ranges from 0.58 to 0.66 in reduced temperature. Triple points are of the order of 0.3 – 0.4 in reduced temperature. The residual Helmholtz energy at zero pressure is calculated from eqn. (66) therefore the expression for the excess Gibbs energy at zero pressure becomes

$$\begin{aligned} \frac{A^E(T, P = 0, \mathbf{x})}{RT} &= \frac{G^E(T, P = 0, \mathbf{x})}{RT} = \frac{G^E(\gamma, \mathbf{x})}{RT} \\ &= \sum_i x_i \ln \frac{\beta(1 - \beta_i)}{\beta_i(1 - \beta)} - \Gamma h(\beta) \\ &\quad + \sum_i x_i \Gamma_{ii} h(\beta_i) + \sum_i x_i \ln \frac{b_i}{b} \end{aligned} \quad (76)$$

where $G^E(\gamma, \mathbf{x})$ denotes the activity coefficient model. Thus any mixing rule for Γ gives a model for the excess Gibbs energy at zero pressure and the other way round, when we solve the equation for the mixture parameter Γ any model for the excess Gibbs energy at zero pressure gives a mixing rule for the Γ -parameter

$$\begin{aligned} \Gamma &= \sum_i x_i \Gamma_{ii} \frac{h(\beta_i)}{h(\beta)} \\ &\quad + \frac{1}{h(\beta)} \left(\sum_i x_i \ln \frac{\beta(1 - \beta_i)}{\beta_i(1 - \beta)} + \sum_i x_i \ln \frac{b_i}{b} - \frac{G^E(\gamma, \mathbf{x})}{RT} \right) \end{aligned} \quad (77)$$

If we combine eqns. (62), (75) and (77) into a new model, we can use accepted low pressure activity coefficient model parameters in $G^E(\gamma, \mathbf{x})$ to correlate the low pressure vapour-liquid equilibrium data with an accuracy similar to the original activity coefficient model because we can hardly distinguish fluid properties at zero pressure from those at low to moderate pressures. However, this approach is limited to temperatures where a solution to eqn. (75) can be obtained, and in order to extend the model to elevated pressures and thus to temperatures where a solution to eqn. (75) no longer exists one can either develop an extrapolation procedure as prescribed by

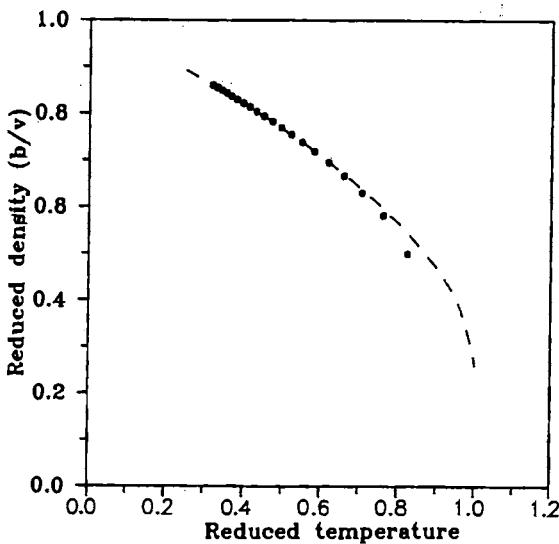


Figure 1: A comparison of liquid densities at saturation (dashed line) and liquid densities at zero pressure (black dots) for a Redlich-Kwong fluid.

Michelsen (1990), or develop an approximate method by assuming that $h(\beta)$ can be considered a constant (Mollerup, 1986).

For pure species $h(\beta_i)$ is only a weak function of the temperature and for mixtures $h(\beta)$ is also a function of the composition, but for practical applications h may be regarded as a constant. If $h(\beta_i) = h(\beta)$, it implies that the reduced densities of the pure species β_i and of the mixture β is a constant β_0 therefore eqn. (77) reduces to

$$\Gamma = \sum_i x_i \Gamma_{ii} - \frac{1}{h(\beta_0)} \left(\sum_i x_i \ln \frac{b}{b_i} + \frac{G^E(\gamma, \mathbf{x})}{RT} \right) \quad (78)$$

Any mixing rule can be applied for the b -parameter. At the normal boiling point $h(\beta_0)$ is of the order of 0.55 for the Redlich-Kwong-Soave equation of state therefore

$$\Gamma = \sum_i x_i \Gamma_{ii} - \frac{1}{0.55} \left(\sum_i x_i \ln \frac{b}{b_i} + \frac{G^E(\gamma, \mathbf{x})}{RT} \right) \quad (79)$$

It may be expedient to validate this approximation. To do so, we calculate the reduced reference fugacity f at zero pressure. The fugacity is calculable

from the residual Gibbs energy

$$\begin{aligned} RT \ln \varphi &= RT \ln \frac{f}{P} = G^r(T, P) \\ &= A^r(T, v) + (Pv - RT) - RT \ln(Pv/RT) \end{aligned}$$

and thus at zero pressure

$$\ln \frac{f}{RT} = \frac{A^r(T, v)}{RT} - 1 - \ln v$$

and when inserting eqn. (62) the result is

$$\ln \frac{fb}{RT} = \ln \frac{f}{P_c} \frac{\Omega_b}{T_r} = -\ln(1-\beta) - \Gamma h(\beta) + \ln \beta - 1 \quad (80)$$

We investigate two cases, first a case where β is calculated from eqn. (75), and second a case where $\beta = 0.73$ corresponding to $\ln(1+\beta) = 0.55$. When β is a constant we can extrapolate to any temperature. The two cases are compared with the fugacity at the saturation line and above the critical temperature the fugacity is calculated along the critical isochore because the critical isochore is the natural extension of the vapour pressure curve because the two curves have equal slopes at the critical point. The comparison is shown in Figure 2, where the dashed line is the reduced fugacity of the saturated phases fb/RT and its extension along the critical isochore, the black dots are the case where β is calculated from eqn. (75) and the open squares are the reduced zero pressure fugacity calculated with $\beta = 0.73$. The comparison shows that the exact zero pressure fugacity hardly is distinguishable from the fugacity at saturation, and that the suggested approximation with a value of $h(\beta) = 0.55$ ensures a good agreement between the zero pressure fugacity and the fugacity at saturation over a wide range of temperatures.

The zero pressure mixing rule does not prescribe a particular mixing rule for the b -parameter. If accepted parameters are used in the activity coefficient model, it is possible to make an *a priori prediction* of vapour-liquid equilibria at elevated pressures.

6 An equation of state from the local composition model

We have shown how activity coefficient models can be derived from the van der Waals fluid model. Similar derivations can be performed from other fluid models. The van Laar activity coefficient model was derived from the van der Waals equation of state, but we can also do it the other way round and derive an equation of state from an activity coefficient model. Thus from the van

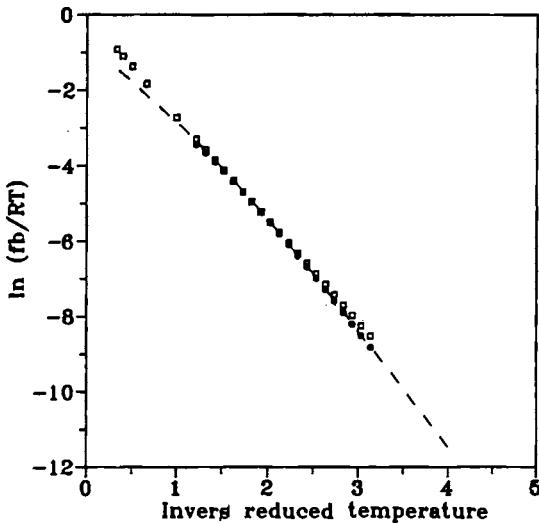


Figure 2: A comparison of f_b/RT at zero pressure calculated with $\beta = 0.73$ (open squares), with β calculated from eqn. (75) (black dots) and f_b/RT at the saturated pressure and the extension along the critical isochore (dashed line).

Laar model we will inevitable get the van der Waals equation of state, but what will an equation of state corresponding to a local composition model look like? From eqns. (31)-(33) we notice that the main feature of a local composition model is that the residual energy of a mixture is

$$U^r = \sum_i x_i \frac{\sum_j \psi_j \exp\left(-\frac{U_{ji}^r}{RT}\right) U_{ji}^r}{\sum_j \psi_j \exp\left(-\frac{U_{ji}^r}{RT}\right)} \quad (81)$$

where ψ_j a statistical weight.

Let us compare the expression in eqn. (81) to the expression we calculate from a cubic equation of state when we use van der Waals' mixing rule, eqn. (5). In the local composition model U_{ji} was considered to be independent of temperature. Similarly, in this derivation we will assume that the a -parameter in eqn. (63) is temperature independent. When the model for the Helmholtz energy is eqn. (62) and the a - and b -parameters are indepen-

dent of temperature, the energy of the mixture is

$$U = -\Gamma h(\beta) \quad (82)$$

When we adopt the van der Waals mixing rule for a is, the result is

$$\begin{aligned} U^{vdW} &= -\sum_i x_i \sum_j x_j a_{ij}^{vdW} \frac{h(\beta)}{b} \\ &= \sum_i x_i \sum_j x_j U_{ij}^{vdW} \end{aligned} \quad (83)$$

where the interaction energy U_{ij}^{vdW} is

$$U_{ij}^{vdW} = -\frac{a_{ij}^{vdW}}{b} h(\beta) \quad (84)$$

To compare the van der Waals model, eqn. (83), with the local composition model, we put $\psi_j = x_j$ in eqn. (81). When we compare the two models we shall observe that the two expression become almost similar only when the energies are quite small, i.e. at high temperature or low density. However, we know from experience that the van der Waals model is appropriate for mixtures of non-polar fluids like hydrocarbons where U not necessarily is small. Therefore, when we incorporate the local composition model into an equation of state, we shall retain the van der Waals model for mixtures of non-polar fluids like hydrocarbons, and thus the local composition model shall be an excess over the van der Waals model. That is

$$U^{LC} = U^r - U^{vdW} = \sum_i x_i \frac{\sum_j x_j \exp\left(-\frac{U_{ji}^r - U_{ji}^{vdW}}{RT}\right) (U_{ji}^r - U_{ji}^{vdW})}{\sum_j x_j \exp\left(-\frac{U_{ji}^r - U_{ji}^{vdW}}{RT}\right)} \quad (85)$$

where of course $U_{ii}^r = U_{ii}^{vdW}$ but $U_{ji}^r \neq U_{ji}^{vdW}$.

To derive a model for the residual Helmholtz energy we shall integrate eqn. (85) with respect to $1/T$ from T_0 to T when $T_0 \rightarrow \infty$. The density dependent local composition (DDLC) contribution to the residual Helmholtz energy is

$$\frac{A^{LC}}{RT} = -\sum_i x_i \ln \sum_j x_j E_{ji} \quad (86)$$

and when adding this term to the classical model the extended model is

$$\frac{A^r(T, v, \mathbf{x})}{RT} = \frac{A^{cubic}}{RT} + \frac{A^{LC}}{RT} = -\ln(1 - \beta) - \frac{a}{RTb} h(\beta) - \sum_i x_i \ln \sum_j x_j E_{ji} \quad (87)$$

In eqn. (87) a is calculated using the conventional mixing rule. The last term is a correction to the conventional equation of state derived from the local composition model. The function E_{ji} is by definition

$$E_{ji} = \exp \left(\frac{a_{ij} - a_{ij}^{vdW}}{RTb} h(\beta) \right) \quad (88)$$

E_{ij} is unity for pure fluids because $a_{ii} = a_{ii}^{vdW}$ and for hydrocarbons where $a_{ij} = a_{ij}^{vdW}$ otherwise a_{ij} is an adjustable parameter. The mixture parameters a and b are calculated using the conventional mixing rules

$$a = \sum_i x_i \sum_j x_j a_{ji}^{vdW} \quad (89)$$

$$b = \sum_i x_i \sum_j x_j b_{ji} \quad (90)$$

In mixtures the term $\sum_i x_i \ln \sum_j x_j E_{ji}$ accounts for polar-polar and polar-nonpolar molecular interactions. This kind of modelling approach ensures that the conventional mixing rules can be used when appropriate, that is when $a_{ij} = a_{ij}^{vdW}$.

Figure 3 shows a correlation of Henry's constant for methane and nitrogen in water. The model combine the Soave-Redlich-Kwong equation of state with the local composition term. The model correctly predicts a maximum in Henry's constant corresponding to a minimum in the solubility which cannot be established using the van der Waals mixing rules. Correlation of phase diagrams of water - light hydrocarbons are shown by Mollerup and Clark (1989).

Correlation of gas solubilities in water is important for prediction of the hydrate-water-gas equilibrium pressures. Figures 4-5 show the predicted equilibrium pressures of hydrates containing nitrogen, hydrogen sulphide and carbon dioxide. The Kihara potential parameters in the van der Waals and Platteeuw's model were fitted to the ice-hydrate equilibrium line. We are therefore able to predict the hydrate-water-gas equilibrium line and investigate the influence of gas solubility on the predicted equilibrium pressures. Figure 6 shows the dissociation pressures of carbon dioxide over a wide range of pressures (Lundgaard and Mollerup, 1991, 1992). The derivatives of eqn. (87) are derived in Section 8.

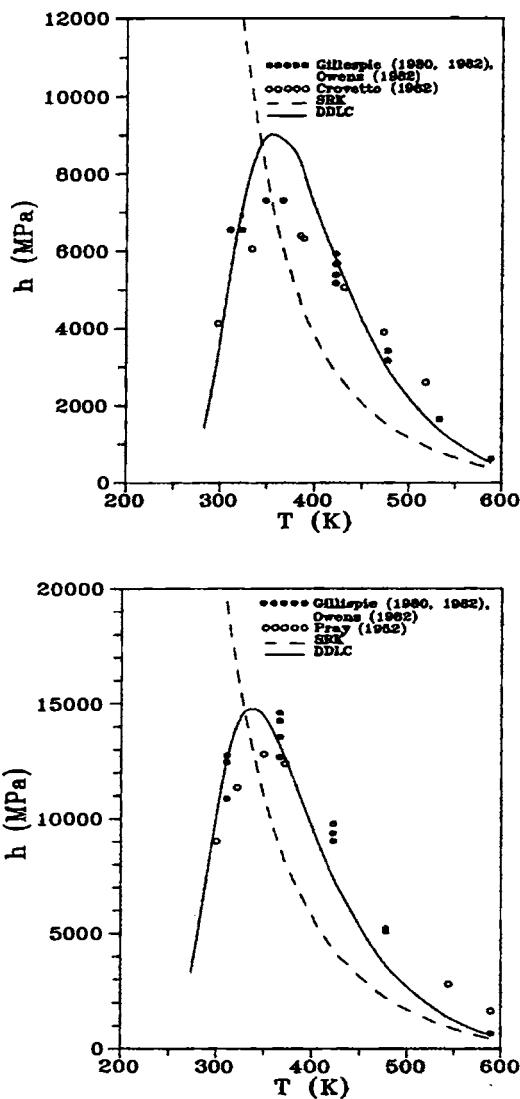


Figure 3: Henry's constants for methane (top) and nitrogen (bottom) in water calculated with the Soave-Redlich-Kwong equation of state (SRK), dashed line, and the Local Composition-SRK model (DDLC), full line. From Mollerup (1985).

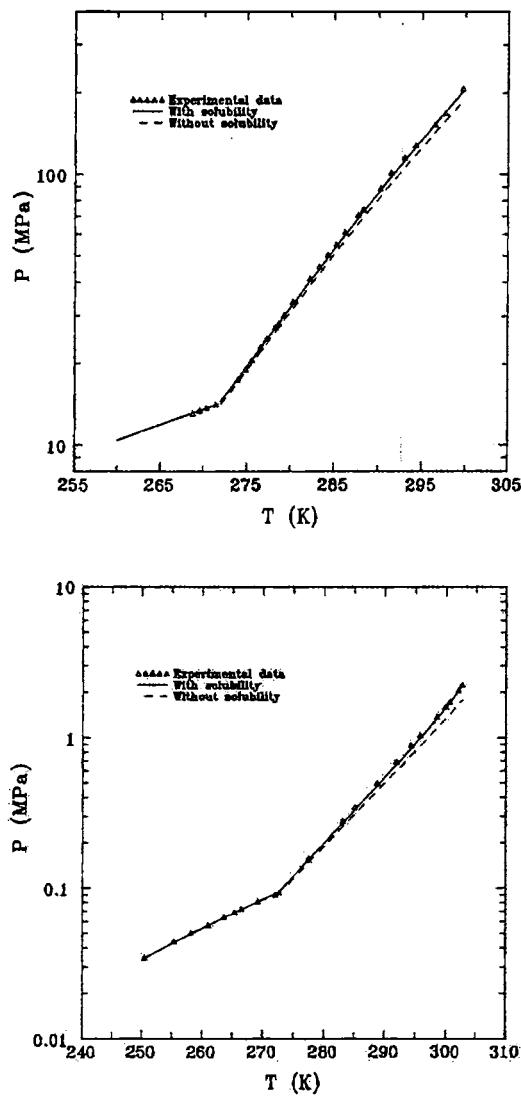


Figure 4: The influence of gas solubility on the calculated dissociation pressures of nitrogen-water-hydrate (top) and hydrogen sulfide-water-hydrate (bottom). Fugacities and gas solubilities are calculated with the SRK equation of state and the DDLC model. The parameters in the Kihara core model have been fitted to the points at the gas-ice-hydrate line and the gas-water-hydrate line is a prediction.

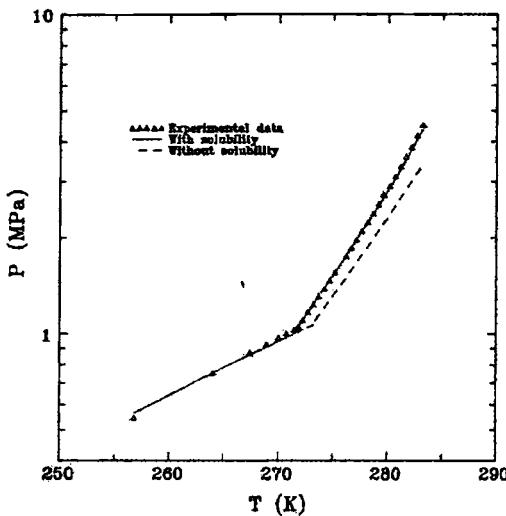


Figure 5: The influence of gas solubility on the calculated dissociation pressure of carbon dioxide-water-hydrate. Fugacities and gas solubilities are calculated with the SRK equation of state and the DDLC model. The parameters in the Kihara core model have been fitted to the points at the gas-ice-hydrate line and the gas-water-hydrate line is a prediction.

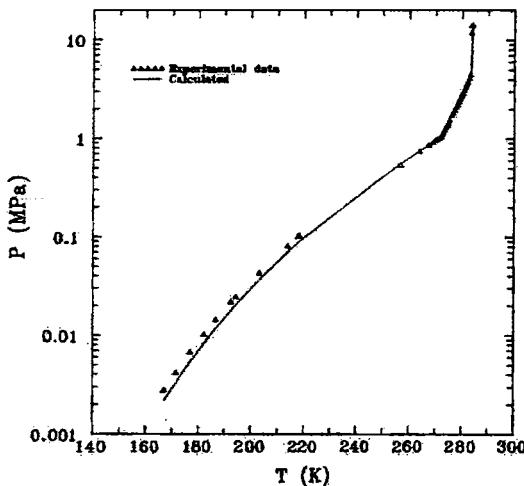


Figure 6: Experimental and calculated dissociation pressure of carbon dioxide-hydrate.

7 The derivatives of excess Gibbs energy models

To calculate the derivatives of excess Gibbs energy models we replace the mole fractions by mole numbers. The total excess Gibbs energy must of course be a homogeneous function of degree one in the mole numbers. The activity coefficient equals the partial molar excess Gibbs energy

$$\ln \gamma_i(T, P, \mathbf{n}) = \frac{\bar{G}_i^E(T, P, \mathbf{n})}{RT} = \left(\frac{\partial}{\partial n_i} \frac{G^E(T, P, \mathbf{n})}{RT} \right)_{T, P, n_j} \quad (91)$$

and compositional or temperature derivatives are found by repeating the differentiation. The first partial derivative with respect to composition is a homogeneous function of degree zero in the mole numbers, and the second partial derivative with respect to composition is a homogeneous function of degree minus one in the mole numbers.

The local composition excess Helmholtz energy model

As the first example we use the expression from eqns. (36) and (37)

$$\begin{aligned} \frac{G^E(T, \mathbf{x})}{RT} &= \frac{A^E(T, \mathbf{x})}{RT} \\ &= - \sum_i x_i \ln \sum_j \frac{\psi_j}{\sum_k \psi_k} \exp \left(-\frac{\Delta U_{ji}}{RT} \right) - \frac{S^E(T \rightarrow \infty)}{R} \end{aligned} \quad (92)$$

where we, in accord with previous assumptions, assume that $\psi_j = x_j s_j$ where s_j is a constant of proportionality in the statistical weight. In Wilson's formula the constant of proportionality is the molar liquid volume. We *replace the mole fractions by mole numbers* and define some auxiliary variables to make the notation easier

$$\lambda_{jk} = s_j \exp \left(-\frac{\Delta U_{jk}}{RT} \right) \quad (93)$$

$$E_k = \sum_j n_j \lambda_{jk} \quad (94)$$

and

$$S_\psi = \sum_j n_j s_j \quad (95)$$

The first term in eqn. (92), the residual term, is in terms of the auxiliary variables

$$F^R(T, \mathbf{n}) = - \sum_k n_k \ln E_k + n \ln S_\psi \quad (96)$$

where

$$n = \sum_k n_k \quad (97)$$

Eqn. (96) is a homogeneous function of degree one in the mole numbers. Differentiation with respect to n_i yields

$$\left(\frac{\partial F^R}{\partial n_i} \right)_{T, n_j} = F_i^R = -\ln E_i - \sum_k n_k \frac{\lambda_{ik}}{E_k} + \ln S_\psi + n \frac{s_i}{S_\psi} \quad (98)$$

This expression must be a homogeneous function of degree zero in the mole numbers. Repeating the differentiation gives

$$\begin{aligned} \left(\frac{\partial^2 F^R}{\partial n_i \partial n_j} \right)_T &= F_{ij}^R \\ &= -\frac{\lambda_{ji}}{E_i} - \frac{\lambda_{ij}}{E_j} + \sum_k n_k \frac{\lambda_{ik} \lambda_{jk}}{E_k^2} + \frac{s_j}{S_\psi} + \frac{s_i}{S_\psi} - n \frac{s_i s_j}{S_\psi^2} \end{aligned} \quad (99)$$

This expression must be symmetric in i and j and a homogeneous function of degree minus one in the mole numbers. Furthermore,

$$\left(\frac{\partial F^R}{\partial T} \right)_n = F_T^R = - \sum_k n_k \frac{1}{E_k} \left(\frac{\partial E_k}{\partial T} \right)_n \quad (100)$$

and from eqn. (98)

$$\begin{aligned} \left(\frac{\partial^2 F^R}{\partial n_i \partial T} \right)_{n_j} &= F_{iT}^R \\ &= -\frac{1}{E_i} \left(\frac{\partial E_i}{\partial T} \right)_n - \sum_k n_k \left(\frac{1}{E_k} \frac{d\lambda_{ik}}{dT} - \frac{\lambda_{ik}}{E_k^2} \left(\frac{\partial E_k}{\partial T} \right)_n \right) \end{aligned} \quad (101)$$

This expression must be a homogeneous function of degree zero in the mole numbers. Provided ΔU_{ij} is temperature independent, the temperature derivatives of the auxiliary variables are

$$\frac{d\lambda_{jk}}{dT} = \frac{\lambda_{jk} \Delta U_{jk}}{RT^2} \quad (102)$$

$$\left(\frac{\partial E_k}{\partial T} \right)_n = \sum_j n_j \frac{d\lambda_{jk}}{dT} \quad (103)$$

As combinatorial term, the last term in eqn. (92), we adopt the Flory-Huggins expression

$$\begin{aligned} F^c(\mathbf{n}) &= -n \frac{S^E(T \rightarrow \infty)}{R} = n \sum_k x_k \ln \frac{\phi_k}{x_k} \\ &= \sum_k n_k \ln \frac{n_j r_k}{\sum_j n_j r_j} \\ &= \sum_k n_k \ln r_k + n \ln n - n \ln S_r \end{aligned} \quad (104)$$

where

$$S_r = \sum_j n_j r_j \quad (105)$$

Eqn. (104) must be a homogeneous function of degree one in the mole numbers. The derivatives are

$$\frac{\partial F^c}{\partial n_i} = F_i^c = \ln r_i + \ln n + 1 - \ln S_r - n \frac{r_i}{S_r} \quad (106)$$

and repeating the differentiation

$$\frac{\partial^2 F^c}{\partial n_i \partial n_j} = F_{ij}^c = \frac{1}{n} - \frac{r_j}{S_r} - \frac{r_i}{S_r} + n \frac{r_i r_j}{S_r^2} \quad (107)$$

This expression must be symmetric in i and j and a homogeneous function of degree minus one in the mole numbers, and eqn. (106) must be a homogeneous function of degree zero. Finally,

$$\frac{\partial F^c}{\partial T} = \frac{\partial^2 F^c}{\partial n_i \partial T} = 0 \quad (108)$$

The excess Gibbs energy and its derivatives are thus calculable as

$$\frac{G^E(T, \mathbf{n})}{RT} = F^R(T, \mathbf{n}) + F^c(\mathbf{n}) \quad (109)$$

$$\ln \gamma_i = F_i^R + F_i^c \quad (110)$$

$$\left(\frac{\partial \ln \gamma_i}{\partial n_j} \right)_T = F_{ij}^R + F_{ij}^c \quad (111)$$

$$\left(\frac{\partial \ln \gamma_i}{\partial T} \right)_n = F_{iT}^R + F_{iT}^c \quad (112)$$

This concludes the derivation.

The local composition excess energy model

In this example we utilise eqn. (34). A combinatorial term $F^c(n)$ can be added if necessary, see eqn. (104).

$$\begin{aligned} \frac{G^E(T, x)}{RT} &= \frac{U^E(T, x)}{RT} \\ &= \sum_i x_i \frac{\sum_j \psi_j \exp\left(-\alpha_{ji} \frac{\Delta U_{ji}}{RT}\right) \frac{\Delta U_{ji}}{RT}}{\sum_j \psi_j \exp\left(-\alpha_{ji} \frac{\Delta U_{ji}}{RT}\right)} \end{aligned} \quad (113)$$

We assume that $\psi_j = x_j s_j$, where s_j is a constant of proportionality in the statistical weight. We replace the mole fractions by mole numbers and define a number of auxiliary variables to make the notation easier

$$\lambda_{jk} = s_j \exp\left(-\alpha_{jk} \frac{\Delta U_{jk}}{RT}\right) \quad (114)$$

$$E_k = \sum_j n_j \lambda_{jk} \quad (115)$$

$$\Lambda_{jk} = s_j \exp\left(-\alpha_{jk} \frac{\Delta U_{jk}}{RT}\right) \frac{\Delta U_{jk}}{RT} = \lambda_{jk} \frac{\Delta U_{jk}}{RT} \quad (116)$$

$$D_k = \sum_j n_j \Lambda_{jk} \quad (117)$$

Finally, we insert the auxiliary variables and write eqn. (113) as

$$F^R(T, n) = \sum_k n_k \frac{D_k}{E_k} \quad (118)$$

This expression must be a homogeneous function of degree one in the mole numbers. Differentiation with respect to n_i yields

$$\left(\frac{\partial F^R}{\partial n_i} \right)_{T, n_j} = F_i^R = \frac{D_i}{E_i} + \sum_k n_k \frac{\Lambda_{ik}}{E_k} - \sum_k n_k \frac{D_k}{E_k^2} \lambda_{ik} \quad (119)$$

This expression must be a homogeneous function of degree zero in the mole numbers. Repeating the differentiation

$$\begin{aligned} \left(\frac{\partial^2 F^R}{\partial n_i \partial n_j} \right)_T = F_{ij}^R &= \frac{\Lambda_{ji}}{E_i} - \frac{D_i}{E_i^2} \lambda_{ji} + \frac{\Lambda_{ij}}{E_j} - \frac{D_j}{E_j^2} \lambda_{ij} \\ &- \sum_k n_k \frac{\Lambda_{ik} \lambda_{jk}}{E_k^2} - \sum_k n_k \frac{\Lambda_{jk} \lambda_{ik}}{E_k^2} + 2 \sum_k n_k \frac{D_k \lambda_{ik} \lambda_{jk}}{E_k^3} \end{aligned} \quad (120)$$

This expression must be symmetric in i and j and a homogeneous function of degree minus one in the mole numbers. Furthermore,

$$\left(\frac{\partial F^R}{\partial T} \right)_n = F_T^R = \sum_k n_k \left(\frac{1}{E_k} \left(\frac{\partial D_k}{\partial T} \right)_n - \frac{D_k}{E_k^2} \left(\frac{\partial E_k}{\partial T} \right)_n \right) \quad (121)$$

and

$$\begin{aligned} \left(\frac{\partial^2 F^R}{\partial n_i \partial T} \right)_{n_j} &= F_{iT}^R = \frac{1}{E_i} \left(\frac{\partial D_i}{\partial T} \right)_n - \frac{D_i}{E_i^2} \left(\frac{\partial E_i}{\partial T} \right)_n \\ &\quad + \sum_k n_k \left(\frac{1}{E_k} \frac{d\Lambda_{ik}}{dT} - \frac{\lambda_{ik}}{E_k^2} \left(\frac{\partial D_k}{\partial T} \right)_n \right) \\ &\quad - \sum_k n_k \frac{1}{E_k^2} \left(\Lambda_{ik} \left(\frac{\partial E_k}{\partial T} \right)_n + D_k \frac{d\lambda_{ik}}{dT} \right) \\ &\quad + 2 \sum_k n_k \frac{D_k \lambda_{ik}}{E_k^3} \left(\frac{\partial E_k}{\partial T} \right)_n \end{aligned} \quad (122)$$

The temperature derivatives of the auxiliary variables are

$$\frac{d\lambda_{jk}}{dT} = \alpha_{jk} \frac{\lambda_{jk} \Delta U_{jk}}{RT^2} = \alpha_{jk} \frac{\Lambda_{jk}}{T} \quad (123)$$

$$\left(\frac{\partial E_k}{\partial T} \right)_n = \sum_j n_j \frac{d\lambda_{jk}}{dT} = \frac{1}{T} \sum_j n_j \alpha_{jk} \Lambda_{jk} \quad (124)$$

$$\frac{d\Lambda_{jk}}{dT} = \left(\frac{d\lambda_{jk}}{dT} - \frac{\lambda_{jk}}{T} \right) \frac{\Delta U_{jk}}{RT} \quad (125)$$

$$\left(\frac{\partial D_k}{\partial T} \right)_n = \sum_j n_j \frac{d\Lambda_{jk}}{dT} = \frac{1}{RT^2} \sum_j n_j \alpha_{jk} \Lambda_{jk} \Delta U_{jk} - \frac{D_k}{T} \quad (126)$$

The activity coefficient and its derivatives are calculable from eqns. (109)-(112).

8 Derivatives of more complex models

Derivatives of more complex models are treated as outlined in Chapter 2, and as implemented in Sections 4, 7 and 7. As an example we take the model shown in eqn. (87). The derivatives of this model are more complex than those of an ordinary equation of state because of the density dependent local composition term. We will not work through all the derivatives in great detail but show examples of how to deal with a complex model. Because

of the definition of the repulsive function h used in this chapter differs from the one used in Chapter 3, we shall write eqn. (87) using a notation similar to the one in Chapter 3. The expression for the reduced residual Helmholtz function of a generic equation of state including the Redlich-Kwong and the Peng-Robinson equations of state is shown in Chapter 3, eqn. (60). When we include the DDLC-term, the model is

$$F = -n g(V, B) - \frac{D(T)}{T} f(V, B) - \sum_i n_i \ln \sum_j \frac{n_j}{n} \lambda_{ji} \quad (127)$$

The first two terms in eqn. (127) are identical with eqn. (60) of Chapter 3 and eqns. (128)-(132) are identical with eqns. (61)-(65) of Chapter 3.

$$g = \ln(1 - B/V) = \ln(V - B) - \ln V \quad (128)$$

$$f = \frac{1}{RB(\delta_1 - \delta_1)} \ln \frac{V + \delta_1 B}{V + \delta_2 B} \quad (129)$$

$$n = \sum_i n_i \quad (130)$$

$$nB = \sum_i n_i \sum_j n_j b_{ij} \quad (131)$$

$$D(T) = \sum_i n_i \sum_j n_j a_{ij}(T) \quad (132)$$

Eqn. (132) is identical with eqn. (89) but the superscript v^{dW} has been omitted. The local composition parameter λ_{ij} is

$$\lambda_{ij} = \lambda_{ji} = \exp(-\alpha_{ij}\beta) \quad (133)$$

where

$$\alpha_{ij}(T) = \alpha_{ji}(T) = k'_{ij} \frac{\sqrt{a_{ii}(T) a_{jj}(T)}}{T} \quad (134)$$

When writing the computer code, one should take advantage of the fact that $k'_{ii} = 0$ and thus $\lambda_{kk} = 1$. The α in eqn. (134) is not identical with α in the SRK and the PR equations of state and β in eqn. (133) is not b/v but

$$\beta = n f(V, B(n)) \quad (135)$$

To calculate the thermodynamic properties we must calculate the partial derivatives as outlined in Section 2 of Chapter 3. The derivatives of the first two terms of eqn. (127) and of eqns. (128)-(132) are given in Section 4 of

Chapter 3. Thus we only have to consider the last term in eqn. (127) which we write in the following manner

$$F^D(\mathbf{n}, \alpha, \beta) = n \ln n - \sum_k n_k \ln E_k \quad (136)$$

where

$$E_k = \sum_l n_l \lambda_{lk}(\alpha_{lk}, \beta) \quad (137)$$

The derivatives of f and B are calculated in Chapter 3. f_V and f_B are derivatives of f with respect to either the volume V or the parameter B . Similarly, the subscripts i or j mean that it is a derivative with respect to n_i or n_j , and a double subscript means that it is a second order derivative. A similar notation will be used for F^D and β .

Differentiation with respect to the volume gives

$$\left(\frac{\partial F^D}{\partial V} \right)_{T, \mathbf{n}} = \left(\frac{\partial F^D}{\partial \beta} \right)_{\mathbf{n}, \alpha} \left(\frac{\partial \beta}{\partial V} \right)_{\mathbf{n}} = F_\beta^D \beta_V \quad (138)$$

from eqn. (136)

$$F_\beta^D = - \sum_k n_k \frac{1}{E_k} \left(\frac{\partial E_k}{\partial \beta} \right)_{\mathbf{n}, \alpha} \quad (139)$$

and from eqn. (137)

$$\left(\frac{\partial E_k}{\partial \beta} \right)_{\mathbf{n}, \alpha} = \sum_l n_l \left(\frac{\partial \lambda_{lk}}{\partial \beta} \right)_\alpha \quad (140)$$

and from eqn. (133)

$$\left(\frac{\partial \lambda_{lk}}{\partial \beta} \right)_\alpha = -\lambda_{lk} \alpha_{lk} \quad (141)$$

combining eqns. (140) and (141) gives

$$\left(\frac{\partial E_k}{\partial \beta} \right)_{\mathbf{n}, \alpha} = \sum_l n_l \left(\frac{\partial \lambda_{lk}}{\partial \beta} \right)_\alpha = - \sum_l n_l \lambda_{lk} \alpha_{lk} = -L_k \quad (142)$$

and finally

$$F_\beta^D = \sum_k n_k \frac{L_k}{E_k} \quad (143)$$

Furthermore

$$\beta_V = n f_V \quad (144)$$

where f_V is the derivative of f with respect to V . This completes the derivation of the derivative of F^D with respect to the volume.

The derivative with respect to the temperature is

$$\left(\frac{\partial F^D}{\partial T} \right)_{V,n} = - \sum_k n_k \frac{1}{E_k} \left(\frac{\partial E_k}{\partial T} \right)_{V,n} \quad (145)$$

and from eqn. (137)

$$\left(\frac{\partial E_k}{\partial T} \right)_{V,n} = \sum_l n_l \left(\frac{\partial \lambda_{lk}}{\partial T} \right)_{V,n} \quad (146)$$

and from eqn. (133) since β does not depend on the temperature

$$\left(\frac{\partial \lambda_{lk}}{\partial T} \right)_{V,n} = -\lambda_{lk} \beta \frac{d\alpha_{lk}}{dT} \quad (147)$$

combining eqn. (146) and (147) gives

$$\left(\frac{\partial E_k}{\partial T} \right)_{V,n} = -\beta \sum_l n_l \lambda_{lk} \frac{d\alpha_{lk}}{dT} \quad (148)$$

to calculate the derivative $d\alpha_{lk}/dT$ we take the natural logarithm of eqn. (134), that is

$$\ln \alpha_{lk} = \ln k'_{lk} - \ln T + \frac{1}{2} \ln a_{ll}(T) + \frac{1}{2} \ln a_{kk}(T)$$

and calculate the derivative. The result is

$$\frac{1}{\alpha_{lk}} \frac{d\alpha_{lk}}{dT} = -\frac{1}{T} + \frac{1}{2a_{ll}} \frac{da_{ll}}{dT} + \frac{1}{2a_{kk}} \frac{da_{kk}}{dT} \quad (149)$$

This completes the derivation of the derivative of F^D with respect the temperature.

The derivative respect to the mole number n_i is

$$\begin{aligned} \left(\frac{\partial F^D}{\partial n_i} \right)_{T,V,n_j} &= \left(\frac{\partial F^D}{\partial n_i} \right)_{\alpha,\beta,n_j} + \left(\frac{\partial F^D}{\partial \beta} \right)_{n,\alpha} \left(\frac{\partial \beta}{\partial n_i} \right)_{V,n_j} \\ &= F_i^D + F_\beta^D \beta_i \end{aligned} \quad (150)$$

$$F_i^D = \ln n + 1 - \ln E_i - \sum_k n_k \frac{\lambda_{ik}}{E_k} \quad (151)$$

Furthermore,

$$\beta_i = f + n f_B B_i \quad (152)$$

where f_B is the derivative of f with respect to B and B_i is the derivative of B with respect to the mole number n_i . This completes the derivation of the first order derivative of F^D with respect to the mole number n_i .

Next we proceed to the second order compositional derivative of F^D . Repeating the differentiation of eqn. (150) with respect to n_j gives

$$\left(\frac{\partial^2 F^D}{\partial n_i \partial n_j} \right)_{T,V} = F_{ij}^D + F_{\beta i}^D \beta_j + F_{\beta j}^D \beta_i + F_{\beta \beta}^D \beta_i \beta_j + F_{\beta}^D \beta_{ij} \quad (153)$$

From eqns. (151) and (137)

$$F_{ij}^D = \frac{1}{n} - \frac{\lambda_{ji}}{E_i} - \frac{\lambda_{ij}}{E_j} + \sum_k n_k \frac{\lambda_{ik}}{E_k} \frac{\lambda_{jk}}{E_k} \quad (154)$$

$$\begin{aligned} F_{\beta i}^D &= -\frac{1}{E_i} \left(\frac{\partial E_i}{\partial \beta} \right)_{n,\alpha} - \sum_k n_k \frac{1}{E_k} \frac{\partial \lambda_{ik}}{\partial \beta} + \sum_k n_k \frac{\lambda_{ik}}{E_k^2} \left(\frac{\partial E_k}{\partial \beta} \right)_{n,\alpha} \\ &= \frac{L_i}{E_i} + \sum_k n_k \frac{\lambda_{ik} \alpha_{ik}}{E_k} - \sum_k n_k \frac{L_k}{E_k} \frac{\lambda_{ik}}{E_k} \end{aligned} \quad (155)$$

From eqn. (143)

$$F_{\beta \beta}^D = \sum_k n_k \frac{L_k^2}{E_k^2} + \sum_k n_k \frac{1}{E_k} \left(\frac{\partial L_k}{\partial \beta} \right)_{n,\alpha} \quad (156)$$

and from eqns. (141) and (142)

$$\left(\frac{\partial L_k}{\partial \beta} \right)_{n,\alpha} = - \sum_l n_l \lambda_{lk} \alpha_{lk}^2 \quad (157)$$

and finally from eqn. (152)

$$\beta_{ij} = f_B B_j + f_B B_i + n f_{BB} B_i B_j + n f_{BB} B_{ij} \quad (158)$$

This completes the derivation of the second derivative of F^D with respect to the mole numbers n_i and n_j .

The second order temperature-compositional derivative is obtained from eqn. (150)

$$\left(\frac{\partial^2 F^D}{\partial T \partial n_i} \right)_V = F_{iT}^D + F_{\beta T}^D \beta_i + F_{\beta}^D \beta_{iT} \quad (159)$$

The last term cancels because β_{iT} is zero. From eqn. (151)

$$\begin{aligned} F_{iT}^D &= -\frac{1}{E_i} \left(\frac{\partial E_i}{\partial T} \right)_{V,n} - \sum_k n_k \frac{1}{E_k} \left(\frac{\partial \lambda_{ik}}{\partial T} \right)_{V,n} \\ &\quad + \sum_k n_k \frac{\lambda_{ik}}{E_k^2} \left(\frac{\partial E_k}{\partial T} \right)_{V,n} \end{aligned} \quad (160)$$

and from eqns. (142) and (145)

$$F_{\beta T}^D = - \sum_k n_k \frac{L_k}{E_k^2} \left(\frac{\partial E_k}{\partial T} \right)_{V,n} - \sum_k n_k \frac{1}{E_k} \left(\frac{\partial^2 E_k}{\partial \beta \partial T} \right)_n \quad (161)$$

and finally from eqns. (141) and (148)

$$\left(\frac{\partial^2 E_k}{\partial \beta \partial T} \right)_{n,\alpha} = \frac{1}{\beta} \frac{\partial E_k}{\partial T} + \beta \sum_l n_l \lambda_{lk} \alpha_{lk} \frac{d\alpha_{lk}}{dT} \quad (162)$$

This completes the derivation of the second derivative of F^D with respect to the mole number n_i and the temperature.

The second order volume-compositional derivative is obtained from eqn. (150)

$$\left(\frac{\partial^2 F^D}{\partial n_i \partial V} \right)_{T,n_j} = F_{\beta i}^D \beta_V + F_{\beta \beta}^D \beta_i \beta_V + F_{\beta}^D \beta_{iV} \quad (163)$$

where the only term we are missing is

$$\beta_{iV} = f_V + n f_{VB} B_i \quad (164)$$

This completes the derivation of the second derivative with respect to the mole number n_i and the volume.

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Chapter 6

Electrolytes

– Ions and Zwitterions

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1 The fundamental equation

Electrolytes are substances that dissociate into electrically charged ions in an aqueous solution. If it dissociates completely, it is called a strong electrolyte and substances that dissociate partially are named weak electrolytes. The substances are those called acids, bases, amphotytes, and salts. In order to develop the thermodynamics of systems containing electrolytes we have to retain a term in the fundamental relation that represents the work done when moving N_i particles of charges $z_i e$ in an electric field of potential ψ . This term is briefly mentioned in Section 1 of Chapter 1 where we derived the fundamental equations of the internal energy. Therefore we use eqn. (18) of Chapter 1 at the following form

$$\begin{aligned} U &= TS - PV + \sum_i \mu_i n_i + \psi \sum_i N_i z_i e \\ &= TS - PV + \sum_i \mu_i n_i + \psi q \end{aligned} \quad (1)$$

where $q = \sum q_i$ and $q_i = N_i z_i e = n_i z_i F$. N_i is the number of particles, z_i the charge number, e is the unit charge and $F = N_A e$ is Faraday's constant which equals 96485.338 C/mole . Finally, N_A is Avogadro's number, $N_A = 6.0221415 \cdot 10^{23} \text{ 1/mole}$. The first three terms are well known. The fourth term contributes to the chemical potential of an ion by an amount $z_i e \psi$ and this

explains why the third term is insufficient to characterise ion-ion equilibrium across a membrane or in an aqueous two-phase system. The importance of the potential ψ will be exemplified in the subsequent section. Actually, the last term is the scalar product of the electric field strength and the total polarisation of the dielectric that in our case simplifies to ψq . The subject is analysed by Münster (1970) in Chapter IX: "Systems in an electric field", and Chapter XI: "Electrochemical systems."

The Helmholtz energy $A = U - TS$ is comprised of a classical contribution, c , and an electric contribution, e ,

$$A = A^c + A^e = -PV + \sum_i \mu_i^c n_i + \sum_i \mu_i^e n_i + \psi q \quad (2)$$

The nature of A^e will be analysed in Sections 4 and 5. The electric contributions need special consideration because electrolytes cannot be analysed using the classical fluid theories because the coulombic potential

$$\Phi(\mathbf{r}) = \frac{1}{4\pi\epsilon} \sum_j \frac{z_j e}{|\mathbf{r} - \mathbf{r}_j|} \quad (3)$$

is so long ranged that the two-body interactions implied by the second virial coefficient do not exist. Thus it is not possible to decompose the many-body problem into a series of two-body, three-body problems, etc. and a straightforward virial expansion is not possible (McQuarrie, 1976). $\Phi(\mathbf{r})$ is the potential at an arbitrary point \mathbf{r} due to the point charges $z_j e$ located at the points \mathbf{r}_j in a medium or permittivity ϵ . In the theory of electrolytes, the medium is characterised by its temperature T , its volume V and its permittivity ϵ . The permittivity depends on the temperature, the molar densities, optical polarizabilities, and electric dipole moments of the species in the medium. Models of the permittivity will be analysed in Section 3.

2 The chemical potentials of ions

The chemical potentials of ions, i.e. the compositional derivatives of the Helmholtz energy (2) at constant temperature T and total volume V , are

$$\begin{aligned} \left(\frac{\partial A}{\partial n_j} \right)_{T,V} &= \left(\frac{\partial A^c}{\partial n_j} \right)_{T,V} + \left(\frac{\partial A^e}{\partial n_j} \right)_{T,V} \\ &= \mu_j^c = \mu_j^c(T, V, \mathbf{n}) + \mu_j^e(T, V, \epsilon, \mathbf{q}) + z_j F \psi \\ &= \mu_j^c(T, V, \mathbf{n}) + \mu_j^{self}(\epsilon, q_j) + \mu_j^{el}(T, V, \epsilon, \mathbf{q}) \\ &\quad + \mu_j^{dip}(T, V, \epsilon, \mathbf{q}) + z_j F \psi \end{aligned} \quad (4)$$

μ_j^{ec} is called the electrochemical potential of component j . $\mu_j^c(T, V, \mathbf{n})$ is the classical term which has been the subject of Chapters 3–5. It is due to the short-range intermolecular forces and it also includes terms accounting for association and hydration. $\mu_j^e(T, V, \epsilon, q)$ is the electric contributions, which we will analyse in Sections 4 and 5 and finally $z_j F\psi$ originates from the last term in eqn. (2). The electric contributions can be further analysed into three contributions μ_j^{self} , μ_j^{el} , and μ_j^{dip} . The potentials μ_j^{self} are the potentials due to the self-energy of charging each ion in the solution in the effective absence of the other ions and these potentials are assumed to be independent of the configuration of the molecules but depend on the permittivity of the solution. The potentials μ_j^{el} originate from the energy due to the mutual electric interactions of the various ions, the so-called background potential (Fowler and Guggenheim, 1965), and finally the potentials μ_j^{dip} account for the interactions between ions and dipolar ions that are also called zwitterions. A dipolar ion is an ion that has a permanent charge distribution and thus a large electric dipole moment even when its net charge is zero. Amino acids are dipolar ions (or zwitterions).

We can apply eqn. (4) to calculate the chemical potential of groups of ionic species which obey the neutrality condition

$$\sum_j \nu_j z_j = 0 \quad (5)$$

ν_j are the stoichiometric coefficients of the ions and assumed to be in integers. The mean electrochemical potential of groups of ions in solution, μ_{\pm} , is the linear combination of the electrochemical potentials of the ions divided by the sum of the stoichiometric coefficients $\nu = \sum_j \nu_j$. That is

$$\nu \mu_{\pm} = \sum_j \nu_j \mu_j^{ec} = \sum_j \nu_j (\mu_j^c(T, V, \mathbf{n}) + \mu_j^e(T, V, \epsilon, q)) \quad (6)$$

The terms containing the electric potential ψ cancel because of the net charge is nought as indicated in eqn. (5).

When groups of electrolytes are distributed between two immiscible phases α and β at identical pressures and temperatures, the equilibrium condition for each of the ionic species is

$$\mu_i^{ec,\alpha} = \mu_i^{ec,\beta} \quad \Leftrightarrow \quad \nu_i \mu_i^{ec,\alpha} = \nu_i \mu_i^{ec,\beta} \quad \text{all } i \quad (7)$$

and in view of eqns. (5) and (6) the equivalent condition is

$$\mu_{\pm}^{\alpha} = \mu_{\pm}^{\beta} \quad (8)$$

Eqn. (8) also applies to a case where the groups of ionic species are not fully dissociated in all phases. We consider the equilibrium between a gas and a liquid phase containing a volatile electrolyte like hydrochloric acid for instance. In this case dissociation will only take place in the liquid phases. Therefore eqn. (7) cannot be applied because the volatile component is not dissociated in all of the phases, but we can apply eqn. (8) if μ_{\pm} , in the gas phase is replaced by the potential of the non-dissociated substance. If the electrolyte is a weak electrolyte, and not fully dissociated in all of the phases, we must apply eqn. (8) and the appropriate dissociation equilibria.

Membrane and ion-exchange equilibria

The usual equilibrium conditions in an isothermal system imply that the pressures are identical in all the phases. However, if the two phases are separated by a semi-permeable membrane that retains some but not all of the charged species or one of the phases contains immobilised charges like an ion-exchange matrix, the pressure in the two phases will not necessarily be exactly alike. Whether a pressure difference is established depends on whether the equilibrium conditions can be fulfilled under the appropriate experimental conditions. We assume that the species are fully dissociated. If the pressures in the two phases are not identical, and the pressure in phase α is P^α and the pressure in phase β is P^β , the equilibrium condition for a molecule that has a net charge of z_j is

$$\mu_j^{ec,\alpha}(P^\alpha) = \mu_j^{ec,\beta}(P^\beta) \quad (9)$$

or the equivalent

$$\mu_j^{c,\alpha}(P^\alpha) + \mu_j^{e,\alpha}(P^\alpha) + z_j^\alpha \psi^\alpha F = \mu_j^{c,\beta}(P^\beta) + \mu_j^{e,\beta}(P^\beta) + z_j^\beta \psi^\beta F \quad (10)$$

If we assume that the partial molar volumes \bar{V}_j are pressure independent and adjust all potentials in phase β to the pressure P^α , then

$$\begin{aligned} \mu_j^{c,\alpha}(P^\alpha) + \mu_j^{e,\alpha}(P^\alpha) + z_j^\alpha \psi^\alpha F \\ = \mu_j^{c,\beta}(P^\alpha) + \mu_j^{e,\beta}(P^\alpha) + z_j^\beta \psi^\beta F + \bar{V}_j^\beta (P^\beta - P^\alpha) \end{aligned} \quad (11)$$

This equation of course also applies to the proton which means that the pH in both phases will not be the same. When the charge numbers z_j of the ions are independent of pH, that is when $z_j^\alpha = z_j^\beta = z_j$, the equilibrium condition becomes

$$\begin{aligned} \mu_j^{c,\alpha}(P^\alpha) - \mu_j^{c,\beta}(P^\alpha) + \mu_j^{e,\alpha}(P^\alpha) - \mu_j^{e,\beta}(P^\alpha) \\ = z_j F (\psi^\beta - \psi^\alpha) + \bar{V}_j^\beta (P^\beta - P^\alpha) \end{aligned} \quad (12)$$

Even if the pressures in the two phases were quite the same, the right-hand side would not be zero because the two electric potentials ψ^α and ψ^β will not be exactly alike unless all charges are distributed evenly in the two phases.

The equilibria for non-ionic species k like water and other non-dissociating species are calculable from the equation

$$\mu_k^{c,\alpha}(P^\alpha) - \mu_k^{c,\beta}(P^\beta) + \mu_k^{e,\alpha}(P^\alpha) - \mu_k^{e,\beta}(P^\beta) = \bar{V}_k^\beta(P^\beta - P^\alpha) \quad (13)$$

Whether a pressure difference $P^\beta - P^\alpha$ will be established depends on whether a pressure difference is necessary in order to satisfy eqn. (13) for all non-electrolyte species k . The electric contributions to the chemical potentials of non-electrolyte species k are minor, but shall not be neglected for several reasons. Firstly, the electric contributions to the Helmholtz energy will contribute to the pressure of the system and secondly, the permittivity of the fluid depends on the charge density and the solvent molarity. If the two phases are separated by a semi-permeable membrane, the pressure difference is denoted the osmotic pressure and when one of the phases is a liquid solution and the other phase is a gel or a chromatographic ion-exchange matrix, the pressure difference is denoted the swelling pressure.

The electric potential – a worked example

The equilibration of ions across a membrane is influenced by the charges carried by impermeable or immobilised ions. Consider the equilibration of a system composed of two compartments. The outer compartment contains a 1:1 salt, sodium chloride, and the inner compartment, which is a dialysis bag, contains a macro-ion of charge z_m of concentration c_m and sodium chloride. The pressures and the temperatures in the two compartments are the same. Since the purpose is to calculate the order of magnitude of the electric potential ψ , we simplify the calculations by assuming that the solution is ‘ideal’, that it, we utilise the approximation that chemical potentials of species of charge z_i is calculable as

$$\mu_i = \mu_i^o - RT \ln c + RT \ln c_i + z_i F\psi = \mu_{c_i}^o + RT \ln c_i + z_i F\psi \quad (14)$$

1. Use the assumptions just stated and show that at equilibrium

$$(c_{\text{Na}^+}^{\text{out}})^2 = c_{\text{Na}^+}^{\text{in}}(c_{\text{Na}^+}^{\text{in}} + z_m c_m)$$

where c_{Na^+} is the concentration of the sodium ion.

2. Use the equation from #1 to calculate the ratio $c_{\text{Na}^+}^{\text{in}}/c_{\text{Na}^+}^{\text{out}}$ when the charge of the macro-ion is +7 and its concentration $c_m = 0.1$ mM. The salt concentration in the outer compartment is 1 mM.

Calculate the $c_{\text{Na}^+}^{in}$ and $c_{\text{Cl}^-}^{in}$ concentrations and the product of $c_{\text{Na}^+}^{in}$ and $c_{\text{Cl}^-}^{in}$. c_{Cl^-} is the concentration of the chloride ion.

3. Use the results from #2 to calculate the difference in the electric potentials ψ (mV) between the inner and the outer compartment.
4. Calculate pH in the inner compartment when pH in the outer compartment is 7. Assume that $c_{\text{H}^+} + c_{\text{OH}^-} = 10^{-14}$.

$F = 96485 \text{ C/mole}$, $R = 8.314 \text{ J/mole K}$, and $T = 298 \text{ K}$. Remember the relationship of units $1 \text{ C} = 1 \text{ J/V}$.

Solution

1. For a 1:1 salt we can write the chemical potential of the salt as

$$\mu_{\pm} = \mu_{\text{Na}^+} + \mu_{\text{Cl}^-} = \mu_{c_{\text{Na}^+}}^o + \mu_{c_{\text{Cl}^-}}^o + RT \ln c_{\text{Na}^+} + RT \ln c_{\text{Cl}^-}$$

The condition of equilibrium is that the chemical potentials of the salt on both sides of the membrane are identical, that is

$$\mu_{\pm}^{in} = \mu_{\pm}^{out} \quad \text{or} \quad c_{\text{Na}^+}^{in} c_{\text{Cl}^-}^{in} = c_{\text{Na}^+}^{out} c_{\text{Cl}^-}^{out}$$

Electroneutrality requires that:

$$\text{outside:} \quad z_{\text{Na}^+} c_{\text{Na}^+}^{out} + z_{\text{Cl}^-} c_{\text{Cl}^-}^{out} = 0$$

$$\text{inside:} \quad z_{\text{Na}^+} c_{\text{Na}^+}^{in} + z_{\text{Cl}^-} c_{\text{Cl}^-}^{in} + z_m c_m = 0$$

and since $z_{\text{Na}^+} = 1$ and $z_{\text{Cl}^-} = -1$, it follows that

$$(c_{\text{Na}^+}^{out})^2 = c_{\text{Na}^+}^{in} (c_{\text{Na}^+}^{in} + z_m c_m)$$

2. The ratio $c_{\text{Na}^+}^{in}/c_{\text{Na}^+}^{out}$ is calculable from the equation

$$\left(\frac{c_{\text{Na}^+}^{in}}{c_{\text{Na}^+}^{out}} \right)^2 + \frac{c_{\text{Na}^+}^{in}}{c_{\text{Na}^+}^{out}} \frac{z_m c_m}{c_{\text{Na}^+}^{out}} - 1 = 0$$

The result is $c_{\text{Na}^+}^{in}/c_{\text{Na}^+}^{out} = 0.71 \text{ mM}$ (0.70948), that is, $c_{\text{Na}^+}^{in} = 0.71 \text{ mM}$ and $c_{\text{Cl}^-}^{in} = 1.41 \text{ mM}$ and $c_{\text{Na}^+}^{in} c_{\text{Cl}^-}^{in} = 1 \text{ (mM)}^2$.

3. At equilibrium the chemical potentials of the ions must fulfil the condition that $RT \ln c^{in} + zF \Delta\psi = RT \ln c^{out}$. The difference in the electric potentials must therefore be $\Delta\psi = -\frac{RT}{zF} \ln(c^{in}/c^{out})$ and since $z = 1$ for the Na^+ ion the potential difference is $\Delta\psi = -\frac{8.314 \cdot 298}{96485} \ln 0.71 = 8.8 \text{ mV}$. A similar result is of course obtained for the negatively charged Cl^- ion $\Delta\psi = \frac{8.314 \cdot 298}{96485} \ln 1.41 = 8.8 \text{ mV}$.

4. In #3 we calculated the ratio c^{in}/c^{out} for a positive monovalent ion to 0.71, therefore $c_{H^+}^{in} = 0.71 \cdot c_{H^+}^{out} = 0.71 \cdot 10^{-7}$ and thus $pH^{in} = 7.15$ and as before $c_{H^+}^{in} c_{OH^-}^{in} = c_{H^+}^{out} c_{OH^-}^{out} = 10^{-14}$.

We observe that the presence of positively charged macro-ions in the inner compartment excludes some positively charged small ions from that compartment. Important is to notice that the pH is different in the two compartments. This is important if proteins are involved because the charge numbers of proteins depend on the pH. The unequal distribution of ions is denoted Donnan exclusion and the electric potential ψ is therefore known as the Donnan potential or the membrane potential.

3 The permittivity

The permittivity of a continuum ϵ is $\epsilon_r \epsilon_0$ where ϵ_r is the relative permittivity and ϵ_0 is the permittivity of vacuum, $\epsilon_0 = 8.854187817 \cdot 10^{-12} \text{ C}^2/\text{J m}$. The relative permittivity of a pure fluid depends on the temperature and the fluid properties like molar density, optical polarizability, and electric dipole moment (Edsall and Wyman, 1958; Kirkwood, 1939).

Kirkwood and Onsager derived an expression for the relative permittivity ϵ_r of a pure fluid

$$\frac{(\epsilon_r - \epsilon_\infty)(2\epsilon_r + \epsilon_\infty)}{(\epsilon_\infty)^2 \epsilon_r} = \frac{n}{V} \frac{N_A}{3\epsilon_0} \left(\alpha + \frac{\delta^2}{3kT} \right) \quad (15)$$

N_A is Avogadro's number, and k is Boltzmann's constant $k = 1.3806503 \cdot 10^{-23} \text{ J/K}$. ϵ_∞ is the relative permittivity at infinite frequency, actually it is the square of the index of refraction, n is the mole number of the solvent, α is the optical polarizability ($\text{C}^2\text{m}^2/\text{J}$) of the solvent and δ is the electric dipole moment ($\text{C}\cdot\text{m}$) of the solvent. The frequency dependence of the permittivity is due to the frequency dependence of the optical polarizability α and the electric dipole moment δ (Atkins and de Paula, 2002). In high density polar fluids, the electric configuration of the molecule is in general altered, and its moment is different from that of the isolated molecule. Actually δ^2 is the average of the product of the moment of the central molecule and the vector sum of the moment of the central plus that of all the neighbours. This sum is in general different in magnitude from the moment of a single molecule (Edsall and Wyman, 1958). To account for the influence of the altered electric configuration we introduce a correction factor β in the expression for the

molar polarizability p

$$p = \frac{N_A}{3\epsilon_0} \left(\alpha + \frac{\beta\delta^2}{3kT} \right) \approx \frac{\beta}{9} \frac{N_A\delta^2}{\epsilon_0 kT} \quad (16)$$

At low frequency we can neglect the optical polarizability α for polar fluids because its contribution is much less than that originating from the dipole moment.

When we write the expression eqn. (15) in the following manner

$$\epsilon_r - \frac{\epsilon_\infty}{2} - \frac{\epsilon_\infty^2}{2\epsilon_r} = \frac{(\epsilon_\infty + 2)^2}{2} \frac{np}{V} \quad (17)$$

it shows, that when the relative permittivity is large in relation to ϵ_∞ , as in strongly polar fluids, eqn. (17) approaches a limiting form where

$$\epsilon_r = \frac{(\epsilon_\infty + 2)^2}{2} \frac{np}{V} = \frac{9}{2} \frac{np}{V} = \frac{n}{V} \frac{\beta N_A \delta^2}{2 \epsilon_0 kT} \quad (18)$$

In this equation we have used the approximation $\epsilon_\infty = 1$. We cannot apply eqn. (18) as it stands to correlate the molar polarizability because it turns out that the parameter β must be a function of temperature, volume, or both in order to match the smoothed experimental data. Figure 1 shows the parameter β for saturated liquid water in the temperature range 273 to 373 K. The data are from *NBS/NRC Steam Tables* by Haar et al. (1983).

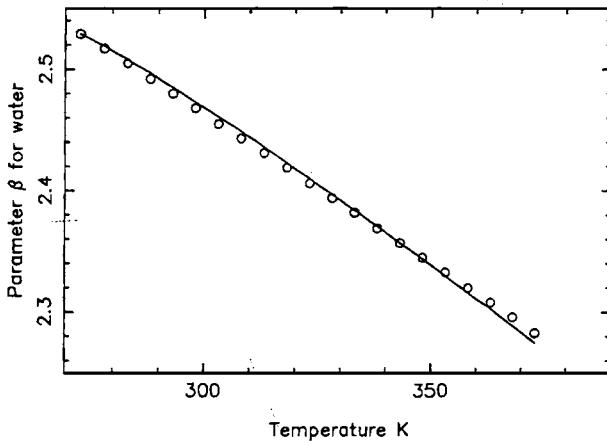


Figure 1: The temperature dependence of the parameter β for saturated liquid water.

If we apply eqn. (16) to correlate the molar polarizability of water it is natural to suggest that, over a limited range of temperature, we can model

the temperature dependence of the molar polarizability using the following expression

$$\begin{aligned} p(T) &= p(T_0) + \frac{\beta_1}{9} \frac{N_A \delta^2}{\epsilon_0 k} \left(\frac{1}{T} - \frac{1}{T_0} \right) \\ &= \frac{\beta_0 - \beta_1}{9} \frac{N_A \delta^2}{\epsilon_0 k T_0} + \frac{\beta_1}{9} \frac{N_A \delta^2}{\epsilon_0 k T} \end{aligned} \quad (19)$$

The molar polarizability $p(T_0)$ at $T_0 = 273.15$ K is 0.3517 litre/mole, the dipole moment of liquid water is $\delta = 8.33 \cdot 10^{-30}$ C·m (Chen et al., 2000), and the value of β at temperature T_0 is $\beta_0 = 2.529$. β_1 is treated as an adjustable parameter. When the upper temperature limit is 373.15 K, the average value of β_1 is determined to 3.201 and thus $\beta_0 - \beta_1 = -0.672$. Comparing eqns. (16) and (19) shows that the suggested temperature dependence of β is

$$\beta(T) = \beta_1 + (\beta_0 - \beta_1) \frac{T}{T_0} \quad (20)$$

The correlation is shown as the full line in Figure 1. The result of the correlation of the relative permittivity of liquid water can be observed as the dashed line in Figure 2. When we developed the correlation (19), we assumed that the molar polarizability of pure water is a function of temperature only, but if we apply similar principles to develop a correlation of the relative permittivity, that is, use eqn. (18) instead of eqn. (16), the suggested model is

$$\varepsilon_r = \varepsilon_r(T_0) + \frac{\beta_1}{2} \frac{N_A \delta^2}{\epsilon_0 k} \left(\frac{n}{VT} - \frac{n}{V_0 T_0} \right) \quad (21)$$

$\varepsilon_r(T_0)$ is the relative permittivity at $T_0 = 273.15$ K, $\varepsilon_r(T_0) = 87.82$, n/V_0 is the molar density at temperature T_0 , and β_1 is treated as an adjustable parameter. When the upper temperature limit is 373.15 K, the adjustable parameter β_1 is determined to 3.1306.

Figure 2 shows the deviation between experimental and correlated values of the relative permittivity of saturated liquid water (full line) in the temperature interval 273–373 K. The model represents the data within ± 0.05 .

The reason why eqn. (21) provides a better correlation than the first approach is, as we will show, that β in this way becomes a function of the density ratio $\rho_0/\rho = V/V_0$ and temperature. Since the molar polarizability, in this context, by definition is $\varepsilon_r V / 4.5 n$, we can calculate the molar polarizability that corresponds to the relative permittivity model eqn. (21), that

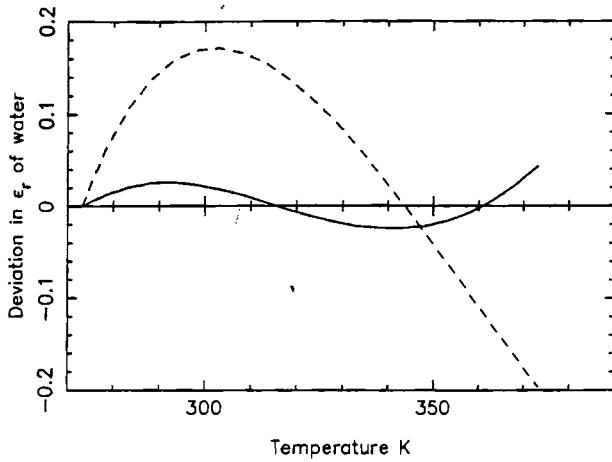


Figure 2: Deviation in the relative permittivity of saturated liquid water at 0 to 100°C. Dashed line model (eqns. (18) and (20)), full line model eqn. (21).

is

$$\begin{aligned} p(T, V) &\equiv \frac{\varepsilon_r V}{4.5 n} = p(T_0) \frac{V}{V_0} + \frac{\beta_1 N_A \delta^2}{9 \varepsilon_0 k} \left(\frac{1}{T} - \frac{V}{V_0 T_0} \right) \\ &= \frac{\beta_0 - \beta_1}{9} \frac{N_A \delta^2}{\varepsilon_0 k T_0} \frac{V}{V_0} + \frac{\beta_1 N_A \delta^2}{9 \varepsilon_0 k T} \end{aligned} \quad (22)$$

As before, β_0 is the value of β at temperature T_0 , $\beta_0 = 2.529$, and $\beta_0 - \beta_1 = -0.601$. Comparing eqns. (16) and eqn. (22) shows that β now depends on temperature as well as volume

$$\beta(T, V) = \beta_1 + (\beta_0 - \beta_1) \frac{T V}{T_0 V_0} \quad (23)$$

The temperature dependence in eqns. (20) and (23) are alike but eqn. (23) also includes a correction for the change in the saturated liquid volume. One cannot expect these simple models to apply over a wider range of temperature, especially not when the critical point is approached. The relative permittivity at the critical point of water is 5.34. Uematsu and Frank (1980) have developed a model of the relative permittivity of water at temperatures from 238 K to 1273 K and pressures up to 1200 MPa.

We can generalise eqn. (18) to include mixtures

$$\varepsilon_r = \frac{4.5}{V} \sum_{i=1}^{NC} n_i p_i = 4.5 \sum_{i=1}^{NC} c_i p_i \quad (24)$$

NC is the number of components and c_i is the molarity. This result is important because it shows that the relative permittivity of a liquid mixture is the volume fraction average of the permittivity of the pure components, that is

$$\varepsilon_r = \frac{1}{V} \sum_{i=1}^{NC} V_i \varepsilon_{r,i} \quad (25)$$

V_i is the pure component volume, $\varepsilon_{r,i}$ is the relative permittivity of pure of species i , and V is the mixture volume. Mixtures of ethanol and water may serve as an example of the application of eqn. (25). No correction has been made for the excess volume. The result is shown in Table 1.

Table 1: Relative permittivity of ethanol-water mixtures at 25°C (Edsall and Wyman, 1958).

Volume % ethanol	Experimental	Calculated
100	24.3	
60	47.9	46.0
40	59.7	56.8
20	70	67.7
0	78.5	

Harvey and Prausnitz (1987) discuss the limitations and extensions of eqn. (25) for mixed solvents.

When we dissolve a salt in water, the relative permittivity decreases. This is caused by a decrease in the molar concentration of water, a reduction of the concentration of 'free' water molecules due to the hydration of the cations, and finally because the addition of salt alters the electric configuration and decreases the influence of dipoles of the neighbour molecules on the moment of the central molecule. The decrease in the molar concentration of water depends on the salt but the decrease in the molar concentration of water is almost a linear function of the salt concentration. Table 2 shows the order of magnitude of the molarity increment of water for some salt solutions. The increments are calculated from the volumetric properties reported in the CRC Handbook of Chemistry and Physics 1997-1998.

However, the decrease in the molar concentration of water with increasing salt concentration is minor compared to the decrease in the relative permittivity of salt solutions. The hydration is most likely a predominant cause. Figures 3-5 show the relative permittivity of some salt solutions in dependence of the salt concentration. The data are from the data collection of

Table 2: The molarity increment of water $\Delta c_{water}/\Delta c_{salt}$ in salt solutions at 20°C.

	Chloride	Bromide	Nitrate	Sulphate
Sodium	-1.1	-1.5	-1.8	-1.4
Potassium	-1.7	-2.0	-2.3	-2.2
Ammonium	-2.1			-3.7

Barthel et al. (1995). It is fairly easy to establish a correlation that fits the general trend of the data. The correlation is

$$\epsilon_r(c_+, c_-) = \epsilon_r^{sat} \left(1 - \sum \frac{a_+ c_+}{1 + 0.160 c_+} - \sum \frac{a_- c_-}{1 + 0.160 c_-} + 0.010(c_+ + c_-) \right) \quad (26)$$

ϵ_r^{sat} is the relative permittivity of pure saturated liquid water and, a_+ and a_- are cation and anion parameters listed in Table 3. The Li^+ parameter is 0.12 exactly. c_+ is the concentration of cation charges $c_+ = z_+ c_{cation}$ where z_+ is the charge number of the cation and c_{cation} is the molar concentration of the cation. $c_{cation} = \nu_+ c_{salt}$ where ν_+ is the stoichiometric coefficient of the cation and c_{salt} is the molar concentration of the salt. Correspondingly c_- is the concentration of anion charges $c_- = z_- c_{anion}$. For CaCl_2 , the concentration of cation charges is equal to two times the molar salt concentration. Similarly, for Na_2SO_4 the concentration of anion charges is equal to two times the molar salt concentration.

Table 3: The parameters for some common ions.

Cation	a_+	Anion	a_-
Li^+	0.12	Cl^-	0.1173
Na^+	0.1062	Br^-	0.1348
K^+	0.0816	NO_3^-	0.1104
Cs^+	0.0650	SO_4^{2-}	0.0022
Mg^{2+}	0.1155		
Ca^{2+}	0.1097		
Ni^{2+}	0.0553		

Solutions of the salts LiCl, NaCl, KCl, CsCl, LiBr, KBr, CsBr, LiNO₃, NaNO₃, KNO₃, Na₂SO₄, NiCl₂, CaCl₂, and MgCl₂ were included in the data base.

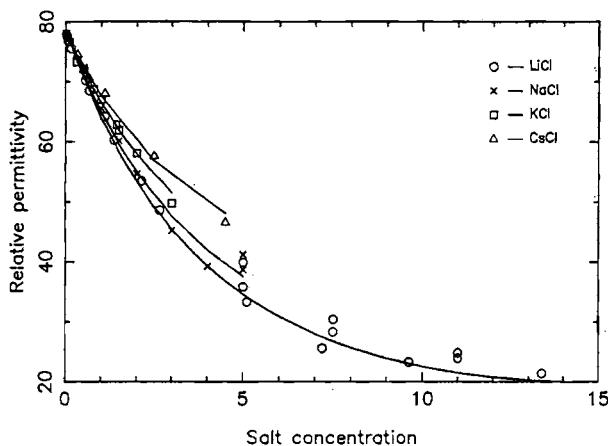


Figure 3: The relative permittivity of chloride salt solutions at 298.15 K.

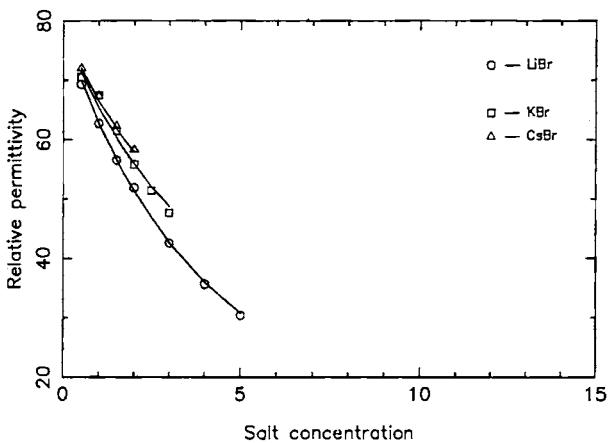


Figure 4: The relative permittivity of bromide salt solutions at 298.15 K.

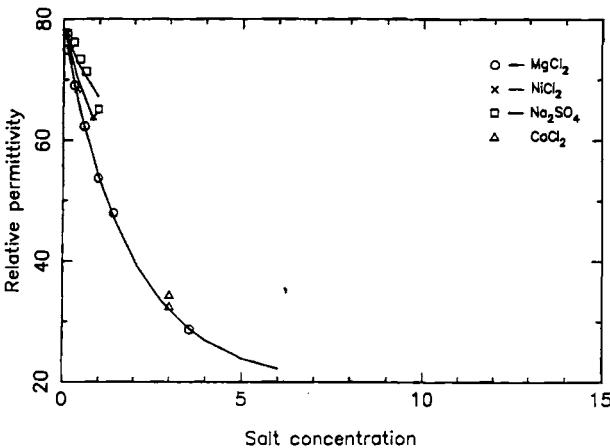


Figure 5: The relative permittivity of solutions containing divalent ions at 298.15 K.

4 The Debye-Hückel equation

In a paper from 1923, *Zur Theorie der Elektrolyte*, Debye and Hückel derive an expression for the change in the Helmholtz energy due to the charging of molecules in solution. The solvent is characterised by its volume V , its temperature T and its relative permittivity ϵ_r . The assembly is completely defined by the number of ions, the nature of the ions and the nature of the medium.

The quotations from the paper by Debye and Hückel (1923) are in German and an English translation is provided immediately after. Debye and Hückel divide the energy U in a classical part and electric part. On page 187 column 2 they write that:

„Die Rechnungen, welche in Folgenden auszuführen sind, unterscheiden sich von den klassischen durch Berücksichtigung der elektrischen Ionenwirkungen. Dementsprechend zerlegen wir U in zwei Bestandteile, einen klassischen Anteil U_k und eine elektrische Zusatzernergie U_e : $U = U_k + U_e$.“

“The calculations which follow differ from the classical calculations in that the electric effect of the ions is taken into account. Accordingly, we divide U into two parts, a classical part U_k and an additional electric energy U_e : $U = U_k + U_e$.“

By using the exact formula $\frac{A}{T} = \int U d\frac{1}{T}$ we can thus divide the Helmholtz energy into a classical part A^c and an additional electric contribution A^e . The classical part is characterised by its independent variables, temperature T , volume V and compositions \mathbf{n} and it includes all contributions that do not involve charges. The electric contribution A^e includes the additional Helmholtz energy generated by charging the molecules. There will of course be some additional contributions not accounted for by A^e and that is among others the charge-dipole and the charge-quadrupole interactions and all induced interactions and associations caused by the introduction of the charges. *The charging process takes place at constant (T, V, \mathbf{n}) and the classical part of the Helmholtz energy A^c is therefore not altered.* In order to derive the expression for A^e we have to assume that the relative permittivity is constant and do not change due to the charging process. However, when we have derived the eventual result, we can relax this constraint. At the time the paper was written and many years after it was a common conviction that essentially the eventual model was or ought to be an excess Gibbs energy model.

Before reporting on their developments, it may be appropriate with a comment on how to read the paper by Debye and Hückel (1923). In their paper the potential G is the Massieu function that equals minus the Helmholtz energy divided by the temperature

$$G = S - \frac{U}{T} \quad (\text{DH1})$$

The independent variables are, besides concentration, volume and temperature, that is

$$dG = \frac{p}{T} dV + \frac{U}{T^2} dV \quad (\text{DH1}')$$

That is, G in Debye and Hückel's paper corresponds to what we denote as $-A/T$. Moreover, Φ is the Massieu-Plank function or potential that equals minus the Gibbs energy divided by the temperature as shown in eqn. (DH4). Since U is divided into a classical part U_k and an additional electric energy U_e the potential G is also divided into two parts calculable from the equation

$$T^2 \frac{\partial G}{\partial T} = U \quad (\text{DH2})$$

That is, according to Debye and Hückel (1923)

$$G = G_k + G_e \quad (\text{DH2}')$$

Their argument for replacing G with Φ in eqn. (DH2) and thus disregarding the PV term is characteristic of the electrolyte thermodynamics of the period

but unfortunately incorrect. Replacing G with Φ corresponds to replacing the Helmholtz energy by the Gibbs energy. In the first column on page 188 Debye and Hückel write:

„Für die praktische Verwertung ist aber das Potential G nicht so gut geeignet, wie die auch von Plank bevorzugte Funktion

$$\Phi = S - \frac{U + pV}{T} \quad (\text{DH4})$$

Wie die Differentialform dieser Definition

$$d\Phi = -\frac{V}{T} dp + \frac{U + pV}{T^2} dT \quad (\text{DH4}')$$

zeigt, sind nämlich beim Potential Φ Druck und Temperatur die naturgemäßen Variablen, und da die überwiegende Mehrzahl der Versuche bei konstantem Druck (und nicht bei konstantem Volumen) ausgeführt wird, ist Φ vorzuziehen. Ein Vergleich von (DH4) mit (DH1) ergibt

$$\Phi = G - \frac{pV}{T} \quad (\text{DH5})$$

ist also nach dem obigen G bekannt, so handelt es sich noch darum, das Zusatzglied $-pV/T$ als Funktion von p und T zu finden und hinzufügen. Mit Rücksicht auf (DH1') kann man schließen

$$\frac{p}{T} = \frac{\partial G}{\partial V} = \frac{\partial G_k}{\partial V} + \frac{\partial G_e}{\partial V} \quad (\text{DH6})$$

und hat so die Zustandsgleichung erhalten, welche bei der Ionenlösung Druck, Volumen und Temperatur miteinander verknüpft. Dieselben kann so interpretiert werden, daß infolge der elektrischen Ionenwirkungen zum äußeren Druck p noch ein elektrischer Zusatzdruck p_e hinzugekommen ist, zu berechnen nach der Beziehung

$$\frac{p_e}{T} = \frac{\partial G_e}{\partial V} \quad (\text{DH6}')$$

Wir werden später nebenbei Gelegenheit haben, diesen elektrischen Druck p_e zu bestimmen, er beträgt für eine wäßrige Lösung z.B. von KCl bei einer Konzentration von 1 Mol pro Liter nur etwa 20 Atm. Es ist also streng genommen nicht richtig, wenn wir für V (als Funktion von p und T) den klassischen Ansatz ohne Berücksichtigung der elektrischen Ionenwirkungen benutzen, da der Druck p_e auch eine Volumänderung hervorruft. Mit Rücksicht

darauf aber, daß die Kompressibilität des Wassers so gering ist, daß 20 Atm. nur eine relative Volumänderung von 0,001 hervorrufen, kann für die meisten Anwendungen der elektrischen Zusatz zu V (als Funktion von p und T) vernachlässigt werden. In sinne dieser Bemerkung werden wir auch Φ zerlegen einen Klassischen Teil und einen elektrischen Zusatzbestandteil "

$$\Phi = \Phi_k + \Phi_e \quad (\text{DH7})$$

"However, for practical evaluations, the potential G is not as suitable as the function preferred by Planck (the Massieu-Plank function)

$$\Phi = S - \frac{U + pV}{T} \quad (\text{DH4})$$

The differential form of this function

$$d\Phi = -\frac{V}{T} dp + \frac{U + pV}{T^2} dT \quad (\text{DH4}')$$

shows, that the characteristic independent variables of the potential Φ are pressure and temperature, and *since the great majority of the experiments are carried out at constant pressure (and not at constant volume)*, Φ is preferable. Subtraction of (DH4) from (DH1) shows that

$$\Phi = G - \frac{pV}{T} \quad (\text{DH5})$$

If G in this equation is known, it remains to find the additional term $-pV/T$ as a function of p and T . With regard to (DH1') and (DH2') we can conclude that

$$\frac{p}{T} = \frac{\partial G}{\partial V} = \frac{\partial G_k}{\partial V} + \frac{\partial G_e}{\partial V} \quad (\text{DH6})$$

and in this way we have obtained the equation of state which relates pressure, volume, and temperature for the ionic solution. (DH6) can be interpreted thus, as a consequence of the electric effect of the ions, an additional electric pressure p_e is added to the external pressure p_k ; the pressure p_e is to be computed from the relation:

$$\frac{p_e}{T} = \frac{\partial G_e}{\partial V} \quad (\text{DH6}')$$

Later we shall determine the electric pressure p_e ; it amounts to approximately 20 atmospheres for an aqueous solution of for instance, KCl at a concentration of 1 mole per litre. Strictly speaking, it is incorrect to use the classical expression for V (as a function of p and T) without regard to the electric effect of the ions, since the pressure p_e causes a change in volume. In view of the low compressibility of water which results in a relative change of volume on 0.001 at a pressure increase of 20 atmospheres, the electric addition to V (as a function of p and T) can be neglected for most application. In view of this remark, we shall also divide Φ in a classical part and an additional electric part."

$$\Phi = \Phi_k + \Phi_e \quad (\text{DH7})$$

In consequence of this statement they put $\Phi_e = G_e$ and therefore

$$\Phi_e = G_e = \int \frac{U_e}{T^2} dT \quad (\text{DH7}')$$

These arguments are strictly speaking not correct. The choice of independent variables do not depend on the experimental conditions and besides the charging process takes place, as their derivation shows, at constant temperature and volume and not at constant temperature and pressure. Moreover, according to eqns. (DH5) and (DH6)

$$\Phi_e = G_e - \frac{p_e V}{T}$$

Regrettably, V in this equation is not a volume change caused by the electric pressure p_e but the total volume of the system that do not alter during the charging process because it takes place at constant T and V as mentioned several times.

With these prefatory remarks we will address the developments of Debye and Hückel (1923). By solving the linearised Poisson-Boltzmann equation they derive equations for the electric potential inside and outside the sphere of radius a_i (equations 17-18' in Debye and Hückel (1923)). The charge of the ion i is located at the centre of a sphere of radius a_i . The radius a_i is the closest distance that any other ion can approach the ion at the centre of the sphere. The electric potential inside the sphere at $r_i \leq a_i$ is divided into two parts, a potential due to charging the ion in the centre of the sphere in the effective absence of the other ions, the self potential, and a potential due to the mutual interactions of the ion with the other charges outside the sphere of radius a_i , the so-called background potential denoted ψ^{el} .

The potential outside the sphere of radius a_i at $r_i \geq a_i$ is

$$\psi_i(r) = \psi_i^{\text{self}} + \psi_i^{\text{el}} = \frac{z_i e}{4\pi\epsilon} \frac{1}{r} \frac{e^{\kappa(a_i - r)}}{1 + \kappa a_i} \quad (27)$$

The potential inside the sphere of radius a_i at $r_i \leq a_i$ is

$$\psi_i(r) = \psi_i^{\text{self}} + \psi_i^{\text{el}} = \frac{z_i e}{4\pi\epsilon} \frac{1}{r} - \frac{z_i e}{4\pi\epsilon} \frac{\kappa}{1 + \kappa a_i} \quad (28)$$

Eqns. (27) and (28) are obtained by combining equations (17), (17') and (18') in the paper by Debye and Hückel, see also the first three equations in the paper on page 193 column two. At the distance $r_i = a_i$ the two potentials are of course identical. κ is the Debye or the shielding length

$$\kappa^2 = \frac{e^2}{\epsilon k T V} \sum_j N_j z_j^2 = \frac{F^2}{\epsilon R T V} \sum_j n_j z_j^2 \quad (29)$$

n_j is the mole number of ion j that is, the number of ions divided by Avogadro's number N_A and F is Faraday's constant.

In order to calculate the additional electric Helmholtz energy, Debye and Hückel calculate the electric energy U_e and obtained A_e by integration with respect to $1/T$. In this analysis we use the partial charging process (Fowler and Guggenheim, 1965; McQuarrie, 1976) to calculate A_e .

The potential of an ion at the distance $r_i = a_i$ that has a fractional charge of $\lambda e z_i$ is

$$\psi_i(\lambda) = \frac{\lambda z_i e}{4\pi\epsilon} \frac{1}{a_i} - \frac{\lambda z_i e}{4\pi\epsilon} \frac{\lambda\kappa}{1 + \lambda\kappa a_i} \quad (30)$$

where λ is a number between 0 and 1.

The total electrostatic Helmholtz energy at $r_i = a_i$ of N_i ions is equal to the electric work to increase each of the charges by an amount $e z_i d\lambda$ at constant temperature T , volume V composition n , and permittivity ϵ . That is

$$\begin{aligned} A^e(T, V, n) &= A^{\text{self}} + A^{\text{el}} = \int_0^1 \sum_i N_i \psi_i(\lambda) z_i e d\lambda \\ &= \int_0^1 \sum_i N_i \frac{\lambda z_i e}{4\pi\epsilon a_i} z_i e d\lambda - \int_0^1 \sum_i N_i \frac{\lambda z_i e}{4\pi\epsilon} \frac{\lambda\kappa}{1 + \lambda\kappa a_i} z_i e d\lambda \end{aligned}$$

$$\begin{aligned}
&= \frac{e^2}{8\pi\epsilon} \sum_i \frac{N_i z_i^2}{a_i} \\
&\quad - \frac{kTV}{4\pi \sum_j N_j z_j^2} \sum_i \frac{N_i z_i^2}{a_i^3} \left[\ln(1 + \kappa a_i) - \kappa a_i + \frac{1}{2}(\kappa a_i)^2 \right] \\
&= \frac{F^2}{8\pi N_A \epsilon} \sum_i \frac{n_i z_i^2}{a_i} - \frac{kTV}{4\pi \sum_j N_j z_j^2} \sum_i n_i z_i^2 \chi_i
\end{aligned} \tag{31}$$

where χ_i is the auxiliary function

$$\chi_i = \frac{1}{a_i^3} \left[\ln(1 + \kappa a_i) - \kappa a_i + \frac{1}{2}(\kappa a_i)^2 \right] \tag{32}$$

The first part of eqn. (31) is the self-energy and the second part is the contribution due to the mutual interactions of the charged molecules. The first part is also known as the self potential or the Born term and this term is not included in the expression derived by Debye and Hückel. The second term in eqn. (31) is exactly identical with eqn. (26) in the paper by Debye and Hückel. Please note that in the paper by Debye and Hückel $n_i = N_i/V$ is the molarity and $c_i = N_i/\sum_j N_j$ is the mole fraction.

It is a common misreading of the paper to conclude that the model derived by Debye and Hückel is restricted to ions of equal distance of closest approach, but as eqn. (31) demonstrates this is not the case. The size parameter a_i in the Debye-Hückel model is not the ionic radius but the closest distance that any other ion can approach the ion looked at, the so-called ‘Annäherungsabstand’, the distance of closest approach. As Debye and Hückel explains on page 192 column one in the paper:

„Die Größe a mißt dann offenbar nicht den Ionenradius, sondern steht für eine Länge, welche einen Mittelwert bildet für den Abstand bis auf welchen die umgebenden, sowohl positiven, wie negativen Ionen an das hervorgehobene Ion herankommen können. Dementsprechend wäre a bei völlig gleichdimensionierten positiven und negativen Ionen z. B. von der Größenordnung des Ionen Durchmessers zu erwarten. Dabei ist im allgemeinen dieser Ionen Durchmesser noch nicht als Durchmesser des wirklichen Ions anzusehen, da die Ionen voraussichtlich ihrer Hydratation entsprechend von einer fest haftenden Schicht Wassermoleküle umgeben zu denken sind.“

"The magnitude a_i , obviously, does not measure the radius of the ion but a length which constitutes the mean value for the distance to which the surrounding ions, positive as well as negative ions, can approach the ion looked at. Correspondingly for positive and negative ions of equal size, for instance, a_i would be expected to be of the order of magnitude of the (hydrated) ion diameter. In general, the ion diameter is not to be considered the diameter of the actual ion, since, most likely, the ions have to be imagined as surrounded by a firmly attached layer of water molecules."

A common misreading, which is strongly supported by Debye and Hückel themselves and many others, is that A^e is not a contribution to the Helmholtz energy but an excess Gibbs energy. But nothing in there derivation supports their arguments.

Fowler and Guggenheim (1965) (§ 917) recite a similar incantation in search of a 'useful meaning of A^{el} '. They use a partial charging process to calculate the increase in free energy F (Helmholtz energy). They write:

"We have up to the present assumed that the volume is invariable, that it is unaffected by pressure and by the charges of the ions. In particular the formula

$$dF^{el} = \psi_\alpha |e| dz_\alpha + \psi_\beta |e| dz_\beta + \dots \quad (\text{FG906-11})$$

states that in the imaginary process of gradually increasing the charges of the ions the increase in free energy F (Helmholtz energy) is equal to the electric work done on the assembly. This implies that there is no other work done on the assembly and in particular no work by the external pressure. This implies indirectly that there is no change in volume during the charging process and therefore, if the solution is compressible, this requires an alternation of pressure to maintain the volume constant. *The only useful meaning of F^{el} (and a similar remark applies to all related quantities) is the excess of F for the actual solution over its value for an ideal solution at the same temperature and at the same pressure.* To evaluate F^{el} and related quantities we must therefore make the integration correspond to the charging of the ions at constant pressure. Superposed on the purely electric work given by the right-hand side of (FG906-11) there will be the work done on the system by the external pressure P . Instead of (FG906-11) we have therefore

$$dF^{el} = \psi_\alpha |e| dz_\alpha + \psi_\beta |e| dz_\beta + \dots - P dV \quad (\text{FG917-1})$$

or since we are assuming P kept constant during the charging process

$$\begin{aligned} dG^{el} &= dF^{el} + d(PV^{el}) \\ &= \psi_\alpha |e| dz_\alpha + \psi_\beta |e| dz_\beta + \dots \end{aligned} \quad (\text{FG917-2})$$

When we insert the values of $\psi_\alpha, \psi_\beta, \dots$ and integrate, we obtain instead of F^{el} the more accurate (excess Gibbs energy) G^{el} .

But the arguments are incorrect as eqns. (31) and (FG906-11) clearly demonstrate. During the charging process we must keep the variables (T, V, n, ϵ) constant in order to perform the integration of the partial charging process. When we keep (T, V, n) constant we also ensure that the classical contributions to the Helmholtz energy A^e are not altered during the charging process. Thus we can calculate the additional (Zusatz) chemical potentials due to the charging of the ions and related properties from the derivatives of A^e . The pressure change P^e is simply $-(\partial A^e / \partial V)_{T,n}$.

5 The chemical potentials and other properties

The model derived in eqn. (31) is often denoted a primitive model because we do not recognise explicitly the molecular nature of the solvent. However, it should also be recognised that the model for A^e is only one of many contributions to the Helmholtz energy of the solution as pointed out above. The model does not include the interactions between charges and dipoles as well as effects induced by the ions. Besides the hydration of ions is not accounted for and this may be important because some water molecules appear to be held so tightly by ions that they are not able to participate in the solution of neutral solutes (McQuarrie, 1976). Another limitation is that the model does, strictly speaking, only apply to dilute solutions.

The model was derived under the assumption that the ions are dissolved in a continuous medium of constant permittivity. Actually the solvent is not a continuous medium, nor is the permittivity constant but this averaging of the influence of the solvent molecules is unavoidable in the derivation. However, when we calculate partial derivatives of A^e from eqn. (31), we have to take into account that the permittivity depends on the solution properties. In dilute solutions the permittivity equals the permittivity of the solvent, but for more concentrated solutions the permittivity decreases due to a reduction of the molar polarizability of the solvent and this has to be taken into account when we calculate the derived properties. In the expressions derived below we assumed that ϵ_∞ is constant.

The electric contribution to the chemical potential of an ion k is calculable as the derivative of A^e with respect to the mole number of the ion n_k at constant T and V . The chemical potentials are

$$\begin{aligned}
 \mu_k^e(T, V, n) &= \left(\frac{\partial A^e}{\partial n_k} \right)_{T,V} = \left(\frac{\partial A^{self}}{\partial n_k} \right)_\epsilon + \left(\frac{\partial A^{self}}{\partial \epsilon} \right)_n \left(\frac{\partial \epsilon}{\partial n_k} \right)_{T,V} \\
 &\quad + \left(\frac{\partial A^{el}}{\partial n_k} \right)_{T,V,\chi} + \sum_i \left(\frac{\partial A^{el}}{\partial \chi_i(\kappa a_i)} \right)_n \frac{\partial \chi_i(\kappa a_i)}{\partial \kappa} \left(\frac{\partial \kappa}{\partial n_k} \right)_{T,V} \\
 &= \frac{F^2 z_k^2}{8\pi N_A \epsilon a_k} - \frac{A^{self}}{\epsilon} \left(\frac{\partial \epsilon}{\partial n_k} \right)_{T,V} \\
 &\quad - \frac{A^{el} z_k^2}{\sum_j n_j z_j^2} - \frac{kTV z_k^2}{4\pi \sum_j n_j z_j^2} \left(\chi_k + \frac{\kappa \sum_i n_i z_i^2 \sigma_i}{2 \sum_j n_j z_j^2} \right) \\
 &\quad + \frac{kTV}{4\pi \sum_j n_j z_j^2} \left(\sum_i n_i z_i^2 \sigma_i \right) \frac{\kappa}{2\epsilon} \left(\frac{\partial \epsilon}{\partial n_k} \right)_{T,V} \tag{33}
 \end{aligned}$$

where

$$\sigma_i = \left(\frac{\partial \chi_i}{\partial \kappa} \right)_{T,V,n} = \frac{1}{a_i^2} \left[\frac{1}{1 + \kappa a_i} + \kappa a_i - 1 \right] = \frac{1}{a_i^2} \frac{(\kappa a_i)^2}{1 + \kappa a_i} \tag{34}$$

Furthermore, we have utilised that the derivatives of the Debye length are

$$\left(\frac{\partial \kappa}{\partial n_k} \right)_{T,V} = \left(\frac{\partial \kappa}{\partial n_k} \right)_{T,V,\epsilon} + \left(\frac{\partial \kappa}{\partial \epsilon} \right)_{T,V,n} \left(\frac{\partial \epsilon}{\partial n_k} \right)_{T,V} \tag{35}$$

$$\left(\frac{\partial \kappa}{\partial n_k} \right)_{T,V,\epsilon} = \frac{\kappa}{2} \frac{z_k^2}{\sum_j n_j z_j^2} \tag{36}$$

$$\left(\frac{\partial \kappa}{\partial \epsilon} \right)_{T,V,n} = -\frac{\kappa}{2\epsilon} \tag{37}$$

The pressure changes due to the charging process by an amount P^e because the charging process takes place a constant temperature and total volume.

The electric pressure is calculable as

$$\begin{aligned}
 -P^e &= \left(\frac{\partial A^e}{\partial V} \right)_{T,n} = \left(\frac{\partial A^{self}}{\partial \varepsilon} \right)_n \left(\frac{\partial \varepsilon}{\partial V} \right)_{T,n} \\
 &\quad + \left(\frac{\partial A^{el}}{\partial V} \right)_{T,n,\chi} + \sum_i \left(\frac{\partial A^{el}}{\partial \chi_i(\kappa a_i)} \right)_n \frac{\partial \chi_i(\kappa a_i)}{\partial \kappa} \left(\frac{\partial \kappa}{\partial V} \right)_{T,n} \\
 &= -\frac{A^{self}}{\varepsilon} \left(\frac{\partial \varepsilon}{\partial V} \right)_{T,n} + \frac{A^{el}}{V} \\
 &\quad + \frac{kTV}{8\pi} \frac{\sum_i n_i z_i^2 \sigma_i}{\sum_j n_j z_j^2} \left(\frac{\kappa}{V} + \frac{\kappa}{\varepsilon} \left(\frac{\partial \varepsilon}{\partial V} \right)_{T,n} \right)
 \end{aligned} \tag{38}$$

In eqn. (38) we have utilised that

$$\left(\frac{\partial \kappa}{\partial V} \right)_{T,n} = -\frac{\kappa}{2V} - \frac{\kappa}{2\varepsilon} \left(\frac{\partial \varepsilon}{\partial V} \right)_{T,n} \tag{39}$$

The composition dependence of the permittivity contributes to the chemical potentials of the solvents and this contribution amounts to

$$\begin{aligned}
 \mu_s^e(T, V, n) &= \left(\frac{\partial A^e}{\partial n_s} \right)_{T,V} \\
 &= \left[\left(\frac{\partial A^{self}}{\partial \varepsilon} \right)_n + \sum_i \left(\frac{\partial A^{el}}{\partial \chi_i(\kappa a_i)} \right)_n \frac{\partial \chi_i(\kappa a_i)}{\partial \kappa} \frac{\partial \kappa}{\partial \varepsilon} \right] \left(\frac{\partial \varepsilon}{\partial n_s} \right)_{T,V} \\
 &= \left[-\frac{A^{self}}{\varepsilon} + \frac{kTV}{8\pi} \frac{\sum_i n_i z_i^2 \sigma_i}{\sum_j n_j z_j^2} \frac{\kappa}{\varepsilon} \right] \left(\frac{\partial \varepsilon}{\partial n_s} \right)_{T,V}
 \end{aligned} \tag{40}$$

The derivative of the Debye length κ with respect to the solvent mole number is non-zero in mixed solvents as analysed in eqn. (24). The derivatives $(\partial \varepsilon / \partial n_s)_{T,V}$, $(\partial \varepsilon / \partial n_k)_{T,V}$ and $(\partial \varepsilon / \partial V)_{T,n}$ must be estimated from an appropriate correlation. The correlation of the relative permittivity of aqueous salt solutions shown in eqn. (26) depends on the mole numbers of the ions n_+ , n_- , the volume V , and the temperature T , but not on the mole number of water in the solution.

Neither μ_k^e nor μ_s^e are activity coefficients but the electric contributions to the chemical potentials of ions and solvents in an electrolyte solution.

6 The molality-scale chemical potential

When reporting experimental measurements on electrolytes, the experimental data are often tabulated in dependence of the molality and besides the definition of the activity coefficients on the molality-scale differs from the classical definition of the activity coefficient. The scope of this section is to explain how to convert molality-scale activity coefficients to classical activity coefficients. In what follows we assume the solvent to be water. To convert from mole fraction to molality we use the identity

$$\frac{x_i}{x_w} = \frac{m_i}{m_0} \quad (41)$$

x_w is the mole fraction of water, m_i the molality of species i and m_0 the molality of pure water, i.e. 55.51 mole/kg. The activity coefficient is defined in eqn. (119) of Section 11 in Chapter 1. According to eqns. (119) and (120) of Section 11 the activity coefficient of species i is calculable from the equation

$$\mu_i(T, P, n) = \mu_i^\circ(T, P) + RT \ln x_i \gamma_i(T, P, n) \quad (42)$$

When we insert the mole fraction x_i from eqn. (41) in eqn. (42), the result is

$$\mu_i(T, P, n) = \mu_i^\circ(T, P) - RT \ln m_0 + RT \ln m_i x_w \gamma_i(T, P, n) \quad (43)$$

The activity coefficient in the molality-scale thermodynamics is defined by the equation

$$\mu_i(T, P, m) = \ddot{\mu}_i^* + RT \ln m_i \ddot{\gamma}_i(T, P, m) \quad (44)$$

where $\ddot{\mu}_i^*$ is the molality-scale reference potential and $\ddot{\gamma}_i$ is a so-called activity coefficient on the molality-scale. Note that $\ln \ddot{\gamma}_i$ is not a partial molar property. Furthermore, the potentials $\ddot{\mu}_i^*$ are those of a (hypothetical) solution of unit molality in which $\ddot{\gamma}_i$ is unity. The potentials $\ddot{\mu}_i^*$ do not have an immediate physical significance. Besides, molality is an inconvenient scale for concentrated solutions because $m_i \rightarrow \infty$ when we reach the pure solute and it is inconvenient for mixed solvents.

Since the chemical potentials in eqns. (43) and (44) must represent the same physical reality, we shall conclude that $\mu_i(T, P, m) = \mu_i(T, P, n)$ and in consequence of this one defines $\ddot{\mu}_i^*$ by the equation

$$\ddot{\mu}_i^* = \mu_i^\circ(T, P) - RT \ln m_0 \quad (45)$$

and thus $\ddot{\gamma}_i$ must be calculable from the equation

$$\ddot{\gamma}_i(T, P, m) = x_w \gamma_i(T, P, n) \quad (46)$$

In most of the available models of $\bar{\gamma}_i(T, P, \mathbf{m})$ the composition vector \mathbf{m} does not include the solvent.

The analysis in this section differs from the discussion in Section 13. In Section 13 we a priori assumed that the activity coefficients have the very same definition and physical significance. This is not the case in this analysis. We follow the conventional approach because our scope is not to obtain a unified framework, but to show how to convert from the molality-scale activity coefficient to the classical activity coefficient. Therefore eqn. (45) is not identical with eqn. (161) of Section 13 in Chapter 1.

In the classical thermodynamics as well as in the molality-scale thermodynamics, a solution is considered ideal when $\gamma_i = 1$ and $\bar{\gamma} = 1$ for all compositions \mathbf{n} or \mathbf{m} . Eqn. (42) conforms to the definition of an ideal mixture, eqn. (111) of Section 10 and this equation, eqn. (111), is in accord with the equation of the chemical potential of a perfect gas, eqn. (95) of Section 7. This means that in the framework of the classical thermodynamics, the perfect gas mixture is an ideal mixture but the ideal mixture is not necessarily a perfect gas mixture.

If the equation

$$\mu_i^{id'}(T, P, \mathbf{m}) = \bar{\mu}_i^* + RT \ln m_0 \quad (47)$$

defines an ‘ideal’ mixture, it has the result that a perfect gas mixture is no longer considered an ideal mixture, and in consequence of this, the molality-scale thermodynamics is not compatible with the classical framework. The difference in ‘ideal’ solution behaviour as reflected in eqns. (42) and (44) is

$$\mu_i^{id}(T, P, \mathbf{n}) - \mu_i^{id'}(T, P, \mathbf{m}) = RT \ln x_w \quad (48)$$

If a solution is considered ‘ideal’ on the molality-scale, $\bar{\gamma}_i = 1$ for all \mathbf{m} , all activity coefficients on the mole number scale, $\gamma_i(T, P, \mathbf{n})$, are $1/x_w$. Activity coefficients reported on the molality-scale must therefore be converted to attain a physical significance.

The molality-scale chemical potential, eqn. (44), offers no advantage over the classical chemical potential, eqn. (42). Only the classical definition conforms to the definition of an ideal mixture that results in the well-known relations for the ideal solution

$$G = \sum_i n_i \mu_i, \quad V = \sum_i n_i v_i \quad \text{and} \quad S = \sum_i n_i s_i - R \sum_i n_i \ln x_i \quad (49)$$

Establishing concentration scale dependent definitions of the ideal and the non-ideal mixture simply makes no sense. Regrettably, some definitions in

thermodynamics are ambiguous which adds to the confusion. The definitions that establish the ideal mixture and the non-ideal mixture must be independent of whether we deal with hydrocarbon mixtures, mixtures of commodity chemicals, polymer mixtures or electrolyte solutions. If we take three (hypothetical) ideal mixtures, one mixture of commodity chemicals (mole fraction scale), another of polymers (volume fraction scale) and a third of aqueous electrolytes (molality-scale) and mix them, in what sense is this mixture then ideal?

7 The electrostatic Helmholtz energy of dipolar ions

In 1932 Scatchard and Kirkwood published a paper dealing with complex ions in electrolyte solutions. In this and a subsequent paper by Kirkwood two years later in 1934, the electric contribution to the Helmholtz energy of a complex ion was derived. A complex ion is an ion that has a permanent charge distribution at its isoelectric point where the net charge is zero. Complex ions include amino acids, peptides and proteins. Amino acids are simple dipolar – or zwitterions. Glycine is an amino acid with one amino and one carboxylic acid group. At its isoelectric point it carries no net charge but it has a very large dipole moment due to the presence of one positive and one negative charge.

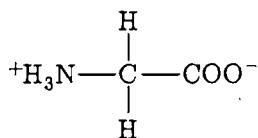


Figure 6: A solute glycine molecule at its isoelectric point.

According to the theory, a complex ion is regarded as a spherical molecule of diameter b having not only a net charge but also multipoles. The distance of closest approach a is larger than or equal to the diameter b . In the monograph by Cohn and Edsall from 1943 Kirkwood concludes that the final result does not differ whether the zwitterion is considered as a sphere or as an ellipse. The work of charging of a complex ion in solution comprises of three contributions. Two of these contributions are similar to the contributions of simple ions. The first contribution is due to the self-energy of charging each ion in the solution in the effective absence of the other ions and this contribution is known as the self potential or the Born potential. This contribution was analysed in Section 4. The second contribution originates from the energy due to the mutual electric interactions of the ions and it is similar to the

Debye-Hückel potential. For complex ions there is a third contribution due to the interaction between the electric dipole and the simple ions in solution.

In this section we calculate the contribution to the Helmholtz energy due to the presence of an electric dipole in a complex ion. The contributions due to the regular charges are calculable from the expressions derived in Section 4.

If the zwitterion has a dipole moment δ , the work of charging due to the formation of a permanent dipole moment δ is (Kirkwood, 1934; Scatchard and Kirkwood, 1932)

$$W(\delta) = -\frac{3}{8\pi \epsilon a^3} \left(\frac{\epsilon}{2\epsilon + \epsilon_{in}} \right)^2 \frac{(\kappa a)^2}{K_2(\kappa a) + \frac{\epsilon - \epsilon_{in}}{2\epsilon + \epsilon_{in}} \left(\frac{b}{a} \right)^3 \frac{(\kappa a)^2}{3}} \quad (50)$$

κ is the Debye length is defined in eqn. (29). ϵ is the permittivity of the surrounding fluid and ϵ_{in} is the permittivity inside the sphere of radius b where $b \leq a$. For dilute solutions Kirkwood derived the expression $K_2(\kappa a) = 1 + \kappa a + \frac{1}{3}(\kappa a)^2$. We assume that $\epsilon_{in} \leq \epsilon$ and if α denotes the ratio ϵ_{in}/ϵ , we write eqn. (50) in a neater form

$$W(\delta) = -\frac{3}{8\pi \epsilon a^3} \left(\frac{1}{2 + \alpha} \right)^2 \frac{(\kappa a)^2}{1 + \kappa a + \frac{(\kappa a)^2}{3} + \frac{1 - \alpha}{2 + \alpha} \left(\frac{b}{a} \right)^3 \frac{(\kappa a)^2}{3}} \quad (51)$$

Since for physical reasons $b \leq a$, and from the assumption $\alpha \leq 1$, we conclude that the term $\frac{1}{3} \frac{1 - \alpha}{2 + \alpha} \left(\frac{b}{a} \right)^3$ must be less than $\frac{1}{6}$, and if ϵ_{in} is of the order of magnitude of ϵ , i.e. $\alpha \approx 1$, this term becomes negligible. Therefore, if we add the two quadratic terms, the maximum value these terms can attain is $\frac{1}{2}(\kappa a)^2$, that is, the expression for the work of charging of a single dipolar ion can be simplified to

$$W(\delta) = -\frac{3}{8\pi \epsilon a^3} \left(\frac{1}{2 + \alpha} \right)^2 \frac{(\kappa a)^2}{1 + \kappa a + \frac{1}{2}(\kappa a)^2} \quad (52)$$

The formula, derived by Kirkwood, for the work of charging due to the formation of a permanent ion-dipole moment is not identical with eqn. (52). He argued that $\alpha \ll 1$ and that essentially $K_2(\kappa a)$ is unity and therefore his equivalent of eqn. (52) is

$$W(\delta) = -\frac{3}{32\pi \epsilon a^3} \frac{\delta^2}{1 + \frac{b^3}{6a^3} (\kappa a)^2} \frac{(\kappa a)^2}{b^3} \quad$$

We do not follow Kirkwood's arguments because the terms proportional to $(\kappa a)^2$ must always be less than κa because κa is a small number. Therefore we prefer to use eqn. (52) to obtain the expressions of the chemical potentials and other derivatives.

The work of charging due to the formation of dipolar ions having permanent dipole moments δ_i is the sum of the individual contributions

$$\begin{aligned} W(\delta) &= \sum_i N_i W_i(\delta) \\ &= -\frac{3}{8\pi\varepsilon} \sum_i \frac{N_i \delta_i^2}{a_i^3} \left(\frac{1}{2 + \alpha_i} \right)^2 \frac{(\kappa a_i)^2}{1 + \kappa a_i + \frac{1}{2}(\kappa a_i)^2} \end{aligned} \quad (53)$$

Since W corresponds to the additional internal configurational energy due to the charging of dipolar ions, the contribution to the configurational Helmholtz energy is calculable as

$$\frac{A^{dip}}{T} = \int U^{dip} d\frac{1}{T} = \int W d\frac{1}{T} \quad (54)$$

The integration is performed at constant temperature T , volume V , composition n , and permittivities ε and ε_{in} . These assumptions are similar to the assumptions made by Debye and Hückel (1923) as well as by Kirkwood (1934), and they are consistent with the continuum theory where the models are derived under the assumption that the ions are dissolved in a continuous medium of constant permittivity as discussed in Section 5. We perform the integration in κ rather than in $\frac{1}{T}$ by utilising the substitution

$$\begin{aligned} 2\kappa d\kappa &= \frac{e^2}{\varepsilon kV} \sum_j N_j z_j^2 d\frac{1}{T} \quad \Leftrightarrow \\ \left(d\frac{1}{T} \right)_{V,N,\varepsilon} &= \frac{2\varepsilon kV \kappa}{e^2 \sum_j N_j z_j^2} d\kappa \end{aligned} \quad (55)$$

The result is

$$\begin{aligned} A^{dip} &= -\frac{3kTV}{4\pi e^2 \sum_j N_j z_j^2} \sum_i \frac{N_i \delta_i^2}{a_i^5} \left(\frac{1}{2 + \alpha_i} \right)^2 \\ &\quad \times \int_0^{\kappa a_i} \frac{(\kappa a_i)^3}{1 + \kappa a_i + \frac{1}{2}(\kappa a_i)^2} d(\kappa a_i) \\ &= -\frac{3N_A RTV}{4\pi F^2 \sum_j n_j z_j^2} \sum_i n_i \delta_i^2 \beta_i \theta_i(\kappa a_i) \end{aligned} \quad (56)$$

where

$$\beta_i = \left(\frac{\epsilon}{2\epsilon + \epsilon_{in,i}} \right)^2 = \left(\frac{1}{2 + \alpha_i} \right)^2, \quad \frac{1}{9} \leq \beta_i \leq \frac{1}{4} \quad (57)$$

and

$$\theta_i(\kappa a_i) = \frac{1}{a_i^5} \left[-4\kappa a_i + (\kappa a_i)^2 + 2 \ln \left(1 + \kappa a_i + \frac{1}{2}(\kappa a_i)^2 \right) + 4 \tan^{-1}(\kappa a_i + 1) - \pi \right] \quad (58)$$

and of course

$$\frac{\partial \theta_i(\kappa a_i)}{\partial \kappa} = \tau_i(\kappa a_i) = \frac{1}{a_i^4} \frac{(\kappa a_i)^3}{1 + \kappa a_i + \frac{1}{2}(\kappa a_i)^2} \quad (59)$$

The simplified equation

If we disregard the second order term in the denominator of eqn. (58) the result is

$$\begin{aligned} A^{dip} &= -\frac{3kTV}{4\pi e^2 \sum_j N_j z_j^2} \sum_i \frac{N_i \delta_i^2}{a_i^5} \left(\frac{1}{2 + \alpha_i} \right)^2 \int_0^{\kappa a_i} \frac{(\kappa a_i)^3}{1 + \kappa a_i} d(\kappa a_i) \\ &= -\frac{3N_A RTV}{4\pi F^2 \sum_j n_j z_j^2} \sum_i n_i \delta_i^2 \beta_i \theta_i(\kappa a_i) \end{aligned} \quad (60)$$

In the simplified case θ_i denotes

$$\theta_i(\kappa a_i) = \frac{1}{a_i^5} \left[\kappa a_i - \frac{1}{2}(\kappa a_i)^2 + \frac{1}{3}(\kappa a_i)^3 - \ln(1 + \kappa a_i) \right] \quad (61)$$

and of course

$$\frac{\partial \theta_i(\kappa a_i)}{\partial \kappa} = \tau_i(\kappa a_i) = \frac{1}{a_i^4} \frac{(\kappa a_i)^3}{1 + \kappa a_i} \quad (62)$$

Eqns. (56) and (60) are identical in form and the only difference is the expressions for the functions θ_i shown in eqns. (58) and (61), respectively.

8 The chemical potentials of dipolar ions and other properties

The model was derived under the assumption that the dipolar ions are dissolved in a continuous medium of constant permittivity as discussed in Section 5. Actually, among others, the permittivity depends on temperature, volume and the molar polarizabilities of the species in the solution. When we calculate the partial derivatives of A^{dip} from eqn. (56) or (60), we have to

take into account that the permittivity of the solution thus depends on the temperature, volume, and composition of the solution.

In this section we consider the contribution to the chemical potential due to the presence of an electric dipole in a complex ion. The contributions due to the regular charges are calculable from the expressions derived in Section 5.

In the expressions, we derive in this section we have assumed that β_i is a constant, that is, we assume that $\epsilon/\epsilon_{in,i}$ independent of the fluid properties. This may be a reasonable approximation but in Section 9: 'Computation of the first and second order derivatives', we have included the derivatives of β_i .

The contribution to the chemical potential of a dipolar ion $\mu_k^{dip}(T, V, n)$ is calculable as the derivative of A^{dip} with respect to the mole number of the dipolar ion n_k at constant T and V . The derivatives of A^{dip} are

$$\begin{aligned} \mu_k^{dip}(T, V, n) &= \left(\frac{\partial A^{dip}}{\partial n_k} \right)_{T, V, \theta} + \sum_i \left(\frac{\partial A^{dip}}{\partial \theta_i(\kappa a_i)} \right)_n \frac{\partial \theta_i(\kappa a_i)}{\partial \kappa} \left(\frac{\partial \kappa}{\partial n_k} \right)_{T, V} \\ &= - \frac{A^{dip} z_k^2}{\sum_j n_j z_j^2} - \frac{3N_A RTV}{4\pi F^2 \sum_j n_j z_j^2} \left(\delta_k^2 \beta_k \theta_k + \frac{\kappa z_k^2}{2} \frac{\sum_i n_i \delta_i^2 \beta_i \tau_i}{\sum_j n_j z_j^2} \right) \\ &\quad + \frac{3N_A RTV}{4\pi F^2 \sum_j n_j z_j^2} \left(\sum_i n_i \delta_i^2 \beta_i \tau_i \right) \frac{\kappa}{2\epsilon} \left(\frac{\partial \epsilon}{\partial n_k} \right)_{T, V} \end{aligned} \quad (63)$$

The derivatives of θ_i are calculable from either eqn. (59) or (62) depending on which model we apply for the function θ .

The pressure changes due to the charging process by an amount P^{dip} because the charging process takes place a constant temperature and total volume. The electrostatic pressure is calculable as

$$\begin{aligned} -P^{dip} &= \left(\frac{\partial A^{dip}}{\partial V} \right)_{T, n} \\ &= \left(\frac{\partial A^{dip}}{\partial V} \right)_{T, \theta} + \sum_i \left(\frac{\partial A^{dip}}{\partial \theta_i(\kappa a_i)} \right)_n \left(\frac{\partial \theta_i(\kappa a_i)}{\partial \kappa} \right)_{T, n} \left(\frac{\partial \kappa}{\partial V} \right)_{T, n} \\ &= \frac{A^{dip}}{V} + \frac{3N_A RTV}{4\pi F^2} \frac{\sum_i n_i \delta_i^2 \beta_i \tau_i}{\sum_j n_j z_j^2} \left(\frac{\kappa}{V} + \frac{\kappa}{\epsilon} \left(\frac{\partial \epsilon}{\partial V} \right)_{T, n} \right) \end{aligned} \quad (64)$$

The derivative of the Debye length with respect to the volume is calculable from eqn. (39). The derivative of the relative permittivity with respect to V must be estimated from an appropriate correlation.

The composition dependence of the permittivity contributes to the chemical potentials of the solvents by the amount

$$\begin{aligned}\mu_s^{dip}(T, V, \mathbf{n}) &= \left(\frac{\partial A^{dip}}{\partial n_s} \right)_{T,V} = \sum_i \left(\frac{\partial A^{dip}}{\partial \theta_i(\kappa a_i)} \right)_n \frac{\partial \theta_i(\kappa a_i)}{\partial \kappa} \frac{\partial \kappa}{\partial \epsilon} \left(\frac{\partial \epsilon}{\partial n_s} \right)_{T,V} \\ &= \frac{3N_A RTV}{4\pi F^2} \sum_i \frac{n_i \delta_i^2 \beta_i \tau_i}{\sum_j n_j z_j^2} \frac{\kappa}{\epsilon} \left(\frac{\partial \epsilon}{\partial n_k} \right)_{T,V}\end{aligned}\quad (65)$$

The derivatives of the Debye length with respect to the permittivity is shown in eqn. (37) and the derivatives of θ_i are calculable from either eqn. (59) or (62) depending on which model we apply. The derivative of the Debye-length κ with respect to the solvent mole number is non-zero in mixed solvents as analysed in eqn. (24). The derivatives of the relative permittivity must be estimated from an appropriate correlation. We have not developed such a correlation, but want to point out that all dipolar species, solvents or solutes, will contribute to the permittivity of the solution.

9 Computation of the first and second order derivatives

It is important to develop a notations which is easy to handle and easy to understand. One can of course write the derivatives the way we did it in the previous section but we find it convenient to simplify it a little. Let F denote a function $F(x, y, \mathbf{n})$. The notation used for the partial derivatives of F are abbreviated in the following way

$$F_x = \left(\frac{\partial F}{\partial x} \right)_{y,n} \quad (66)$$

$$F_y = \left(\frac{\partial F}{\partial y} \right)_{x,n} \quad (67)$$

$$F_i = \left(\frac{\partial F}{\partial n_i} \right)_{x,y,\mathbf{n} \setminus n_i} \quad (68)$$

The notation used for second derivatives are

$$F_{xy} = F_{yx} = \left(\frac{\partial^2 F}{\partial x \partial y} \right)_n \quad (69)$$

$$F_{yi} = F_{iy} = \left(\frac{\partial^2 F}{\partial y \partial n_i} \right)_{x,n \setminus n_i} \quad (70)$$

$$F_{ij} = F_{ji} = \left(\frac{\partial^2 F}{\partial n_i \partial n_j} \right)_{x,y,\mathbf{n} \setminus n_i, n_j} \quad (71)$$

In the extended Newton-Raphson procedure, Section 5 of Chapter 3, we make use of the second derivative of the pressure with respect to the volume. Therefore we have to calculate the third derivative of the Helmholtz function and the auxiliary functions with respect to the volume.

The self potential

The self potential is the first term of eqn. (31)

$$A^{self} = \frac{F^2}{8\pi N_A \epsilon} \sum_{\alpha} \frac{n_{\alpha} z_{\alpha}^2}{a_{\alpha}} \quad (72)$$

The subscript α denotes the running index. To facilitate a neat notation we define two auxiliary functions g and F

$$g = \sum_{\alpha} \frac{n_{\alpha} z_{\alpha}^2}{a_{\alpha}} \quad (73)$$

$$F = \frac{A^{self} 8\pi N_A}{F^2} = \frac{g}{\epsilon} \quad \Leftrightarrow \quad F\epsilon = g \quad (74)$$

Calculation of the derivatives of F is thus straightforward.

Derivatives of g and F

$$g_i = \frac{z_i^2}{a_i} \quad (75)$$

$$F_i \epsilon + F \epsilon_i = g_i \quad \Leftrightarrow \quad F_i = \frac{g_i - F \epsilon_i}{\epsilon} \quad (76)$$

$$F_T \epsilon + F \epsilon_T = g_i \quad \Leftrightarrow \quad F_T = -\frac{F \epsilon_T}{\epsilon} \quad (77)$$

$$F_V \epsilon + F \epsilon_V = g_i \quad \Leftrightarrow \quad F_V = -\frac{F \epsilon_V}{\epsilon} \quad (78)$$

We differentiate once more

$$\begin{aligned} F_{ij} \epsilon + F_i \epsilon_j + F_j \epsilon_i + F \epsilon_{ij} &= 0 \quad \Leftrightarrow \\ F_{ij} &= -\frac{F_i \epsilon_j + F_j \epsilon_i + F \epsilon_{ij}}{\epsilon} \end{aligned} \quad (79)$$

$$\begin{aligned} F_{Ti} \epsilon + F_T \epsilon_i + F_i \epsilon_T + F \epsilon_{Ti} &= 0 \quad \Leftrightarrow \\ F_{Ti} &= -\frac{F_T \epsilon_i + F_i \epsilon_T + F \epsilon_{Ti}}{\epsilon} \end{aligned} \quad (80)$$

$$F_{Vi}\varepsilon + F_V\varepsilon_i + F_i\varepsilon_V + F\varepsilon_{Vi} = 0 \Leftrightarrow \\ F_{Vi} = -\frac{F_V\varepsilon_i + F_i\varepsilon_V + F\varepsilon_{Vi}}{\varepsilon} \quad (81)$$

$$F_{VT}\varepsilon + F_V\varepsilon_T + F_T\varepsilon_V + F\varepsilon_{VT} = 0 \Leftrightarrow \\ F_{VT} = -\frac{F_V\varepsilon_T + F_T\varepsilon_V + F\varepsilon_{VT}}{\varepsilon} \quad (82)$$

$$F_{VV}\varepsilon + F_V\varepsilon_V + F_V\varepsilon_V + F\varepsilon_{VV} = 0 \Leftrightarrow \\ F_{VV} = -\frac{2F_V\varepsilon_V + F\varepsilon_{VV}}{\varepsilon} \quad (83)$$

$$F_{TT}\varepsilon + F_T\varepsilon_T + F_T\varepsilon_T + F\varepsilon_{TT} = 0 \Leftrightarrow \\ F_{TT} = -\frac{2F_T\varepsilon_T + F\varepsilon_{TT}}{\varepsilon} \quad (84)$$

Eqn. (83) is differentiated with respect to V

$$F_{VVV}\varepsilon + 3F_{VV}\varepsilon_V + 3F_V\varepsilon_{VV} + F\varepsilon_{VVV} = 0 \Leftrightarrow \\ F_{VVV} = -\frac{3F_{VV}\varepsilon_V + 3F_V\varepsilon_{VV} + F\varepsilon_{VVV}}{\varepsilon} \quad (85)$$

The Debye-Hückel equation

The electric contribution is the second term of eqn. (31)

$$A^{el} = \frac{kTV}{4\pi \sum_{\alpha} N_{\alpha} z_{\alpha}^2} \sum_{\alpha} n_{\alpha} z_{\alpha}^2 \chi_{\alpha} \quad (86)$$

where according to eqn. (32)

$$\chi_{\alpha}(T, V, \mathbf{n}, \varepsilon) = \frac{1}{a_{\alpha}^3} \left[\ln(1 + \kappa a_{\alpha}) - \kappa a_{\alpha} + \frac{1}{2}(\kappa a_{\alpha})^2 \right] \quad (87)$$

$$\kappa^2 = \frac{F^2}{RTV\varepsilon} \sum_{\alpha} n_{\alpha} z_{\alpha}^2 \quad (88)$$

To facilitate a neat notation we define five auxiliary functions

$$\beta = \frac{F^2}{R} \quad (89)$$

$$q = \sum_{\alpha} n_{\alpha} z_{\alpha}^2 \quad (90)$$

$$b_{\alpha} = \kappa a_{\alpha} \quad (91)$$

$$S = \sum_{\alpha} n_{\alpha} z_{\alpha}^2 \chi_{\alpha} \quad (92)$$

$$F = -\frac{4\pi A^{el}}{k} = \frac{TVS}{q} \quad (93)$$

The Debye length is therefore calculable as

$$\kappa^2 = \frac{\beta q}{TV\epsilon} \quad (94)$$

Calculation of the derivatives is thus straightforward.

Derivatives of q

q is a simple sum that only depends on the mole numbers.

$$q_i = z_i^2 \quad (95)$$

All other derivatives of q are zero.

Derivatives of F

The first order derivatives of F with respect to the independent variables are

$$F = \frac{TVS}{q} \Leftrightarrow Fq = TVS \quad (96)$$

$$F_i q + F q_i = TVS_i \Leftrightarrow F_i = \frac{TVS_i - F q_i}{q} \quad (97)$$

$$F_V q = TS + TVS_V \Leftrightarrow F_V = \frac{TS + TVS_V}{q} \quad (98)$$

$$F_T q = VS + TVS_T \Leftrightarrow F_T = \frac{VS + TVS_T}{q} \quad (99)$$

The second order derivatives of F with respect to the independent variables

$$F_{ij}q + F_i q_j + F_j q_i = TV S_{ij} \Leftrightarrow \\ F_{ij} = \frac{TV S_{ij} - F_i q_j - F_j q_i}{q} \quad (100)$$

$$F_{iV}q + F_V q_i = TS_i + TV S_{iV} \Leftrightarrow \\ F_{iV} = \frac{TS_i + TV S_{iV} - F_V q_i}{q} \quad (101)$$

$$F_{iT}q + F_T q_i = VS_i + TV S_{iT} \Leftrightarrow \\ F_{iT} = \frac{VS_i + TV S_{iT} - F_T q_i}{q} \quad (102)$$

$$F_{VV}q = 2TS_V + TV S_{VV} \Leftrightarrow \\ F_{VV} = \frac{2TS_V + TV S_{VV}}{q} \quad (103)$$

$$F_{TT}q = 2VS_T + TV S_{TT} \Leftrightarrow \\ F_{TT} = \frac{2VS_T + TV S_{TT}}{q} \quad (104)$$

$$F_{VT}q = S + TS_T + VS_V + TV S_{VT} \Leftrightarrow \\ F_{VT} = \frac{S + TS_T + VS_V + TV S_{VT}}{q} \quad (105)$$

and the third order derivative of F with respect to V

$$F_{VVV}q = 3TS_{VV} + TV S_{VVV} \Leftrightarrow \\ F_{VVV} = \frac{3TS_{VV} + TV S_{VVV}}{q} \quad (106)$$

Derivatives of χ_α

It is convenient to multiply χ_α on both sides with a_α^3 before we calculate the derivatives. That is,

$$\chi_\alpha a_\alpha^3 = \ln(1 + b_\alpha) - b_\alpha + \frac{1}{2}b_\alpha^2 \quad (107)$$

Since we have to include the running index, we use the following notation

$$(\chi_\alpha)_\kappa = \frac{\partial \chi_\alpha}{\partial \kappa} = \frac{\partial \chi_\alpha}{\partial b_\alpha} \frac{\partial b_\alpha}{\partial \kappa} = \frac{\partial \chi_\alpha}{\partial b_\alpha} a_\alpha \quad (108)$$

$$(\chi_\alpha)_{\kappa\kappa} = \frac{\partial^2 \chi_\alpha}{\partial \kappa^2} = \frac{\partial}{\partial \kappa} \frac{\partial \chi_\alpha}{\partial b_\alpha} a_\alpha = \frac{\partial^2 \chi_\alpha}{\partial b_\alpha^2} a_\alpha^2 \quad \text{etc.} \quad (109)$$

Consequently, we obtain the derivatives

$$(\chi_\alpha)_\kappa a_\alpha^2 = \frac{1}{1 + b_\alpha} - 1 + b_\alpha \quad (110).$$

$$(\chi_\alpha)_{\kappa\kappa} a_\alpha = -\frac{1}{(1 + b_\alpha)^2} + 1 \quad (111)$$

$$(\chi_\alpha)_{\kappa\kappa\kappa} = \frac{2}{(1 + b_\alpha)^3} \quad (112)$$

Derivatives of S

Eqn. (92) is differentiated once with respect to the variable x , a second time with respect to y , and finally with respect to z . These substitution variables (x, y, z) can be any one of the variables T and V .

$$S_x = \sum_\alpha n_\alpha z_\alpha^2 \frac{\partial \chi_\alpha}{\partial \kappa} \frac{\partial \kappa}{\partial x} = \left(\sum_\alpha n_\alpha z_\alpha^2 (\chi_\alpha)_\kappa \right) \kappa_x = S_{\kappa\kappa x} \quad (113)$$

$$S_{xy} = \left(\sum_\alpha n_\alpha z_\alpha^2 (\chi_\alpha)_{\kappa\kappa} \right) \kappa_x \kappa_y + S_{\kappa\kappa xy} = S_{\kappa\kappa} \kappa_x \kappa_y + S_{\kappa\kappa xy} \quad (114)$$

$$S_{xyz} = S_{\kappa\kappa\kappa} \kappa_x \kappa_y \kappa_z + S_{\kappa\kappa} (\kappa_{xz} \kappa_y + \kappa_x \kappa_{yz} + \kappa_{xy} \kappa_z) + S_{\kappa\kappa xyz} \quad (115)$$

where $S_{\kappa\kappa\kappa} = \sum_\alpha n_\alpha z_\alpha^2 (\chi_\alpha)_{\kappa\kappa\kappa}$.

The compositional derivatives of S are

$$S_i = z_i^2 \chi_i + S_{\kappa\kappa i} \quad (116)$$

$$S_{ij} = z_i^2 (\chi_i)_{\kappa\kappa j} + z_j^2 (\chi_j)_{\kappa\kappa i} + S_{\kappa\kappa} \kappa_i \kappa_j + S_{\kappa\kappa ij} \quad (117)$$

$$S_{iy} = z_i^2 (\chi_i)_{\kappa\kappa y} + S_{\kappa\kappa} \kappa_i \kappa_y + S_{\kappa\kappa iy} \quad (118)$$

Derivatives of the Debye length

We have now calculated the derivatives of q and F and what remains to be done is to calculate the derivatives of the Debye length

$$\kappa^2 = \frac{\beta q}{TV\varepsilon} \quad \Leftrightarrow \quad \kappa^2 TV\varepsilon = \beta q \quad (119)$$

where $\varepsilon = \varepsilon(T, V, \mathbf{n})$.

First order derivatives

$$2\kappa\kappa_i TV\varepsilon + \kappa^2 TV\varepsilon_i = \beta q_i \Leftrightarrow \kappa_i = \frac{\beta q_i - \kappa^2 TV\varepsilon_i}{2\kappa TV\varepsilon} \quad (120)$$

$$2\kappa\kappa_V V\varepsilon + \kappa^2 \varepsilon + \kappa^2 V\varepsilon_V = 0 \Leftrightarrow \kappa_V = -\kappa \frac{\varepsilon + V\varepsilon_V}{2V\varepsilon} \quad (121)$$

$$2\kappa\kappa_T T\varepsilon + \kappa^2 \varepsilon + \kappa^2 T\varepsilon_T = 0 \Leftrightarrow \kappa_T = -\kappa \frac{\varepsilon + T\varepsilon_T}{2T\varepsilon} \quad (122)$$

Second order derivatives

$$2\kappa_j\kappa_i TV\varepsilon + 2\kappa\kappa_{ij} TV\varepsilon + 2\kappa\kappa_i TV\varepsilon_j + 2\kappa\kappa_j TV\varepsilon_i + \kappa^2 TV\varepsilon_{ij} = 0 \Leftrightarrow \kappa_{ij} = -\frac{\kappa_j\kappa_i \varepsilon + \kappa\kappa_i \varepsilon_j + \kappa\kappa_j \varepsilon_i + \frac{1}{2}\kappa^2 \varepsilon_{ij}}{\kappa \varepsilon}. \quad (123)$$

$$2\kappa_{Vi} V\varepsilon + 2\kappa_V V\varepsilon_i + \kappa_i \varepsilon + \kappa \varepsilon_i + \kappa_i V\varepsilon_V + \kappa V\varepsilon_{Vi} = 0 \Leftrightarrow \kappa_{Vi} = -\frac{2\kappa_V V\varepsilon_i + \kappa_i \varepsilon + \kappa \varepsilon_i + \kappa_i V\varepsilon_V + \kappa V\varepsilon_{Vi}}{2V\varepsilon} \quad (124)$$

$$2\kappa_{Ti} T\varepsilon + 2\kappa_T T\varepsilon_i + \kappa_i \varepsilon + \kappa \varepsilon_i + \kappa_i T\varepsilon_T + \kappa T\varepsilon_{Ti} = 0 \Leftrightarrow \kappa_{Ti} = -\frac{2\kappa_T T\varepsilon_i + \kappa_i \varepsilon + \kappa \varepsilon_i + \kappa_i T\varepsilon_T + \kappa T\varepsilon_{Ti}}{2T\varepsilon} \quad (125)$$

$$2\kappa_{VV} V\varepsilon + 3\kappa_V V\varepsilon_V + 3\kappa_V \varepsilon + 2\kappa \varepsilon_V + \kappa V\varepsilon_{VV} = 0 \Leftrightarrow \kappa_{VV} = -\frac{3\kappa_V V\varepsilon_V + 3\kappa_V \varepsilon + 2\kappa \varepsilon_V + \kappa V\varepsilon_{VV}}{2V\varepsilon} \quad (126)$$

$$2\kappa_{TT} T\varepsilon + 3\kappa_T T\varepsilon_T + 3\kappa_T \varepsilon + 2\kappa \varepsilon_T + \kappa T\varepsilon_{TT} = 0 \Leftrightarrow \kappa_{TT} = -\frac{3\kappa_T T\varepsilon_T + 3\kappa_T \varepsilon + 2\kappa \varepsilon_T + \kappa T\varepsilon_{TT}}{2T\varepsilon} \quad (127)$$

$$2\kappa_{VT}V\epsilon + 2\kappa_VV\epsilon_T + \kappa_{TE} + \kappa_{ET} + \kappa_TV\epsilon_V + \kappa V\epsilon_{TV} = 0 \quad \Leftrightarrow$$

$$\kappa_{VT} = -\frac{2\kappa_VV\epsilon_T + \kappa_{TE} + \kappa_{ET} + \kappa_TV\epsilon_V + \kappa V\epsilon_{TV}}{2V\epsilon} \quad (128)$$

or the equivalent

$$2\kappa_{TV}T\epsilon + 2\kappa_TT\epsilon_V + \kappa_V\epsilon + \kappa_V + \kappa_VT\epsilon_T + \kappa TE_{VT} = 0 \quad \Leftrightarrow$$

$$\kappa_{TV} = -\frac{2\kappa_TT\epsilon_V + \kappa_V\epsilon + \kappa_V + \kappa_VT\epsilon_T + \kappa TE_{VT}}{2T\epsilon} \quad (129)$$

Third order derivative with respect to V

$$2\kappa_{VVV}V\epsilon + 5\kappa_{VV}\epsilon + 5\kappa_{VV}V\epsilon_V + 8\kappa_V\epsilon_V$$

$$+ 4\kappa_VV\epsilon_{VV} + 3\kappa\epsilon_{VV} + \kappa V\epsilon_{VVV} = 0 \quad \Leftrightarrow$$

$$\kappa_{VVV} = -\frac{5\kappa_{VV}\epsilon + 5\kappa_{VV}V\epsilon_V + 8\kappa_V\epsilon_V}{2V\epsilon}$$

$$-\frac{4\kappa_VV\epsilon_{VV} + 3\kappa\epsilon_{VV} + \kappa V\epsilon_{VVV}}{2V\epsilon} \quad (130)$$

Derivatives with respect to the solvent mole number n_s

$$2\kappa\kappa_s\epsilon + \kappa^2TV\epsilon_s = 0 \quad \Leftrightarrow \quad \kappa_s = -\frac{\kappa\epsilon_s}{2\epsilon} \quad (131)$$

$$2\kappa_s\kappa_s\epsilon + 2\kappa\kappa_{ss}\epsilon_s + 2\kappa\kappa_s\epsilon_s + \kappa^2\epsilon_{ss} = 0 \quad \Leftrightarrow$$

$$\kappa_{ss} = -\frac{2\kappa_s^2\epsilon + 4\kappa\kappa_s\epsilon_s + \kappa^2\epsilon_{ss}}{2\kappa\epsilon} \quad (132)$$

The Kirkwood equation

The interactions between the dipolar ions and the simple ions contribute to the Helmholtz energy. The expression is shown in eqn. (56) or (60). The two expressions are identical in form and the only difference is the expression for the auxiliary function θ_α .

$$A^{dip} = -\frac{3N_A RTV}{4\pi F^2 \sum_\alpha n_\alpha z_\alpha^2} \sum_\alpha n_\alpha \beta_\alpha \delta_\alpha^2 \theta_\alpha \quad (133)$$

where $\theta_\alpha(T, V, n, \epsilon)$ is either, eqn. (58)

$$\theta_\alpha = \frac{1}{a_\alpha^5} \left[-4\kappa a_\alpha + (\kappa a_\alpha)^2 + 2\ln(1 + \kappa a_\alpha + \frac{1}{2}(\kappa a_\alpha)^2) \right. \\ \left. + 4\tan^{-1}(\kappa a_\alpha + 1) - \pi \right] \quad (134)$$

or eqn. (61)

$$\theta_\alpha = \frac{1}{a_\alpha^5} \left[\kappa a_\alpha - \frac{1}{2} (\kappa a_\alpha)^2 + \frac{1}{3} (\kappa a_\alpha)^3 - \ln(1 + \kappa a_\alpha) \right] \quad (135)$$

We define four auxiliary functions

$$q = \sum_{\alpha} n_{\alpha} z_{\alpha}^2 \quad (136)$$

$$b_{\alpha} = \kappa a_{\alpha} \quad (137)$$

$$S = \sum_{\alpha} n_{\alpha} \beta_{\alpha} \delta_{\alpha}^2 \theta_{\alpha} \quad (138)$$

$$F = -\frac{4\pi F^2 A^{dip}}{3N_A R} = \frac{TVS}{q} \quad (139)$$

The functional forms of the derivatives of F are thus identical with the derivatives of F in the Debye-Hückel equation, eqn. (96), when remembering that the sum S is a different function.

Derivatives of θ_{α}

It is convenient to use the following notation

$$(\theta_{\alpha})_{\kappa} = \frac{\partial \theta_{\alpha}}{\partial \kappa} = \frac{\partial \theta_{\alpha}}{\partial b_{\alpha}} \frac{\partial b_{\alpha}}{\partial \kappa} = \frac{\partial \theta_{\alpha}}{\partial b_{\alpha}} a_{\alpha} \quad (140)$$

$$(\theta_{\alpha})_{\kappa\kappa} = \frac{\partial^2 \theta_{\alpha}}{\partial \kappa^2} = \frac{\partial}{\partial \kappa} \frac{\partial \theta_{\alpha}}{\partial b_{\alpha}} a_{\alpha} = \frac{\partial^2 \theta_{\alpha}}{\partial b_{\alpha}^2} a_{\alpha}^2 \quad \text{etc.} \quad (141)$$

Before we calculate the derivatives of θ_{α} it is convenient to multiply on both sides with a_{α}^5 .

When

$$a_{\alpha}^5 \theta_{\alpha} = -4b_{\alpha} + b_{\alpha}^2 + 2 \ln(1 + b_{\alpha} + \frac{1}{2}b_{\alpha}^2) + 4 \tan^{-1}(b_{\alpha} + 1) - \pi \quad (142)$$

then the derivatives are

$$a_{\alpha}^5 (\theta_{\alpha})_{\kappa} = -4a_{\alpha} + 2b_{\alpha}a_{\alpha} + 2 \frac{a_{\alpha} + b_{\alpha}a_{\alpha}}{1 + b_{\alpha} + \frac{1}{2}b_{\alpha}^2} + \frac{4a_{\alpha}}{1 + (b_{\alpha} + 1)^2} \quad \Leftrightarrow$$

$$a_{\alpha}^4 (\theta_{\alpha})_{\kappa} = \frac{b_{\alpha}^3}{1 + b_{\alpha} + \frac{1}{2}b_{\alpha}^2} \quad (143)$$

$$a_\alpha^4(\theta_\alpha)_{\kappa\kappa}(1 + b_\alpha + \frac{1}{2}b_\alpha^2) + a_\alpha^4(\theta_\alpha)_\kappa(a_\alpha + b_\alpha a_\alpha) = 3\beta_\alpha^2 a_\alpha \quad \Leftrightarrow$$

$$a_\alpha^3(\theta_\alpha)_{\kappa\kappa} = \frac{3b_\alpha^2 - a_\alpha^4(\theta_\alpha)_\kappa(1 + b_\alpha)}{1 + b_\alpha + \frac{1}{2}b_\alpha^2} \quad (144)$$

$$a_\alpha^3(\theta_\alpha)_{\kappa\kappa\kappa}(1 + b_\alpha + \frac{1}{2}b_\alpha^2) + a_\alpha^3(\theta_\alpha)_{\kappa\kappa}(a_\alpha + b_\alpha a_\alpha) = 6\beta_\alpha a_\alpha - a_\alpha^4(\theta_\alpha)_{\kappa\kappa}(1 + b_\alpha) - a_\alpha^4(\theta_\alpha)_\kappa a_\alpha \quad \Leftrightarrow$$

$$a_\alpha^2(\theta_\alpha)_{\kappa\kappa\kappa} = \frac{6b_\alpha - 2a_\alpha^3(\theta_\alpha)_{\kappa\kappa}(1 + b_\alpha) - a_\alpha^4(\theta_\alpha)_\kappa}{1 + b_\alpha + \frac{1}{2}b_\alpha^2} \quad (145)$$

When

$$a_\alpha^5 \theta_\alpha = b_\alpha - \frac{1}{2}b_\alpha^2 + \frac{1}{3}b_\alpha^3 - \ln(1 + b_\alpha) \quad (146)$$

then the derivatives are

$$a_\alpha^4(\theta_\alpha)_\kappa = 1 - b_\alpha + b_\alpha^2 - \frac{1}{1 + b_\alpha} = \frac{b_\alpha^3}{1 + b_\alpha} \quad (147)$$

$$a_\alpha^3(\theta_\alpha)_{\kappa\kappa} = -1 + 2b_\alpha + \frac{1}{(1 + b_\alpha)^2} \quad (148)$$

$$a_\alpha^2(\theta_\alpha)_{\kappa\kappa\kappa} = 2 - \frac{2}{(1 + b_\alpha)^3} \quad (149)$$

Derivatives of S

In the Debye-Hückel equation the sum S is $S = \sum_\alpha n_\alpha z_\alpha^2 \chi_\alpha$. In the Kirkwood equation the sum S has the following form $S = \sum_\alpha n_\alpha \beta_\alpha \delta_\alpha^2 \theta_\alpha$.

We observe that if we can assume that $\beta_\alpha \delta_\alpha^2$ is independent of the solution properties, the mathematical structure of the two summations becomes similar. That is, $S = \sum_\alpha n_\alpha f_\alpha$ where f_α is either $z_\alpha^2 \chi_\alpha$ or $\beta_\alpha \delta_\alpha^2 \theta_\alpha$. In this passage we treat the general case where β_α depends on the permittivities.

x and y denotes either T or V

$$S_x = \sum_\alpha n_\alpha \beta_\alpha \delta_\alpha^2 \frac{\partial \theta_\alpha}{\partial \kappa} \frac{\partial \kappa}{\partial x} + \sum_\alpha n_\alpha \frac{\partial \beta_\alpha}{\partial \varepsilon} \delta_\alpha^2 \theta_\alpha \frac{\partial \varepsilon}{\partial x}$$

$$= S_\kappa \kappa_x + S_\beta \varepsilon_x \quad (150)$$

where $S_\kappa = \sum_\alpha n_\alpha \beta_\alpha \delta_\alpha^2 (\theta_\alpha)_\kappa$ and $S_\beta = \sum_\alpha n_\alpha (\beta_\alpha)_\epsilon \delta_\alpha^2 \theta_\alpha$.

$$\begin{aligned} S_{xy} &= \left(\sum_\alpha n_\alpha \beta_\alpha \delta_\alpha^2 (\theta_\alpha)_{\kappa\kappa} \right) \kappa_x \kappa_y + S_\kappa \kappa_{xy} \\ &\quad + \left(\sum_\alpha n_\alpha (\beta_\alpha)_{\epsilon\epsilon} \delta_\alpha^2 \theta_\alpha \right) \epsilon_x \epsilon_y + S_\beta \epsilon_{xy} \\ &= S_{\kappa\kappa} \kappa_x \kappa_y + S_\kappa \kappa_{xy} + S_\beta \beta \epsilon_x \epsilon_y + S_\beta \epsilon_{xy} \end{aligned} \quad (151)$$

$$\begin{aligned} S_{xyz} &= S_{\kappa\kappa\kappa} \kappa_x \kappa_y \kappa_z + S_{\kappa\kappa} (\kappa_{zz} \kappa_y + \kappa_x \kappa_{yz} + \kappa_{xy} \kappa_z) + S_\kappa \kappa_{xyz} \\ &\quad + S_{\beta\beta\beta} \epsilon_x \epsilon_y \epsilon_z + S_{\beta\beta} (\epsilon_{zz} \epsilon_y + \epsilon_x \epsilon_{yz} + \epsilon_{xy} \epsilon_z) + S_\beta \epsilon_{xyz} \end{aligned} \quad (152)$$

where $S_{\kappa\kappa\kappa} = \sum_\alpha n_\alpha \beta_\alpha \delta_\alpha^2 (\theta_\alpha)_{\kappa\kappa\kappa}$ and $S_{\beta\beta\beta} = \sum_\alpha n_\alpha (\beta_\alpha)_{\epsilon\epsilon\epsilon} \delta_\alpha^2 \theta_\alpha$.

The compositional derivatives of S are

$$S_i = \beta_i \delta_i^2 \theta_i + S_\kappa \kappa_i + S_\beta \epsilon_i \quad (153)$$

$$\begin{aligned} S_{iy} &= \beta_i \delta_i^2 \theta_{ik} \kappa_y + S_{\kappa\kappa} \kappa_i \kappa_y + S_\kappa \kappa_{iy} \\ &\quad + \beta_{i\epsilon} \delta_i^2 \theta_i \epsilon_y + S_{\beta\beta} \epsilon_i \epsilon_y + S_\beta \epsilon_{iy} \end{aligned} \quad (154)$$

$$\begin{aligned} S_{ij} &= \beta_i \delta_i^2 (\theta_i)_\kappa \kappa_j + \beta_j \delta_j^2 (\theta_j)_\kappa \kappa_i + S_{\kappa\kappa} \kappa_i \kappa_j + S_\kappa \kappa_{ij} \\ &\quad + (\beta_i)_\epsilon \delta_i^2 \theta_i \epsilon_j + (\beta_j)_\epsilon \delta_j^2 \theta_j \epsilon_i + S_{\beta\beta} \epsilon_i \epsilon_j + S_\beta \epsilon_{ij} \end{aligned} \quad (155)$$

The derivatives of κ are listed in the section dealing with the Debye-Hückel equation.

Derivatives of β_α

We assume that the relative permittivity inside the molecule $\epsilon_{in,\alpha}$ is constant. The parameter β_α is defined in eqn. (57).

$$\beta_\alpha = \left(\frac{\epsilon}{2\epsilon + \epsilon_{in,\alpha}} \right)^2 = \left(\frac{\epsilon_r}{2\epsilon_r + \epsilon_{r,in,\alpha}} \right)^2 = f^2 \quad (156)$$

$$(\beta_\alpha)_\epsilon = \frac{\partial \beta_\alpha}{\partial \epsilon} = 2ff_\epsilon \quad (157)$$

$$(\beta_\alpha)_{\epsilon\epsilon} = \frac{\partial^2 \beta_\alpha}{\partial \epsilon^2} = 2ff_\epsilon + 2f_\epsilon^2 \quad (158)$$

$$f_\epsilon = \frac{1 - 2f}{2\epsilon + \epsilon_{in,\alpha}} \quad (159)$$

$$f_{\epsilon\epsilon} = \frac{-4f_\epsilon}{2\epsilon + \epsilon_{in,\alpha}} \quad (160)$$

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Chapter 7

Excess Gibbs Energy Models in Equations of State

Introduction

Cubic equations of state with a single interaction parameter for each binary pair have been very successful in correlating equilibrium properties of mixtures of non-polar components, in particular hydrocarbons. Their accuracy is much less satisfactory for mixtures consisting of polar components (e.g. acetone-water) and for mixtures containing both polar and non-polar components, such as alcohol-hydrocarbon mixtures. Their accuracy is somewhat improved provided two binary interaction parameters per pair (for the b -parameter as well as for the α -parameter) are used but still cannot match that of activity coefficient expressions such as Wilson, UNIQUAC or NRTL.

On the other hand, several drawbacks are associated with the 'gamma-phi' approach, where the liquid phase is described by an excess Gibbs energy model and the vapour phase by an equation of state. Such a model cannot generate a closed phase boundary or a vapour-liquid critical point, and, in particular, the treatment of non-condensable components is cumbersome. It is therefore of interest to combine the best features from the two approaches, i.e. the completeness of the equation of state with the flexibility and accuracy of the activity coefficient model. One manner in which this can be accomplished is by utilizing an excess Gibbs energy expression to generate equation of state mixing rules.

1 Excess Gibbs energy from a cubic equation of state

We shall consider a cubic equation of state of the general form

$$P = \frac{RT}{v - b} - \frac{a}{(v + \delta_1 b)(v + \delta_2 b)} \quad (1)$$

where a and b are mixture parameters and δ_1 and δ_2 are constants. For convenience we shall replace the mixture parameter a by α , where $a = \alpha b RT$. Eqn. (1) thus becomes

$$\frac{P}{RT} = \frac{1}{v - b} - \alpha \frac{b}{(v + \delta_1 b)(v + \delta_2 b)} \quad (2)$$

The *mixture fugacity* f_{mix} is then given by the expression

$$\ln \left(\frac{f_{mix} b}{RT} \right) = \frac{Pv}{RT} - 1 - \ln \left(\frac{v - b}{b} \right) - \frac{\alpha}{\delta_2 - \delta_1} \ln \left(\frac{v + \delta_2 b}{v + \delta_1 b} \right) \quad (3)$$

We mark pure components by their index and apply eqn. (3) for the pure component fugacities of all components in the mixture

$$\ln \left(\frac{f_i b_i}{RT} \right) = \frac{Pv_i}{RT} - 1 - \ln \left(\frac{v_i - b_i}{b_i} \right) - \frac{\alpha_i}{\delta_2 - \delta_1} \ln \left(\frac{v_i + \delta_2 b_i}{v_i + \delta_1 b_i} \right) \quad (4)$$

For a mixture of composition \mathbf{z} the reduced molar excess Gibbs energy thus becomes

$$\frac{g^E(T, P, \mathbf{z})}{RT} = \ln f_{mix}(T, P, \mathbf{z}) - \sum_i z_i \ln f_i(T, P) \quad (5)$$

Next, we shall use eqn. (5) together with eqns. (1) and (2) to derive simplified expressions for g^E at two different sets of conditions, namely in the limits of infinite pressure and that of zero pressure.

2 Infinite pressure. The Huron-Vidal mixing rule.

When eqns. (3) and (4) are substituted into eqn. (5), we arrive at

$$\begin{aligned} \frac{g^E}{RT} &= \frac{P}{RT} \left(v - \sum_i z_i v_i \right) - \left(\ln(v - b) - \sum_i z_i \ln(v_i - b_i) \right) \\ &\quad - \frac{1}{\delta_2 - \delta_1} \left(\alpha \ln \left(\frac{v + \delta_2 b}{v + \delta_1 b} \right) - \sum_i z_i \alpha_i \ln \left(\frac{v_i + \delta_2 b_i}{v_i + \delta_1 b_i} \right) \right) \end{aligned}$$

In the limit $P \rightarrow \infty$, $v \rightarrow b$ and $v_i \rightarrow b_i$. The individual terms above are reduced as follows: For the first term,

$$\begin{aligned} \frac{P}{RT} \left(v - \sum_i z_i v_i \right) &= \frac{P}{RT} \left((v - b) - \sum_i z_i (v_i - b_i) \right) + \frac{P}{RT} \left(b - \sum_i z_i b_i \right) \\ &= 1 - \alpha \frac{b(v - b)}{(v + \delta_2 b)(v + \delta_1 b)} - \sum_i z_i \left(1 - \alpha_i \frac{b_i(v_i - b_i)}{(v_i + \delta_2 b_i)(v_i + \delta_1 b_i)} \right) \\ &\quad + \frac{P}{RT} \left(b - \sum_i z_i b_i \right) \approx \frac{P}{RT} \left(b - \sum_i z_i b_i \right) \text{ for } P \text{ large} \end{aligned}$$

For the second term we rewrite eqn. (2),

$$\begin{aligned} \frac{1}{v - b} &= \frac{P}{RT} + \alpha \frac{b}{(v + \delta_2 b)(v + \delta_1 b)} \\ &= \frac{P}{RT} \left(1 + \frac{RT}{P} \alpha \frac{b}{(v + \delta_2 b)(v + \delta_1 b)} \right) \end{aligned}$$

and

$$\begin{aligned} \ln(v - b) &= -\ln \frac{P}{RT} - \ln \left(1 + \frac{RT}{P} \alpha \frac{b}{(v + \delta_2 b)(v + \delta_1 b)} \right) \\ &\approx -\ln \frac{P}{RT} \text{ for } P \rightarrow \infty \end{aligned}$$

Similarly, $\ln(v_i - b_i) \rightarrow -\ln \frac{P}{RT}$, and therefore

$$\ln(v - b) - \sum_i z_i \ln(v_i - b_i) \rightarrow 0 \text{ for } P \rightarrow \infty$$

Finally, for the last term,

$$\begin{aligned} \frac{\alpha}{\delta_2 - \delta_1} \ln \frac{v + \delta_2 b}{v + \delta_1 b} &\approx \frac{\alpha}{\delta_2 - \delta_1} \ln \frac{b + \delta_2 b}{b + \delta_1 b} = \alpha \Delta \\ \text{with } \Delta &= \frac{1}{\delta_2 - \delta_1} \ln \frac{1 + \delta_2}{1 + \delta_1} \end{aligned}$$

The last term therefore becomes $-\Delta(\alpha - \sum_i z_i \alpha_i)$. Consequently, the excess Gibbs energy at very high pressure becomes

$$\frac{g_{\infty}^E}{RT} \equiv \lim_{P \rightarrow \infty} \frac{g^E}{RT} = \frac{P}{RT} \left(b - \sum_i z_i b_i \right) - \Delta \left(\alpha - \sum_i z_i \alpha_i \right) \quad (6)$$

Provided we chose the linear mixing rule $b = \sum_i z_i b_i$ for the b -parameter the excess Gibbs energy remains finite at infinite pressure, and we obtain the simple relation

$$\alpha = \sum_i z_i \alpha_i - \frac{1}{\Delta} \frac{g_{\infty}^E}{RT} \quad (7)$$

between the mixture parameter α and the excess Gibbs energy at infinite pressure.

The derivation given above is essentially identical to that given originally (Huron and Vidal, 1979). Huron and Vidal further proposed that eqn. (7) was used as a mixing rule for the α -parameter, where one of the conventional excess Gibbs energy expressions was substituted for g_{∞}^E . The number of adjustable parameters in the resulting equation of state would thus become equal to that of the chosen excess Gibbs energy model. In this manner they were able to correlate excellently over a wide temperature range the behaviour of the acetone-water mixture. In contrast very poor results were obtained with the classical mixing rule for the a -parameter.

Equally important but less commonly known, Huron and Vidal also showed that the excess Gibbs energy expression in eqn. (7) could be chosen and parameterised in such a manner that the results of classical mixing rules are reproduced exactly. They suggested the use of a modified NRTL expression,

$$\frac{g_{\infty}^E}{RT} = \sum_i z_i \frac{\sum_j z_j b_j \exp\left(-\alpha_{ji} \frac{C_{ji}}{RT}\right) C_{ji}}{\sum_j z_j b_j \exp\left(-\alpha_{ji} \frac{C_{ji}}{RT}\right)} \quad (8)$$

where C_{ji} and C_{ij} represent interaction energies for the ij -pair, and $\alpha_{ij} = \alpha_{ji}$ the non-randomness parameter for the pair. The specific choice

$$\begin{aligned} \alpha_{ij} &= 0, \quad C_{ji} = g_{ji} - g_{ii}, \quad g_{ii} = -\alpha_i RT \Delta \\ \text{and } g_{ji} &= -2 \sqrt{\frac{b_i b_j}{b_i + b_j}} \sqrt{g_{ii} g_{jj}} (1 - k_{ij}) \end{aligned} \quad (9)$$

was shown to reproduce exactly the classical mixing rule for the a -parameter with the binary interaction coefficient k_{ij} . This implies that e.g. in equilibrium calculations for mixtures containing a large number of hydrocarbons and in addition, water and methanol, existing binary interaction parameters between the hydrocarbon components can be preserved while flexibility is obtained using the general NRTL expression for the remaining pair interactions.

3 Zero pressure. Modified Huron-Vidal mixing rules.

Unfortunately, the ability of the Huron-Vidal mixing rule to reproduce existing equation of state results is not matched by a corresponding general ability to reproduce the behaviour of existing excess Gibbs energy models without a re-parameterization. Parameters for g^E models are normally correlated from data at near-atmospheric pressure. When such parameters are used in connection with eqn. (7), the resulting values from the equation of state excess Gibbs energy will differ substantially from those of the underlying excess Gibbs energy model. An example is given for a mixture of acetone (1) and water (2) in Figure 1 below where the Wilson expression is used for the excess Gibbs energy. The following model parameters are used: $V_1 = 74.05$, $V_2 = 18.07$ (cm³/mole), $A_{12}/R = 172.57$, $A_{21}/R = 733.39$ (K).

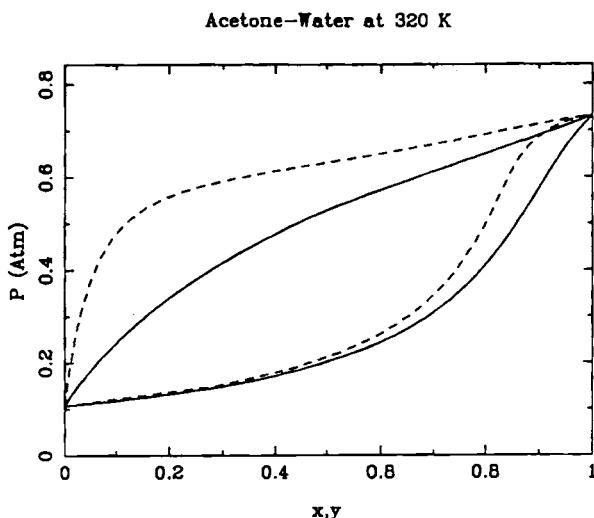


Figure 1: P_{xy} diagram for the acetone-water mixture at 320 K. Solid lines: Equation of state with Huron-Vidal mixing rule. Dashed lines: Activity coefficient model.

We shall therefore return to eqns. (1)-(5) in order to derive an expression for the equation of state excess Gibbs energy at zero pressure. Setting $P = 0$ and introducing the dimensionless volume $u = v/b$, eqn. (3) becomes

$$\ln \frac{f_{mix,0} b}{RT} = -1 - \ln(u - 1) - \frac{\alpha}{\delta_2 - \delta_1} \ln \frac{u + \delta_2}{u + \delta_1} \quad (10)$$

where u is the positive root of

$$0 = \frac{1}{u-1} - \frac{\alpha}{(u+\delta_1)(u+\delta_2)} \quad (11)$$

Similarly, for the pure components,

$$\ln \frac{f_{i,0} b_i}{RT} = -1 - \ln(u_i - 1) - \frac{\alpha_i}{\delta_2 - \delta_1} \ln \frac{u_i + \delta_2}{u_i + \delta_1} \quad (12)$$

where u_i is determined from α_i using eqn. (11). We may here note, that the right hand side of eqn. (11), with $u(\alpha)$ determined by eqn. (10), is a function, Q , of α only. This function is shown in Figure 2 below. Similarly, the right hand side of eqn. (12) is the same function of α_i . Combining eqns. (10) and (12) we obtain

$$\ln \frac{f_{mix,0} b}{RT} - \sum_i z_i \ln \frac{f_{i,0} b_i}{RT} = Q(\alpha) - \sum_i z_i Q(\alpha_i)$$

or

$$\frac{g_0^E}{RT} + \sum_i z_i \ln \frac{b}{b_i} = Q(\alpha) - \sum_i z_i Q(\alpha_i) \quad (13)$$

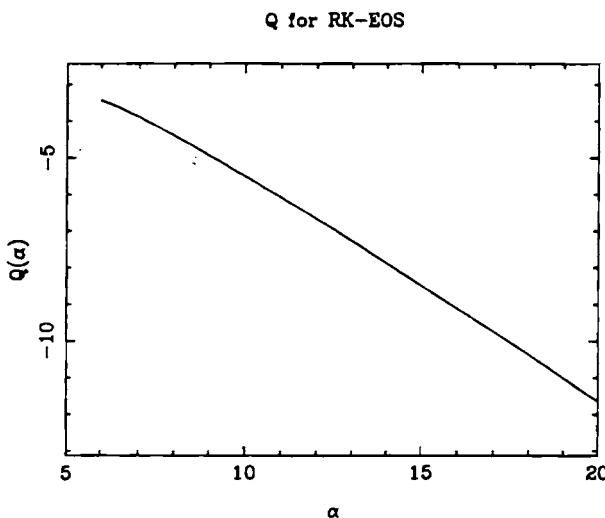


Figure 2: Plot of $Q(\alpha)$

If we substitute an excess Gibbs energy model expression for g_0^E and let eqn. (13) define the mixing rule for α , the resulting equation of state will

exactly reproduce the behaviour of the excess Gibbs energy model at zero pressure – and thus also at low to moderate pressures, since the pressure effect on liquid fugacities is very modest. The resulting mixing rule is implicit and must be solved numerically for α . In practice this is not a problem as the Q -function is very simple.

The development in the form above was originally presented by Michelsen (1990), who also observed that the Q -function was well approximated by a straight line,

$$Q(\alpha) \approx q_0 + q_1 \alpha$$

Substitution of this approximation results in the *explicit* mixing rule

$$\alpha = \sum_i z_i \alpha_i + \frac{1}{q_1} \left(\frac{g_0^E}{RT} + \sum_i z_i \ln \frac{b}{b_i} \right) \quad (14)$$

The form of this mixing rule is remarkable close to that of the Huron-Vidal mixing rule and it was therefore called the Modified Huron-Vidal mixing rule (MHV-1). Based on the observation that the majority of the data used for correlating excess Gibbs energy model parameters had pure component α -values for the SRK-equation in the range 9 – 14 Michelsen suggested a value of $q_1 = -0.593$ ($\delta_1 = 0$, $\delta_2 = 1$) as the best straight-line approximation for Q with this equation.

The straight-line approximation resolves a different problem, namely that Q is only defined provided

$$\alpha \geq \delta_1 + \delta_2 + 2 + 2\sqrt{\delta_1 \delta_2 + \delta_1 + \delta_2 + 1}$$

For lower values of α the quadratic equation determining u has no solution. This corresponds to the case where the equation of state has no liquid-like roots for the density at zero pressure. The MHV-1 mixing rule, however, can be used regardless of the pure component and mixture α -values and can therefore also be used for mixtures containing supercritical components.

The variation of the equation of state excess Gibbs energy with pressure is illustrated in Figure 3. We note that the effect of pressure is very modest below 1000 bar. The zero pressure approximation can thus safely be used for calculation at liquid phase properties, as noted earlier.

An analytic treatment of the effects of pressure is also possible. The excess volume, $v^E = v(z, T, P) - \sum_i z_i v_{ii}(T, P)$, is equal to the pressure derivative of the excess Gibbs energy. We may therefore write

$$\frac{g^E(z, T, P)}{RT} - \frac{g^E(z, T, P=0)}{RT} = \int_0^P \frac{v^E}{RT} dP \quad (15)$$

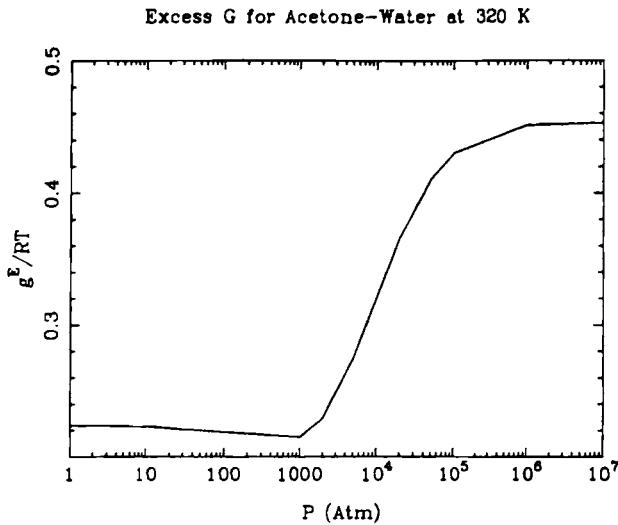


Figure 3: Variation of $g^E/(RT)$ with pressure for acetone-water mixture.

From the equation of state

$$\frac{v}{RT} = \frac{b}{RT} + \frac{1}{P + \frac{a}{(v + \delta_1 b)(v + \delta_2 b)}} \quad (16)$$

and therefore,

$$\begin{aligned} \frac{v^E}{RT} &= \frac{b}{RT} - \sum_i \frac{z_i b_{ii}}{RT} + \frac{1}{P + \frac{a}{(v + \delta_1 b)(v + \delta_2 b)}} \\ &\quad - \sum_i \frac{z_i}{P + \frac{a_{ii}}{(v_{ii} + \delta_1 b_{ii})(v_{ii} + \delta_2 b_{ii})}} \\ &= \frac{b - \sum_i z_i b_{ii}}{RT} - \sum_i z_i \left(\frac{\frac{1}{P + \frac{a}{(v + \delta_1 b)(v + \delta_2 b)}}}{P + \frac{a_{ii}}{(v_{ii} + \delta_1 b_{ii})(v_{ii} + \delta_2 b_{ii})}} \right) \quad (17) \end{aligned}$$

With a linear mixing rule for the b -parameter the first term is identically zero. If we further assume that the liquid phase volumes can be approximated by the corresponding b -value (or even the less restrictive 'constant packing' assumption that the liquid volumes are proportional to the b -values), we arrive at the explicit result

$$\begin{aligned} \int_0^P \frac{v^E}{RT} dP \\ = \sum_i z_i \ln \left(\frac{P + \frac{a}{(\delta_1 + 1)(\delta_2 + 1)b^2}}{P + \frac{a_{ii}}{(\delta_1 + 1)(\delta_2 + 1)b_{ii}^2}} \right) - \sum_i z_i \ln \frac{ab_{ii}^2}{a_{ii}b^2} \quad (18) \end{aligned}$$

and, in particular,

$$\int_0^\infty \frac{v^E}{RT} dP = - \sum_i z_i \ln \frac{ab_{ii}^2}{a_{ii}b^2} = \sum_i z_i \ln \frac{b}{b_{ii}} - \sum_i z_i \ln \frac{\alpha}{\alpha_i} \quad (19)$$

or

$$\begin{aligned} \frac{g_0^E}{RT} + \sum_i z_i \ln \frac{b}{b_{ii}} &= \frac{g_\infty^E}{RT} + \sum_i z_i \ln \frac{\alpha}{\alpha_i} \\ &= -\Delta \left(\alpha - \sum_i z_i \alpha_i \right) + \sum_i z_i \ln \frac{\alpha}{\alpha_i} \quad (20) \end{aligned}$$

If an excess Gibbs energy model expression is substituted for g_0^E , this yields a simple (but implicit) mixing rule for α which can be used for any equation of state of the general form of eqn. (1) and which does not involve individual empirical constants like that used in MHV-1. Figure 4 shows the Pxy -phase diagram for acetone-water, calculated with eqn. (20) as the mixing rule for the α -parameter. We may note that the mixing rule of eqn. (20) corresponds to that of eqn. (13) if we take $Q(\alpha) = \ln \alpha - \Delta \alpha$. An expansion of the Q -function of eqn. (13) from $\alpha = \infty$ yields

$$\frac{dQ}{d\alpha} = -\Delta + \frac{1}{\alpha} + \left(\frac{\delta_1 + \delta_2}{2} + 1 \right) \frac{1}{\alpha^2} + \dots$$

and eqn. (20) where $dQ/d\alpha = -\Delta + 1/\alpha$ therefore matches the two dominant terms of this series. A potential drawback of the mixing rule is that it can only be applied for mixtures where α (and $-dQ/d\alpha$) is positive. Highly supercritical components might therefore create a problem. The third term in the expansion from infinity can also be matched provided we take

$$Q(\alpha) = -\Delta \alpha + \ln \left(\alpha - \left(\frac{\delta_1 + \delta_2}{2} + 1 \right) \right)$$

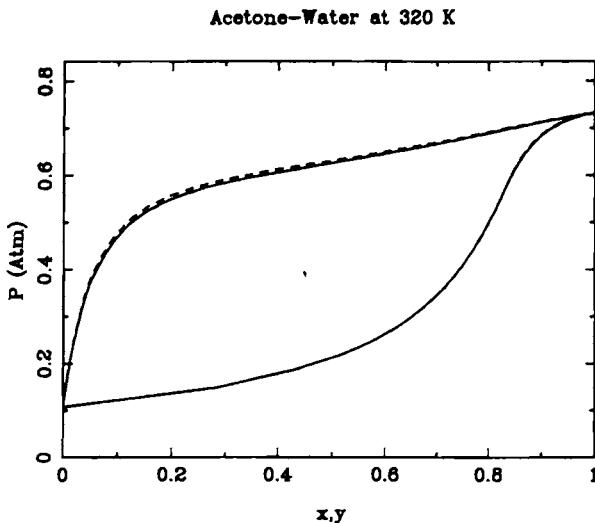


Figure 4: P_{xy} diagram for acetone-water at 320 K using the mixing rule of eqn. (20). Solid line: Equation of state. Dashed line: Activity coefficient model.

This improves the match to an activity coefficient model expression but obviously increases the potential problems with supercritical components.

The mixing rules given by eqns. (14) and (20) are both capable of reproducing the phase behaviour obtained with the underlying activity coefficient model. Formally, they can also be used to extrapolate to higher temperatures and pressures, where the 'gamma-phi' approach as such would be inapplicable. In most cases the results of such extrapolations agree well with experimental data (Dahl and Michelsen, 1990). An example is shown in Figure 5.

4 The Wong-Sandler approach

The Huron-Vidal mixing rule and its modifications suffer from the drawback that the second virial coefficient does not exhibit a quadratic composition dependence. This led Wong and Sandler (1992) to propose a new mixing rule that incorporates an excess Gibbs energy expression in the same manner as the Huron-Vidal mixing rule, i.e.

$$\alpha = \sum_i z_i \alpha_i - \frac{1}{\Delta} \frac{g_{AM}^E}{RT} \quad (21)$$

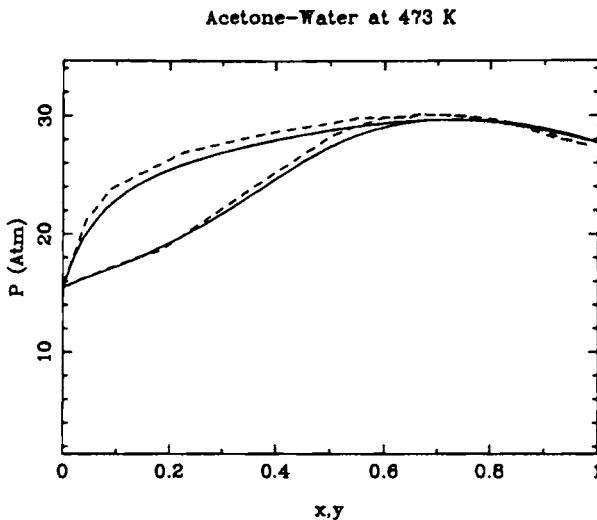


Figure 5: Acetone-water at 473 K with mixing rule of eqn. (20). Solid line: predictions. Dashed line: experimental.

but in addition specifies the mixing rule for the b -parameter by

$$b(\alpha - 1) = \sum_i \sum_j z_i z_j d_{ij} \quad (22)$$

where

$$d_{ij} = \frac{1}{2} (b_{ii}(\alpha_i - 1) + b_{jj}(\alpha_j - 1))(1 - k_{ij}) \quad (23)$$

Note that the product $b(1 - \alpha)$ is proportional to the second virial coefficient which is thereby forced to be a quadratic function of composition. The binary interaction coefficient k_{ij} in eqn. (23) is determined in such a manner that for a binary ij -mixture the excess Gibbs energy of the activity coefficient model at a specified temperature equals that of the equation of state at $z_1 = 0.5$. In general this enables Wong and Sandler to obtain a reasonable match between the behaviour of the activity coefficient model and that of the equation of state. As an example the acetone-water phase diagram used earlier, calculated with the Wong-Sandler mixing rules, is shown in Figure 6.

It is noteworthy that the Wong-Sandler mixing rule has been shown to provide excellent results, in general better than those of the MHV-mixing rules, when it is used for extrapolating to higher temperatures. It is, however, questionable whether this can be ascribed to their ability to provide the

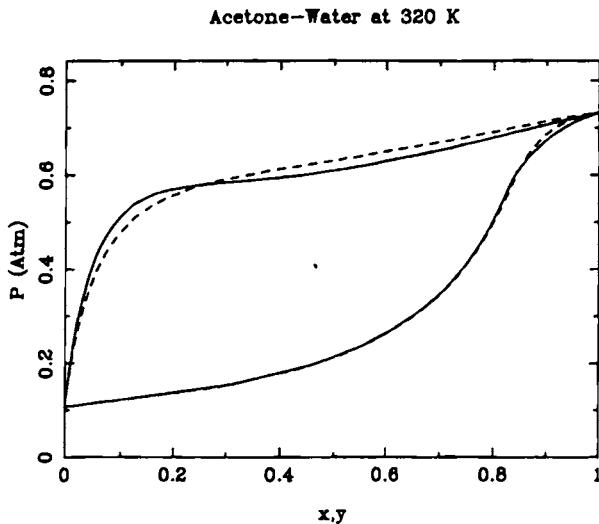


Figure 6: P_{xy} diagram for acetone-water mixture with Wong-Sandler mixing rule. Solid line: Wong-Sandler. Dashed line: Activity coefficient model.

theoretically correct form for the composition dependence of the second virial coefficient, since the difference between fugacity coefficients calculated by the MHV-mixing rules and the Wong-Sandler mixing rule is much larger for the liquid phase than for the vapour phase (Michelsen and Heidemann, 1996). Michelsen and Heidemann suggested that the success of the Wong-Sandler mixing rule could be ascribed to defects in the ability of the underlying excess Gibbs energy model to represent excess enthalpy.

Since the mixing rule for the b -parameter in the MHV-mixing rules can be chosen freely, it is evidently possible to obtain a quadratic composition dependence for the second virial coefficient with the mixing rules by including eqn. (22) as the mixing rule for b . Tochigi et al. (1994) tried this with MHV-1 without any significant effect on the resulting predictions.

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The suggestion to perform the match at zero pressure rather than at infinite pressure originates from Mollerup (1986), and the first successful practical attempt to combine a zero-pressure match with a mixing rule that could be applied at all conditions is that of Heidemann and Kokal (1990). Modifica-

tions have followed rapidly. The MHV-mixing rules proposed by Michelsen (1990) yielded a good match to the excess Gibbs energy expression with very simple expressions for the mixture parameter. Holderbaum and Gmehling (1991) proposed an MHV-1 analogue with a slightly different choice of q_1 , and Tassios and coworkers (1994) have proposed the LCVM-model, a linear combination of the original and the modified Huron-Vidal mixing rules.

The ability of the excess Gibbs energy model based equations of state to formally incorporate supercritical components is of importance e.g. for the calculation of gas solubility. The parameters describing the interactions between the gaseous and the liquid components clearly cannot be obtained from existing activity coefficient model correlations but have to be re-evaluated within the equation of state framework. Examples of parameter tables describing interactions between gas components and liquid components are: MHV-2 (Dahl et al., 1991), PSRK (Horstmann et al., 2000) and for LCVM (Voutsas et al., 1996).

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Chapter 8

General Equations of Phase Equilibrium

Introduction

Calculation of phase equilibrium is of importance for dimensioning of multi-stage separation cascades, as well as for single stage units. In the calculation of multistage columns the equilibrium equations for the individual stages are coupled through overall material balances, and such columns are most efficiently treated by algorithms which simultaneously solve the material balances and the equilibrium relations. The present work does not treat such systems but concentrates on single stage equilibrium, where, as a general rule, the overall composition of the equilibrium mixture is specified.

Satisfactory prediction of multiphase equilibrium requires that adequate thermodynamic models for the fluid phases are available. The methods described here deal primarily with the case where the same equation of state is used for calculating all properties for all phases.

In this chapter a general set of equations that must be satisfied in almost any phase equilibrium calculation is presented. We demonstrate that all problems require two *specifications* and concepts like *trivial solutions* and *stability analysis* are introduced. Finally, variable transformations and the selection of independent variables for solving the equilibrium equations are discussed.

1 The basic equilibrium equations

We consider the case of two-phase equilibrium in a C -component mixture of overall composition \mathbf{z} . Mixture mole fractions in the liquid and vapour phases are denoted \mathbf{x} and \mathbf{y} , respectively, and a necessary condition of equilibrium is

that the chemical potential for each component is the same in the two phases, i.e.

$$\mu_i^l = \mu_i^v, \quad i = 1, 2, \dots, C \quad (1)$$

or, equivalently, that the fugacities of the individual components have the same value,

$$\hat{f}_i^l = \hat{f}_i^v, \quad i = 1, 2, \dots, C \quad (2)$$

Let the overall fraction of vapour phase be β . A material balance for each component yields C relations,

$$\beta y_i + (1 - \beta)x_i = z_i, \quad i = 1, 2, \dots, C \quad (3)$$

Finally, mole fractions in the liquid and the vapour phase must sum to unity, yielding one additional relation, conveniently written in the form

$$\sum_{i=1}^C (y_i - x_i) = 0 \quad (4)$$

Our thermodynamic model enables us to calculate component fugacities, given temperature, pressure (or volume) and phase composition, i.e.,

$$\hat{f}_i^l = \hat{f}_i(T, P, \mathbf{x}), \quad \hat{f}_i^v = \hat{f}_i(T, P, \mathbf{y}) \quad (5)$$

and eqns. (2), (3) and (4) thus yields $2C + 1$ relations between the $2C + 3$ unknown, \mathbf{x} , \mathbf{y} , T , P and the vapour fraction, β . In order to define the phase equilibrium problem, two *specification equations* are needed. The specification equations can be written in the general form

$$q_1(\mathbf{x}, \mathbf{y}, T, P, \beta) = 0, \quad q_2(\mathbf{x}, \mathbf{y}, T, P, \beta) = 0 \quad (6)$$

and typically correspond to fixing two of the independent variables T , P and β , or, alternatively, fixing one of these variables, e.g. P , and in addition specifying an overall property of the mixture, such as total enthalpy, H , total entropy, S , or total volume, V .

The type of specification strongly affects our choice of solution procedure. Certain specifications, e.g. (P, T) , (P, H) , (P, S) or (T, V) enable us to formulate the equilibrium calculation as a minimization of a thermodynamic state function and guarantees a unique, valid solution. For other specifications, e.g. (T, β) and (P, β) multiple solutions to the equations may be possible, or a solution may not even exist.

Phase equilibrium calculations involving more than two phases require an extension of the set of eqns. (2)-(4). Each new phase introduces $C + 1$

additional variables, the C mole fractions and the overall phase fraction, and correspondingly $C + 1$ equations, representing equality of fugacity and summation of mole fractions. Thus, the number of 'free' specifications remains at 2, regardless of the number of phases.

2 The trivial solution

An important problem associated with the use of equations of state is the potential existence of the so-called *trivial solution*, i.e. a solution with liquid and vapour phases of identical composition and with identical properties, leading to automatic satisfaction of eqns. (2)-(4). The trivial solution may be the only valid solution for the given set of specifications, e.g. for a (P, T) specification in the single phase region, but unless precautions are taken it is frequently encountered under conditions where the correct solution corresponds to two equilibrium phases, in particular when inadequate initial estimates are used.

The problem with the trivial solution is particularly pronounced in the critical region. At the critical point the vapour and the liquid phase have identical composition, and in the critical region, i.e. the vicinity of the critical point, the equilibrium compositions are 'close', i.e.,

$$x_i \approx y_i \approx z_i \quad (7)$$

Calculations in this region are particularly likely to converge to the trivial solution unless initial estimates of high quality are used.

3 Verifying the solution; Stability analysis.

The condition of equal component fugacities in the fluid phases is only a necessary condition for equilibrium. The equilibrium mixture is stable at the current (T, P) if and only if the total Gibbs energy is at its *global minimum*.

The change in Gibbs energy by transferring δn_i moles of component i from the liquid phase to the vapour phase is

$$\delta G = (\mu_i^v - \mu_i^l) \delta n_i \quad (8)$$

At the global minimum, δG must be zero for any transfer of material, yielding the equality of chemical potential (or of fugacity) condition as a necessary condition of equilibrium.

Let us next consider a phase of composition z , with chemical potentials $\mu(z)$. Assume that an infinitesimal amount δe of a new phase of molar composition w is formed. The change in Gibbs energy associated with formation

of the new phase is then

$$\delta G = \delta e \sum_{i=1}^C w_i (\mu_i(\mathbf{w}) - \mu_i(\mathbf{z})) \quad (9)$$

the amount of component i transferred being $w_i \delta e$. A *necessary condition* for stability of the phase of composition \mathbf{z} is thus that δG is non-negative for any positive δe , i.e.

$$\sum_{i=1}^C w_i (\mu_i(\mathbf{w}) - \mu_i(\mathbf{z})) \geq 0 \quad (10)$$

for any composition \mathbf{w} . This is the *tangent plane condition* of Gibbs.

A solution to the phase equilibrium equations (2)-(4) has identical chemical potential for each component in all phases. This implies that the vapour phase composition and the liquid phase composition have identical tangent planes, and stability analysis by means of the tangent plane distance will thus yield identical results for both phases, or for all phases, when more than two 'equilibrium' phases are present.

For a binary mixture a graphical interpretation of the equilibrium and stability conditions is illustrative. The molar *Gibbs energy of mixing*, g_z^{mix} , is plotted against the mole fraction z of component 1,

$$g_z^{\text{mix}} = z(\mu_1 - \mu_1(z=1)) + (1-z)(\mu_2 - \mu_2(z=0)) \quad (11)$$

The use of the Gibbs energy of mixing is purely a matter of convenience, and for the following derivation we shall instead for notational convenience use the mixture molar Gibbs energy, given by

$$g_z = z\mu_1 + (1-z)\mu_2 \quad (12)$$

Consider a split of the mixture F into two new phases of composition x and y ($y > x$), respectively, represented by points A and B in Figure 1. From the material balance the fraction β of the y -phase is given by

$$\beta y + (1-\beta)x = z \quad (13)$$

The combined Gibbs energy g_2 of the two phases is

$$g_2 = \beta g_y + (1-\beta)g_x \quad (14)$$

and the change in Gibbs energy from the split of the original phase into two new phases is

$$\Delta g = g_2 - g_z = \beta g_y + (1-\beta)g_x - g_z \quad (15)$$

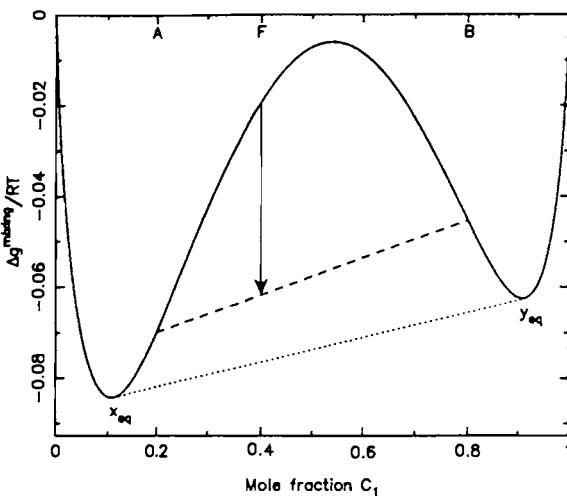


Figure 1: Gibbs Energy of mixing for binary mixture (CH_4 - H_2S at 190 K, 4.56 MPa)

The equation for the chord connecting (x, g_x) to (y, g_y) is

$$g_{\text{cord}}(w) = g_x + \frac{g_y - g_x}{y - x} (w - x) \quad (x < w < y) \quad (16)$$

and we observe by substitution (or by means of the lever arm rule) that

$$g_{\text{cord}}(z) = g_x + \frac{g_y - g_x}{y - x} (z - x) = (1 - \beta)g_x + \beta g_y = g_2 \quad (17)$$

The split into two phases yields a decrease in the Gibbs energy provided $g_2(z) < g_z$, and the equilibrium state corresponds to the largest possible decrease, which is obtained when the cord connecting (x, g_x) to (y, g_y) is the common tangent to the g -curve, at compositions x_{eq} and y_{eq} . Phase compositions in the range $x_{eq} < z < y_{eq}$ are unstable and split into two equilibrium phases whereas those outside this range are stable.

The slope of the tangent to the g -curve can be determined as follows; we may formally write $g(z) = G(n_1, n_2)$ where $n_1 = z$ and $n_2 = 1 - z$. Then,

$$\frac{dg}{dz} = \frac{\partial G}{\partial n_1} \frac{dn_1}{dz} + \frac{\partial G}{\partial n_2} \frac{dn_2}{dz} = \mu_1 - \mu_2 \quad (18)$$

The equation for the tangent to the Gibbs energy curve at z is given by

$$\begin{aligned}
 t(w) &= g_z + \left(\frac{dg}{dz} \right)_z (w - z) \\
 &= z\mu_{1,z} + (1 - z)\mu_{2,z} + (w - z)(\mu_{1,z} - \mu_{2,z}) \\
 &= w\mu_{1,z} + (1 - w)\mu_{2,z}
 \end{aligned} \tag{19}$$

and the distance from the tangent line to the Gibbs energy curve at w becomes

$$\begin{aligned}
 TPD(w) &= g_w - t(w) = w(\mu_{1,w} - \mu_{1,z}) + (1 - w)(\mu_{2,w} - \mu_{2,z}) \\
 &= \sum_i w_i (\mu_{i,w} - \mu_{i,z})
 \end{aligned} \tag{20}$$

If the tangent plane distance at composition w is negative, it is evident that we can choose the y -phase composition $y = w$ and locate an x -phase composition $x < z$ such that the phase split yields a decrease in the Gibbs energy.

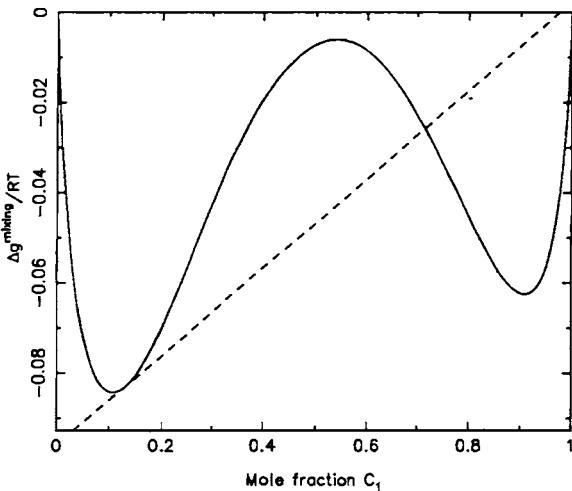


Figure 2: Tangent ‘plane’ for mixture of Figure 1 at $z = 0.13$.

The tangent plane condition is evidently a necessary condition for stability. It is easily shown that it is also a sufficient condition. Consider for

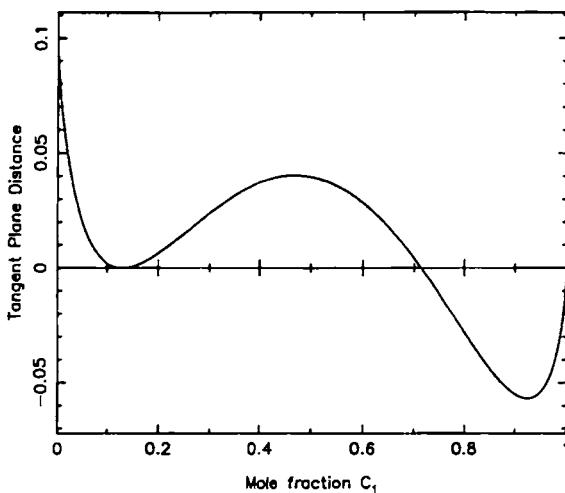


Figure 3: Tangent plane distance plot showing instability at $z = 0.13$.

example a K -phase distribution with mole fractions \mathbf{x} , satisfying the condition of equal chemical potentials, i.e.

$$\mu_i(\mathbf{x}^1) = \mu_i(\mathbf{x}^2) = \cdots = \mu_i(\mathbf{x}^K) = (\mu_i^*) \quad (21)$$

The total Gibbs energy of this mixture is

$$G^* = \sum_{k=1}^K \sum_{i=1}^C n_i^k \mu_i^* = \sum_{i=1}^C z_i \mu_i^* \quad (22)$$

The mixture is unstable if and only if there exists a different phase distribution with a lower total Gibbs energy. Assume that such a distribution exists, consisting of L phases of composition \mathbf{y} and with overall phase fractions $\beta_1, \beta_2, \dots, \beta_L$, where the chemical potentials are $\boldsymbol{\mu}(\mathbf{y}^1) = \boldsymbol{\mu}(\mathbf{y}^2) = \cdots = \boldsymbol{\mu}(\mathbf{y}^L) = \hat{\boldsymbol{\mu}}$. Then,

$$\hat{G} = \sum_{i=1}^C z_i \hat{\mu}_i < G^* \quad (23)$$

or,

$$\hat{G} - G^* = \sum_{i=1}^C z_i (\hat{\mu}_i - \mu_i^*) \leq 0 \quad (24)$$

From the overall material balance,

$$z_i = \sum_{l=1}^L \beta_l y_i^l \quad (25)$$

and eqn. (5) can be written

$$\sum_{l=1}^L \beta_l \sum_{i=1}^C y_i^l (\bar{\mu}_i - \mu_i^*) < 0 \quad (26)$$

or

$$\sum_{l=1}^L \beta_l TPD^l < 0 \quad (27)$$

which requires that the tangent plane condition is violated for the original phase distribution. **The tangent plane is thus a necessary and sufficient condition for stability.**

Verifying that the tangent plane condition is satisfied is not a trivial task, as it requires a search over the entire composition space. Methods for practical implementation of the tangent plane analysis will be discussed in detail later. For the present purpose we shall assume that the tangent plane condition for stability is satisfied provided an extensive search does not reveal violations.

For certain practically important specifications, e.g. (P, T) , (P, H) , (P, S) and (V, T) , satisfaction of the tangent plane condition not only implies that we have located a valid solution to the phase equilibrium calculation but also that this solution is unique. For a range of other specifications satisfaction of the condition only verifies that the solution is proper, whereas the possible existence of alternative, equally valid solutions is not ruled out. As an example, consider dewpoint calculations at specified pressure in the retrograde region, where two solutions are frequently expected.

Application of the tangent plane condition is not limited to the yes/no question of stability. Locating a trial phase composition yielding a negative TPD usually provides a good starting point for subsequent calculation of the correct phase distribution.

4 Alternative formulation of equations; Equilibrium factors

The set of equations (2)-(4) can be reduced to a smaller set by introducing equilibrium factors, defined by

$$K_i = \frac{y_i}{x_i} \quad (28)$$

Substituting this expression into the material balance equations yields

$$x_i = \frac{z_i}{1 - \beta + \beta K_i} \quad (29)$$

and

$$y_i = \frac{K_i z_i}{1 - \beta + \beta K_i} \quad (30)$$

and phase mole fractions x and y can thus be calculated from the K -factors and the phase fraction β . Substituting

$$\hat{f}_i^l = x_i \hat{\varphi}_i^l P, \quad \hat{f}_i^v = y_i \hat{\varphi}_i^v P \quad (31)$$

into the equilibrium equations yield the following C relations

$$K_i = \frac{\hat{\varphi}_i^l}{\hat{\varphi}_i^v}, \quad i = 1, 2, \dots, C \quad (32)$$

together with the summation of mole fraction relation

$$\sum_{i=1}^C (y_i - x_i) = \sum_{i=1}^C \frac{z_i(K_i - 1)}{1 - \beta + \beta K_i} = 0 \quad (33)$$

Combined with the two specification equations we thus obtain $C + 3$ equations in the $C + 3$ variables, i.e., the C K -factors, β , T and P . The fugacity coefficients of eqn. (32) depend on temperature, pressure and the phase compositions x and y , where the latter are given in terms of the K -factors and β , by eqns. (29) and (30). An arbitrary set of values for these variables will not in general result in 'mole fractions' from eqns. (29) and (30) that add to unity. For the purpose of evaluating fugacity coefficients, the x and y vectors are formally treated as vectors of mole numbers.

The K -factors will frequently span a range of several decades, and in order to obtain a suitable scaling we prefer to use their logarithm as the actual independent variables.

5 Molar flows

In equilibrium calculations that can be formulated as minimization problems it is often advantageous to use molar amounts as the independent variables. Liquid and vapour amounts (per unit feed) are related to the corresponding mole fractions by

$$l_i = (1 - \beta)x_i, \quad v_i = \beta y_i \quad (34)$$

and the material balance simply becomes

$$l_i + v_i = z_i \quad (35)$$

At specified (T, P) the equilibrium calculation can be formulated as

$$\min G(l, v) \quad (36)$$

subject to the set of linear constraints $l + v = z$, or as the *un-constrained minimization*

$$\min G(v, l(v)), \quad \text{with } l = z - v \quad (37)$$

thus reducing the number of independent variables to C . In multiphase calculations the number of independent variables similarly becomes $C(F-1)$, F being the number of phases.

6 Ideal solutions

In a vapour phase at low pressure, and in a liquid mixture containing very similar components at subcritical conditions, the fugacity coefficients depend only weakly on the phase composition. Mixtures with composition independent fugacity coefficients are called ideal mixtures, and for such mixtures the equilibrium calculation can usually be reformulated in such a manner that only a single or two independent variables are needed. As an example, consider the *PT*-flash. The liquid and vapour phase fugacity coefficients are now known, and the only equation remaining is the *Rachford-Rice* equation, eqn. (33) that must be solved for the vapour fraction, β .

Many important solution procedures for equilibrium calculations for non-ideal mixtures are based on an implicit assumption of ideal solution behaviour. Such procedures use nested loops, where an 'ideal mixture' calculation is converged in an inner loop and non-ideality is taken into account by 'updating' fugacity coefficients in an outer loop. This approach is frequently remarkably efficient, even for highly non-ideal mixtures, but its most important application is for generating 'reasonable' initial estimates for algorithms involving the full set of independent variables.

Chapter 9

Stability Analysis and Critical Points

Introduction

The tangent plane condition for phase stability was introduced in Chapter 8. In this chapter we shall derive formulations of the tangent plane condition which can form the basis for a computational implementation of a stability investigation.

The *critical point* for a mixture is a limiting point on the two-phase co-existence curve where the compositions of the equilibrium phases become identical. The conditions at which criticality occurs are readily derived from the properties of the tangent plane surface. We derive such criteria for binary and multicomponent mixtures and briefly discuss their computational implementations.

1 Stability analysis

We consider a C -component mixture of composition \mathbf{z} at specified temperature and pressure. The *necessary and sufficient condition* for stability of this mixture is that the tangent plane distance function, $TPD(\mathbf{w})$,

$$TPD(\mathbf{w}) = \sum_i w_i (\mu_i(\mathbf{w}) - \mu_i(\mathbf{z})) \quad (1)$$

is *non-negative* for any trial phase composition \mathbf{w} . It is normally more convenient to rewrite the condition in terms of fugacity coefficients. We substitute

$$\begin{aligned}\mu_i(T, P, \mathbf{w}) &= \mu_i^*(T, P_0) + RT \ln \frac{\hat{f}_i(T, P, \mathbf{w})}{P_0} \\ &= \mu_i^*(T, P_0) + RT \left(\ln w_i + \ln \frac{P}{P_0} + \ln \hat{\varphi}_i(T, P, \mathbf{w}) \right)\end{aligned}\quad (2)$$

and define the *reduced tangent plane distance* by

$$\begin{aligned}tpd(\mathbf{w}) &= \frac{TPD(\mathbf{w})}{RT} = \sum_i w_i (\ln w_i + \ln \hat{\varphi}_i(\mathbf{w}) - \ln z_i - \ln \hat{\varphi}_i(\mathbf{z})) \\ &= \sum_i w_i (\ln w_i + \ln \hat{\varphi}_i(\mathbf{w}) - d_i)\end{aligned}\quad (3)$$

with $d_i = \ln z_i + \ln \hat{\varphi}_i(\mathbf{z})$.

In order to verify stability we must ensure that $tpd(\mathbf{w})$ is non-negative for all valid phase compositions and for all phase models in consideration. When different phase models can be used for a given phase composition \mathbf{w} , e.g. an activity coefficient model for the liquid phase and an equation of state for the vapour phase, we select the properties (i.e. the fugacity coefficients) for the phase model yielding the lower Gibbs energy.

A computational approach can be based on the fact that the tangent plane condition is non-negative everywhere if and only if it is non-negative at all its minima. Our recommended implementation of the tangent plane condition is

- i) Locate all (local) minima of the tangent plane distance.
- ii) Check that the value of tpd is non-negative at all the minima. If a negative value of tpd is encountered during the search for the local minima, the mixture is known to be unstable.

Conditions for local minima

The function to be minimised is the reduced tangent plane distance,

$$tpd(\mathbf{w}) = \sum_i w_i (\ln w_i + \ln \hat{\varphi}_i(\mathbf{w}) - d_i)\quad (4)$$

subject to the constraint that w must represent a valid phase composition, i.e.,

$$\begin{aligned} w_i &\geq 0, \quad i = 1, 2, \dots, k, \\ w_i &= 0, \quad i = k + 1, \dots, C, \\ \sum_i w_i - 1 &= 0 \end{aligned} \tag{5}$$

where components that are allowed to be present in the phase model in consideration are indexed $1, 2, \dots, k$, and those that are not allowed have indices $k + 1, k + 2, \dots, C$. Usually, all components can be present in all phases, i.e. $k = C$. Exceptions are e.g. gas hydrates, where only water and specific light gases and light hydrocarbons can be present in the hydrate phase, and pure solids, where $k = 1$. For convenience we shall assume in the following that $k = C$. The logarithmic dependence on component mole fractions ensures that at a minimum of tpd , all mole fractions are positive, and we may therefore replace the constraints by

$$\begin{aligned} w_i &> 0, \quad i = 1, 2, \dots, C, \\ \sum_i w_i - 1 &= 0 \end{aligned} \tag{6}$$

The conditions that must be satisfied at a minimum of the tangent plane distance subject to these constraints can be derived from the corresponding Lagrangian function (Fletcher, 1981)

$$\mathcal{L}(w, \lambda) = \sum_i w_i (\ln w_i + \ln \hat{\varphi}_i - d_i) - \lambda \left(\sum_i w_i - 1 \right) \tag{7}$$

At all *stationary points* (i.e. minima, maxima and saddle points) the following conditions must be satisfied

$$\frac{\partial \mathcal{L}}{\partial w_i} = \ln w_i + \ln \hat{\varphi}_i - d_i + 1 - \lambda = 0, \quad i = 1, 2, \dots, C \tag{8}$$

and

$$\frac{\partial \mathcal{L}}{\partial \lambda} = - \sum_i w_i + 1 = 0 \tag{9}$$

which yields a set of $C + 1$ equations for the $C + 1$ unknown (w, λ) . The value of tpd at a stationary point is

$$tpd^{SP} = \sum_i w_i (\ln w_i + \ln \hat{\varphi}_i - d_i) = \sum_i w_i (\lambda - 1) = \lambda - 1 \tag{10}$$

Stability thus requires that the Lagrange multiplier λ is greater than or equal to 1 at all stationary points.

The stationarity condition can also be written as

$$\ln \hat{f}_i(\mathbf{w}) = \ln \hat{f}_i(\mathbf{z}) + \lambda - 1, \quad \text{or} \quad \mu_i(\mathbf{w}) = \mu_i(\mathbf{z}) + RT(\lambda - 1) \quad (11)$$

showing that the stationary points for the tangent plane distance are characterised by a constant difference between the chemical potentials at the composition \mathbf{w} and at the composition \mathbf{z} . The slope of the tangent to the g -curve for a binary mixture is the difference in chemical potentials between the two components, $\mu_1 - \mu_2$. At the stationary points for the tangent plane distance, $\mu_1(w) - \mu_2(w) = \mu_1(z) - \mu_2(z)$, and the stationary points are thus found where the tangent to the g -curve is parallel to the tangent at z . An example is shown in Figure 1, where parallel tangents are drawn corresponding to the (unstable) composition $z = 0.13$.

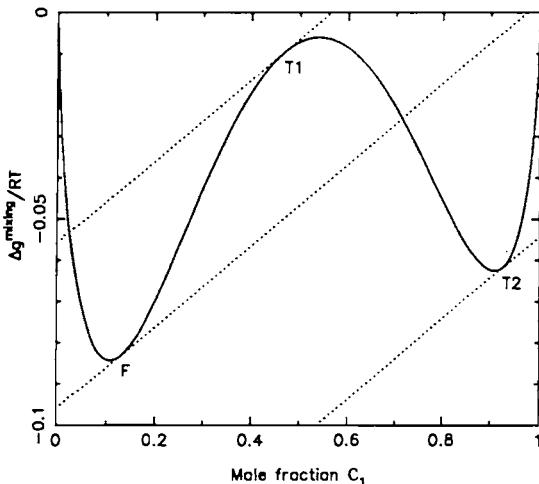


Figure 1: Parallel tangents for unstable binary mixture.

Alternative formulations

We shall next show that an unconstrained formulation of the tpd -minimization is possible. Consider the function

$$tm(\mathbf{W}) = 1 + \sum_i W_i (\ln W_i + \ln \hat{\varphi}_i(\mathbf{W}) - d_i - 1) \quad (12)$$

where the W_i are composition variables that are formally treated as mole numbers. The stationary points of tm satisfy

$$\frac{\partial tm}{\partial W_i} = \ln W_i + \ln \hat{\varphi}_i(\mathbf{W}) - d_i = 0, \quad i = 1, 2, \dots, C \quad (13)$$

and at the stationary points we obtain

$$tm^{SP} = 1 - W_T, \quad \text{where } W_T = \sum_i W_i \quad (14)$$

The molar composition of the phase \mathbf{W} is given by $w_i = W_i/W_T$, and obviously, $\hat{\varphi}_i(\mathbf{W}) = \hat{\varphi}_i(\mathbf{w})$. This shows that a minimum of tm is also a minimum of tpd , corresponding to $\lambda = 1 - \ln W_T$. Our condition for stability therefore is that W_T must be less than or equal to 1 at all stationary points of tm . The modified tangent plane function can be written as

$$\begin{aligned} tm(\mathbf{W}) &= 1 + W_T \sum_i w_i (\ln W_T + \ln w_i + \ln \hat{\varphi}_i - d_i - 1) \\ &= (1 - W_T + W_T \ln W_T) + W_T tpd(\mathbf{w}) \end{aligned} \quad (15)$$

The first term on the RHS of this equation is always positive. A negative value of tm therefore implies a negative value of tpd and thus an unstable mixture.

Solution methods

A very simple algorithm for determining the stationary points of tm (i.e. the solutions of eqn. (12)) is the *successive substitution method*,

$$\ln W_i^{(k+1)} = d_i - \ln \hat{\varphi}_i(\mathbf{W}^{(k)}) \quad (16)$$

where the phase composition at iteration $k+1$ is determined from properties calculated at the composition from the previous iteration. When the composition dependence of the fugacity coefficients is weak, convergence will be rapid. It is readily shown that the successive substitution, if convergent, will converge to a local minimum of the modified tangent plane distance. Although some examples of divergent behaviour are given by Heidemann and Michelsen (1995), the iteration is convergent in the vast majority of practically important cases. However, in the vicinity of the mixture critical point the rate of convergence can be intolerably low, and a second order convergence method may be preferable. The obvious choice is Newton's method for minimization, where, in addition to the gradient vector,

$$g_i = \ln W_i + \ln \hat{\varphi}_i - d_i \quad (17)$$

the Hessian matrix is also required,

$$H_{ij} = \frac{\partial g_i}{\partial W_j} = \frac{1}{W_i} \delta_{ij} + \frac{\partial \ln \hat{\varphi}_i}{\partial W_j} \quad (18)$$

The Newton correction is calculated from

$$\mathbf{H} \Delta \mathbf{W} + \mathbf{g} = \mathbf{0}, \quad \mathbf{W}^{(k+1)} = \mathbf{W}^{(k)} + \Delta \mathbf{W} \quad (19)$$

and in most cases the method is rapidly convergent. When the Hessian matrix is near-singular or has negative eigenvalues, the Newton correction may, however, 'overstep' the solution or even fail to reduce the objective function. It is therefore preferable to use a 'trust region' modification where the correction step is calculated from

$$(\mathbf{H} + \eta \mathbf{S}) \Delta \mathbf{W} + \mathbf{g} = \mathbf{0} \quad (20)$$

where \mathbf{S} is a preselected diagonal matrix with positive elements, and the parameter η is chosen such that

- i) $\mathbf{H} + \eta \mathbf{S}$ is a positive definite matrix,
- ii) The magnitude of the correction step is smaller than a prescribed limit, and
- iii) The resulting step yields a decrease in the objective function.

This can always be accomplished by choosing η sufficiently large. In practice the conditions are satisfied for $\eta = 0$ in most steps. The favourable convergence properties of Newton's method are therefore retained but the precautions serve to safeguard against difficult cases and to overcome inadequate initial estimates.

A particularly advantageous form results when the variable substitution $\alpha_i = 2\sqrt{W_i}$ is used. We obtain

$$g_i = \frac{\partial tm}{\partial \alpha_i} = \sqrt{W_i} (\ln W_i + \ln \hat{\varphi}_i - d_i) \quad (21)$$

and

$$H_{ij} = \delta_{ij} + \sqrt{W_i W_j} \frac{\partial \ln \hat{\varphi}_i}{\partial W_j} + \frac{1}{2} \frac{g_i}{\alpha_i} \delta_{ij} \quad (22)$$

The last term can be neglected without effect on the rate of convergence since it vanishes at the solution, and in this modification the Hessian matrix reduces to the Identity matrix if the fugacity coefficients are composition independent, indicating an optimal scaling of the independent variables in the minimization problem. Our choice of \mathbf{S} with this choice of independent variables is $\mathbf{S} = \mathbf{I}$, the Identity matrix.

Trivial solutions

It is worthwhile to notice that the composition \mathbf{z} of the phase investigated for stability represents a stationary point for the tangent plane distance. The stationary point is a minimum provided the Hessian matrix is positive definite, i.e., satisfies the condition

$$\mathbf{e}^T \mathbf{H} \mathbf{e} > 0 \quad (23)$$

for any non-zero vector \mathbf{e} . Positive definiteness implies that all eigenvalues of the Hessian matrix are positive. The requirement for positive definiteness at a minimum can be seen as follows. We investigate the tangent plane distance in the vicinity of \mathbf{z} by substituting $\mathbf{W} = \mathbf{z} + \mathbf{e}$, where \mathbf{e} is small. A Taylor series expansion of $tm(\mathbf{W})$ from $\mathbf{W} = \mathbf{z}$ yields

$$tm(\mathbf{W}) = tm(\mathbf{z}) + \mathbf{g}(\mathbf{z})^T \mathbf{e} + \frac{1}{2} \mathbf{e}^T \mathbf{H}(\mathbf{z}) \mathbf{e} + \dots = \frac{1}{2} \mathbf{e}^T \mathbf{H}(\mathbf{z}) \mathbf{e} + \dots \quad (24)$$

since $tm(\mathbf{z}) = 0$ and $\mathbf{g}(\mathbf{z}) = 0$. When $\mathbf{H}(\mathbf{z})$ is positive definite, the dominant term in the Taylor series expansion of the tangent plane distance is positive, indicating that the trivial solution $\mathbf{W} = \mathbf{z}$ is a local minimum. If $\mathbf{H}(\mathbf{z})$ has one or more negative eigenvalues, the tangent plane distance can become negative arbitrarily close to \mathbf{z} showing that the mixture is unstable. A mixture for which $\mathbf{H}(\mathbf{z})$ has negative eigenvalues is called *intrinsically unstable*. For a binary mixture intrinsic instability is found where the curvature of the g -curve is negative. If exactly one eigenvalue of $\mathbf{H}(\mathbf{z})$ is zero and the remaining are positive, the mixture is at the *limit of intrinsic stability* (for a ternary mixture, the *spinodal curve*).

Selection of initial estimates

Verification of stability requires that the global minimum of the tangent plane distance is determined and therefore necessitates that we locate all local minima or at least verify that their value of the tpd is non-negative. In general this is likely to be a very time-consuming, if not impossible, task. A less ambitious approach is to perform the search for local minima with a number of judiciously selected initial estimates in the hope that these searches will uncover at least all negative minima. Guidelines for initiating such searches will be discussed in the Chapters 10 and 11. For certain models, however, it can be shown that the tpd -function has a unique local minimum and therefore only requires a single search. This is the case provided the model Gibbs energy surface is *convex*, i.e., models that satisfy

$$g(\theta \mathbf{x}_1 + (1 - \theta) \mathbf{x}_2) < \theta g(\mathbf{x}_1) + (1 - \theta) g(\mathbf{x}_2), \quad 0 < \theta < 1 \quad (25)$$

or, equivalently, that the Hessian matrix is positive definite everywhere. It is evident that ideal solutions have this property, and in addition the Wilson activity coefficient model can be shown to be convex. For most other models, convexity cannot be determined in advance.

2 Calculation of critical points

The *critical point* for a mixture of specified composition is the set of conditions (e.g. T and P) at which the mixture and the equilibrium phase have identical composition and density. Points on the phase boundary at 'close to critical' conditions are characterised by nearly identical phase compositions and phase densities. In the following we shall derive the criteria that must be satisfied at a critical point. These criteria will first be derived for binary mixtures, for which plots of the Gibbs energy of mixing and tangent plane distance provide convenient illustrations, and subsequently extended to mixtures containing an arbitrary number of components. Finally, criteria for higher order (tricritical, tetracritical) critical points are discussed.

Binary mixtures

The phase diagram for a mixture containing 50% methane and 50% carbon dioxide is shown in Figure 2. The mixture critical point is 251.95 K, 8.50

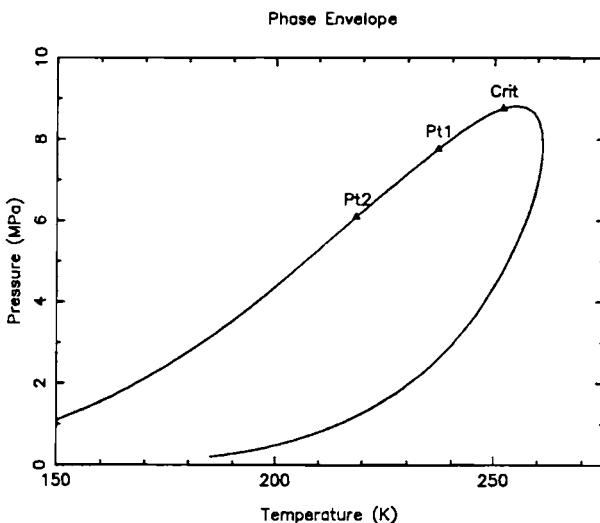


Figure 2: Phase diagram for a mixture containing 50% C₁ and 50% CO₂.

MPa, and two additional points are marked on the phase boundary, Pt.1 at 236.8 K, 7.56 MPa and Pt.2 at 218.5 K, 5.93 MPa. The composition of one of the equilibrium phases at all 3 points is thus 50% C₁, 50% CO₂.

Gibbs energy of mixing plots for all 3 points are shown in Figure 3. The region of immiscibility is determined by the common tangent to the curves, and we observe a characteristic flat portion of the g excess curve at $x = 0.5$ at critical conditions. The features characterizing a critical point appear more

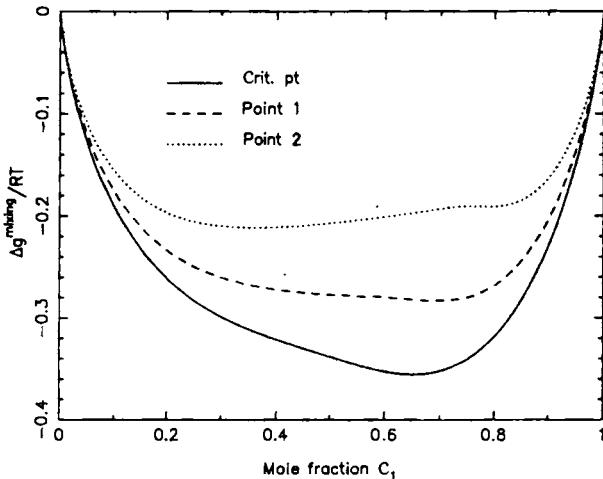


Figure 3: Gibbs energy of mixing plots for mixtures of methane and carbon dioxide.

clearly on a tangent plane distance plot, based on a test phase composition of $z = 0.5$, corresponding to the composition of one of the equilibrium phases. This plot is shown in Figure 4. A minimum in tpd with a value of zero is found at the test phase composition as well as at the equilibrium phase composition, and as the critical point is approached, the composition difference between the test phase and the equilibrium phase decreases and the two minima move together. If the equilibrium phase methane mole fraction is y , the tangent plane distance can be approximated by

$$tpd(x) \cong K(x - z)^2(x - y)^2 = Ks^2(s - a)^2 \quad (26)$$

with $s = x - z$ and $a = y - z$. At the critical point, the composition difference between the equilibrium phases becomes equal to zero, and we obtain for the

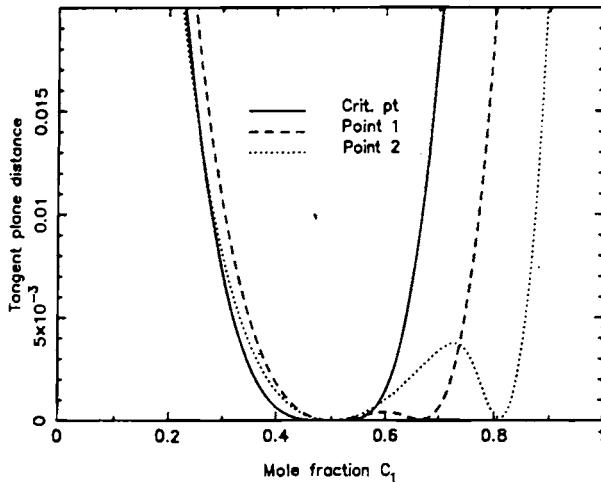


Figure 4: Tangent plane distance plot for C_1 -CO₂ mixtures.

critical mixture

$$tpd(s) \cong Ks^4 \quad (27)$$

The tangent plane distance and its first derivative is by definition zero at $s = 0$, and the criticality conditions for a binary mixture can thus be expressed

$$tpd^{(2)}(s) = tpd^{(3)}(s) = 0 \quad \text{at } s = 0 \quad (28)$$

In order to calculate the second and the third derivative of the tangent plane distance numerically, we can utilise that the first derivative is easily calculated. From $x_1 = z_1 + s$, $x_2 = z_2 - s$, we obtain

$$\frac{d(tpd)}{ds} = (\ln x_1 + \ln \hat{\varphi}_1(x) - d_1) - (\ln x_2 + \ln \hat{\varphi}_2(x) - d_2) \quad (29)$$

with $d_i = \ln z_i + \ln \hat{\varphi}_i(z)$. The second and the third derivatives of the tangent plane distance are next calculated by numerical differentiation of the first derivative by means of the difference relations

$$\frac{df}{ds} \cong \frac{f(s + \epsilon) - f(s - \epsilon)}{2\epsilon}, \quad \frac{d^2f}{ds^2} \cong \frac{f(s + \epsilon) - 2f(s) + f(s - \epsilon)}{\epsilon^2} \quad (30)$$

where ϵ is chosen suitably small, e.g. 0.001. Since the derivative of the tangent plane distance always has a value of zero at the test phase composition ($s =$

0), we obtain the very simple criticality conditions

$$\frac{d(tpd)}{ds} = 0 \quad \text{at } s = \epsilon \text{ and at } s = -\epsilon \quad (31)$$

Multicomponent mixtures

When more than two components are present in the mixture, graphical illustrations of excess Gibbs energy of mixing and of tangent plane distances are much less useful in deriving criticality conditions. A simple example will be shown here for a ternary mixture of methane, ethane and carbon dioxide. At a mixture composition of 30% C₁, 30% C₂ and 40% CO₂ the critical point is found at 269.5 K, 6.72 MPa. The Gibbs energy of mixing diagram at this temperature and pressure is shown in Figure 5, as a contour plot. It is difficult to locate the critical composition in this diagram. A tangent plane distance

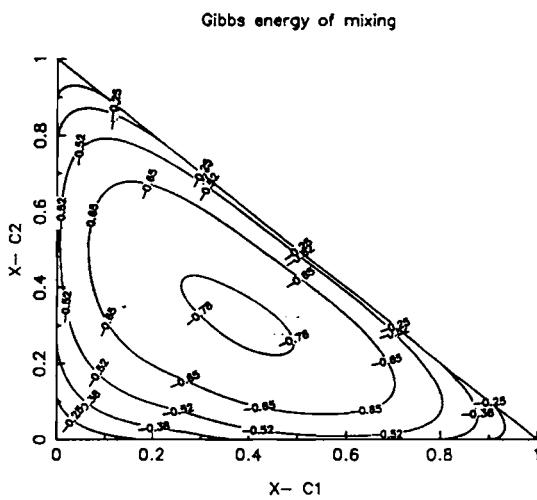


Figure 5: Gibbs energy of mixing diagram for C₁-C₂-CO₂ at 269.5 K, 6.72 MPa.

contour plot using the critical composition as the test phase composition is shown in Figure 6. The tangent plane plot is here characterised by very elongated contours round the critical composition. It is illustrative to compare the tangent plane plot for the critical mixture to a similar plot calculated at T = 266.4 K, 5.44 MPa, corresponding to a point on the phase boundary in the vicinity of the mixture critical point, Figure 7. We here observe two minima, corresponding to the test phase composition and the equilibrium phase

composition. As the distance between the equilibrium phase compositions

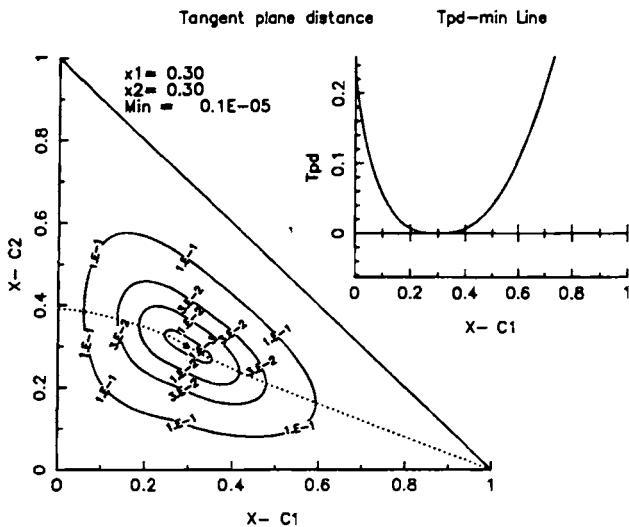


Figure 6: Tangent plane plot for critical ternary mixture.

decreases the minima move together, the final result being the characteristic elongated contours at a critical point. If we connect the two minima by a straight line, the variation of the tangent plane distance along this line will correspond to that observed for a binary mixture.

It is possible to obtain a quantitative description corresponding to that for the binary system as follows: We define the function

$$t^*(s) \equiv \min tpd(\mathbf{x}) \quad (32)$$

subject to the constraints

$$x_1 - z_1 - s = 0; \quad \sum_{i=1}^C x_i - 1 = 0 \quad (33)$$

This objective function fixes one mole fraction x_1 as the *independent variable* through the variable s . Remaining mole fractions are determined such that tpd is minimised and the summation of mole fraction constraint is satisfied. Solving the minimization problem defined by eqns. (7) and (8) in dependence of the 'distance parameter's reduces the tangent plane distance to a function of the single variable s . The locus of local minima is the dashed line shown

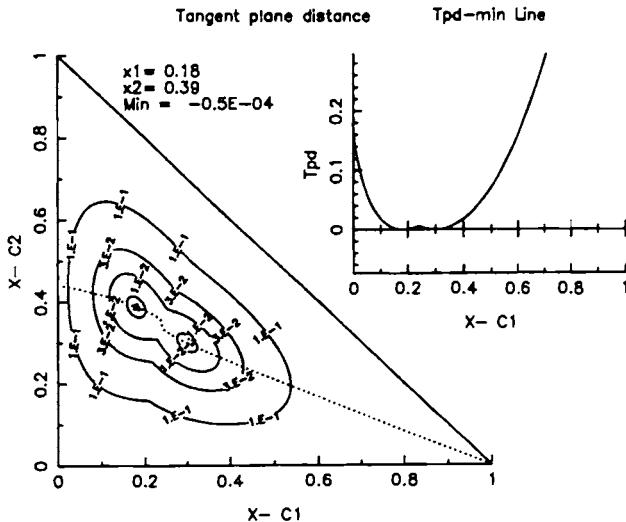


Figure 7: Tangent plane distance plot for near-critical mixture of C_1 - C_2 - CO_2 .

in the contour plot for the tangent plane distance in Figures 6 and 7, and the variation along this line is shown in the inserted upper right plots. As for the binary case, at a critical point this reduced tangent plane distance must satisfy

$$t^*(s) \cong K s^4 \quad (34)$$

or, equivalently,

$$\frac{d^2 t^*}{ds^2} = \frac{d^3 t^*}{ds^3} = 0 \quad \text{at } s = 0 \quad (35)$$

A numerical solution is conveniently performed by means of *Lagrange multipliers*. The Lagrange function corresponding to the objective function of eqns. (7) and (8) is

$$\begin{aligned} \mathcal{L}(\mathbf{x}, \lambda) = & \sum_i x_i (\ln x_i + \ln \hat{\varphi}_i(\mathbf{x}) - d_i) - \lambda_1(x_1 - z_1 - s) \\ & - \lambda_2 \left(\sum_i x_i - 1 \right) \end{aligned} \quad (36)$$

and the following relations must be satisfied at the minimum

$$\ln x_1 + \ln \hat{\varphi}_1(\mathbf{x}) - d_1 - \lambda_1 - \lambda_2 = 0 \quad (37)$$

$$\ln x_i + \ln \hat{\varphi}_i(\mathbf{x}) - d_i - \lambda_2 = 0, \quad i = 2, 3, \dots, C \quad (38)$$

$$x_1 - z_1 - s = 0 \quad (39)$$

$$1 - \sum_i x_i = 0 \quad (40)$$

At the solution of this set of equations, the Lagrange multiplier λ_1 equals dt^*/ds , and evaluation of the criticality criteria thus only requires solution of eqns. (12)-(15) at two s -values, i.e. $s = \epsilon$ and $s = -\epsilon$. The equations are readily solved, e.g. by Newton's method. The evaluation of the criticality conditions can, however, be simplified further. The calculation of the reduced tangent plane distance defines a curve of minimizing compositions, $\mathbf{x} = \mathbf{x}(s)$, in composition space, with $\mathbf{x}(s=0) = \mathbf{z}$. The tangent to this curve at $s=0$ is

$$\hat{\mathbf{x}}(s) = \mathbf{z} + s \mathbf{a} \quad (41)$$

where $\mathbf{a} = (dx/ds)_{s=0}$.

It is easily shown that the second derivative of t^* at $s=0$ is equal to the second derivative of the tangent plane distance, evaluated along $\hat{\mathbf{x}}(s)$. The third derivatives are in general not identical but differ by an amount proportional to the second derivative. As a consequence, we can replace the derivative conditions for t^* with derivative conditions for the tangent plane distance, evaluated along $\hat{\mathbf{x}}(s)$, and explicit determination of t^* is unnecessary. The vector \mathbf{a} is readily determined by linearizing eqns. (13)-(16) at $s=0$. From the Jacobian matrix given by

$$J_{ij} = \frac{1}{z_i} \delta_{ij} + \left(\frac{\partial \ln \hat{\varphi}_i}{\partial n_j} \right)_{T,P,\mathbf{n}=\mathbf{z}} \quad (42)$$

the elements of \mathbf{a} can be calculated from

$$a_1 = 1, \quad (43)$$

$$\sum_{j=2}^C (z_1 J_{1j} + (1-z_1) J_{ij}) a_j + z_1 J_{11} + (1-z_1) J_{1i} = 0, \\ i = 2, 3, \dots, C \quad (44)$$

and, in addition, we get

$$\frac{d\lambda_1(s=0)}{ds} = \frac{1}{1-z_1} \sum_{j=1}^C J_{1j} a_j \quad (45)$$

The second derivative is thus obtained as a byproduct of the calculation, and only the third derivative requires numerical differentiation.

3 Practical determination of the critical point

The procedure described above enable us to determine whether a given mixture is critical at a specified T and P . To determine the mixture critical temperature and pressure, the calculation must be supplemented with an iterative procedure for adjusting T and P in order to satisfy the criticality conditions. A simple and easily implemented procedure would be Newton's method by means of numerical derivatives with respect to T and P . Such a procedure, however, is encumbered with the drawback that quite accurate initial estimates are required in order to obtain convergence. A much preferable approach, suggested by Heidemann and Khalil (1980) with a somewhat different implementation, is based on the use of temperature and volume as the independent variables. Let the test phase of composition \mathbf{z} have the temperature T and the molar volume v^0 . The tangent plane distance for a trial phase at temperature T , total composition \mathbf{n} and total volume V can be written

$$tpd(T, V, \mathbf{n}) = \sum_i n_i (\ln \hat{f}_i(T, V, \mathbf{n}) - \ln \hat{f}_i(T, v^0, \mathbf{z})) - \frac{V}{RT} (P(T, V, \mathbf{n}) - P^0) \quad (46)$$

where $P^0 = P(T, v^0, \mathbf{z})$. The tangent plane distance is a homogeneous function of degree one in (\mathbf{n}, V) and therefore allows us to replace V by v^0 and consider \mathbf{n} as the only independent variables. The criticality conditions for the tangent plane distance written in this form are completely identical to those that apply using T and P as the independent variables, but the iterative search for T and v^0 is much more well-behaved.

In the Heidemann-Khalil approach the matrices of second and third composition derivatives of tpd are calculated at $\mathbf{n} = \mathbf{z}$,

$$\begin{aligned} M_{ij} &= \left(\frac{\partial^2 tpd}{\partial n_i \partial n_j} \right)_{T,V} = \left(\frac{\partial \ln \hat{f}_i}{\partial n_j} \right)_{T,V} \\ N_{ijk} &= \left(\frac{\partial^3 tpd}{\partial n_i \partial n_j \partial n_k} \right)_{T,V} = \left(\frac{\partial^2 \ln \hat{f}_i}{\partial n_j \partial n_k} \right)_{T,V} \end{aligned} \quad (47)$$

Nested loops are used to solve for the critical temperature and volume. In the inner loop the volume is kept fixed and the temperature is determined from the condition

$$\det \mathbf{M} = 0 \quad (48)$$

When the condition of a zero determinant is satisfied, a scaled solution to the set of homogeneous equations,

$$\mathbf{M} \Delta \mathbf{n} = \mathbf{0} \quad (49)$$

is determined, and the second criticality condition

$$\sum_i \sum_j \sum_k N_{ijk} \Delta n_i \Delta n_j \Delta n_k = 0 \quad (50)$$

is used to adjust the volume in the outer loop. Heidemann and Khalil (1980) recommended for initial estimates T as the arithmetic average of the component critical temperatures,

$$T = \sum_i z_i T_{ci}$$

and v^0 as 4 times the equation of state covolume and convergence is generally unproblematic. The major drawback of the Heidemann-Khalil approach, the requirement for second composition derivatives of the fugacities, is easily circumvented by means of a numerical evaluation of the second criticality condition.

Later modifications by Michelsen essentially aim at refining the procedure of Heidemann and Khalil by means of a simultaneous solution procedure for the two equations, a reduced set of derivatives and by a more economical evaluation of the derivatives required in the iterative search. The matrix \mathbf{M} is calculated as in the Heidemann-Khalil method, and we define

$$n_i = z_i + s u_i \sqrt{z_i} \quad (51)$$

where \mathbf{u} is a normalised vector, $\mathbf{u}^T \mathbf{u} = 1$. Then,

$$\left. \frac{\partial^2 tpd}{\partial s^2} \right|_{s=0} = \sum_i \sum_j u_i u_j \sqrt{z_i z_j} M_{ij} = \mathbf{u}^T \mathbf{M}^* \mathbf{u} \quad (52)$$

where $M_{ij}^* = \sqrt{z_i z_j} M_{ij}$. We select \mathbf{u} to be the eigenvector of \mathbf{M}^* corresponding to the smallest eigenvalue, $\mathbf{M}^* \mathbf{u} = \lambda_1 \mathbf{u}$, and therefore,

$$\left. \frac{\partial^2 tpd}{\partial s^2} \right|_{s=0} = \lambda_1 \quad (53)$$

The first criticality condition is that $\lambda_1 = 0$, the equivalent of the Heidemann-Khalil determinant criterion. The second criticality condition becomes

$$c = \left. \frac{\partial^3 tpd}{\partial s^3} \right|_{s=0} = 0 \quad (54)$$

where \mathbf{u} is kept fixed during the differentiation. This latter derivative is evaluated numerically from

$$\begin{aligned} \left. \frac{\partial^3 tpd}{\partial s^3} \right|_{s=0} &\approx \frac{1}{\epsilon^2} \left(\left. \frac{\partial tpd}{\partial s} \right|_{s=-\epsilon} - 2 \left. \frac{\partial tpd}{\partial s} \right|_{s=0} + \left. \frac{\partial tpd}{\partial s} \right|_{s=\epsilon} \right) \\ &= \frac{1}{\epsilon^2} \left(\left. \frac{\partial tpd}{\partial s} \right|_{s=-\epsilon} + \left. \frac{\partial tpd}{\partial s} \right|_{s=\epsilon} \right) \end{aligned} \quad (55)$$

where ϵ is chosen suitably small (10^{-3} - 10^{-4}). The numerical calculation only requires evaluation of the fugacities at a perturbed composition. A similar procedure can of course be used for evaluating the second criticality condition in the Heidemann-Khalil approach. Michelsen in addition derived fairly complex but computationally efficient expressions from which the derivatives of λ_1 and c with respect to the independent variables (temperature and volume) could be calculated and used Newton's method for determining the critical point. Alternatively, additional robustness is possible when the critical point is determined by minimizing the function $\lambda_1^2 + c^2$.

Each iterative step in the Michelsen approach requires a single evaluation of the partial composition derivatives of the (log) fugacities and a single factorization of the matrix of partial derivatives (determining the eigenvector and eigenvalue by inverse iteration). Calculation of c and the temperature and volume derivatives require additional calculations of the fugacities and their temperature and volume derivatives. The Heidemann-Khalil initialization is used, and convergence is usually readily obtained.

4 Higher order critical points

A tricritical point represents a limiting situation with 3 equilibrium phases of identical composition. The criteria for tricriticality are very easily derived from the properties of $t^*(s)$. In addition to the second and third derivatives at $s = 0$, the fourth and fifth derivative must also be equal to zero. Evaluation of these derivatives cannot be performed by means of the straight line approximation only but requires numerical determination of $t^*(s)$, followed by numerical differentiation. As four conditions must be satisfied at a tricritical point, the search involves two composition variables in addition to temperature and pressure/volume.

Critical points of still higher order can be determined similarly, an increase in order by one requiring that two additional derivatives of $t^*(s)$ are equal to zero.

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The practical application of the tangent plane condition of Gibbs in connection with phase equilibrium was demonstrated by Baker et al. (1982), and a computational approach based on minimizing the tangent plane distance was suggested by Michelsen (1982), who also gave guidelines for its use in connection with multiphase equilibrium calculations. Recently, there has been considerable interest in the use of global methods for resolving the stability question. The methodology used comprise global optimization methods, as developed by Floudas and coworkers (e.g. McDonald and Floudas (1995, 1996)) for specific models, interval analysis (Hua et al., 1996) and continuation methods (Sun and Seider, 1995).

A general method for the calculation of critical points in multicomponent mixtures was first formulated by Peng and Robinson (1977). Their approach was based on the 'Gibbs determinants' using pressure and temperature as the iteration variables, and a similar methodology using volume and temperature was proposed by Baker and Luks (1978). The computational inefficiency of these methods were overcome in the method of Heidemann and Khalil (1980), where the second Gibbs determinant condition was replaced by a cubic form. Later, Michelsen (1984) refined the Heidemann-Khalil approach. Finally, a general methodology for determination of higher order critical points was proposed by Michelsen and Heidemann (1988).

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Chapter 10

The Isothermal Two-Phase Flash

Introduction

The isothermal flash calculation, i.e. equilibrium calculation at specified T and P , is probably the most important equilibrium calculation. The fixation of both temperature and pressure also makes the isothermal flash the calculation for which a robust and reliable algorithm is most easily written. For this reason, equilibrium calculations involving alternative specifications are frequently solved by ‘overiteration’, using an isothermal flash calculation in the inner loop, combined with an outer loop for adjustment of either temperature and pressure.

An important feature of the isothermal equilibrium is that the correct solution represents the global minimum in Gibbs energy. Using molar amounts as the independent variable and eliminating the amounts in one phase by means of the overall material balance enables us to solve the equilibrium calculation as an unconstrained minimization problem. The use of this approach provides a level of safety which could not otherwise be obtained. Each iterative step can be tested against the previous for a reduction in mixture Gibbs energy, and unproductive iteration steps can be corrected to prevent divergence.

A complicating factor in these equilibrium calculations is that the number of equilibrium phases may not be known in advance. In many practical applications we may be certain that at most two phases, a liquid and a vapour, are present at equilibrium, but if liquid demixing can occur it is necessary to verify the stability of the two-phase equilibrium mixture. Mixtures capable of forming multiple liquid phases are best handled by alternative use of Gibbs energy minimization for solving the equilibrium calculation for the current (assumed) number of equilibrium phases, and of stability analysis by

means of the tangent plane condition for solution verification and potential introduction of new phases. In this chapter, we shall only consider methods for calculation of two-phase equilibrium, starting with the classical successive substitution method. In addition, the computational aspects of tangent plane stability analysis are discussed.

1 Successive substitution and the Rachford-Rice equation

For mixtures forming ideal solutions in both phases the *PT*-flash is particularly simple, since the equilibrium factors,

$$K_i = \frac{\hat{\varphi}_i^l(T, P)}{\hat{\varphi}_i^v(T, P)} \quad (1)$$

are now known in advance. It is therefore only necessary to solve eqn. (33) in Chapter 8, the Rachford-Rice equation, for β

$$g(\beta) = \sum_{i=1}^C (y_i - x_i) = \sum_{i=1}^C z_i \frac{K_i - 1}{1 - \beta + \beta K_i} = 0 \quad (2)$$

The equation is easily solved, e.g. by Newton's method, using

$$g'(\beta) = - \sum_{i=1}^C z_i \frac{(K_i - 1)^2}{(1 - \beta + \beta K_i)^2} < 0 \quad (3)$$

The function g is thus monotonically decreasing, and a solution in the interval $(0, 1)$ exists provided

$$g(0) = \sum_{i=1}^C z_i K_i - 1 > 0 \quad (4)$$

and

$$g(1) = 1 - \sum_{i=1}^C \frac{z_i}{K_i} < 0 \quad (5)$$

At the solution liquid and vapour mole fractions are subsequently calculated from

$$x_i = \frac{z_i}{1 - \beta + \beta K_i}, \quad y_i = \frac{K_i z_i}{1 - \beta + \beta K_i} \quad (6)$$

Violation of the conditions (4) and (5) correspond to a subcooled liquid ($\beta = 0$) or a superheated vapour ($\beta = 1$), respectively.

Normally, very few iterations are required to solve eqn. (2) using Newton's method, but some situations require special attention. If a very volatile component (like hydrogen) is present in small amount in the feed and the

solution is located close to $\beta = 0$, the derivative of g may become very large, leading to a substantial number of iterations being required. Similar considerations apply with a very heavy component present in trace amounts when the iterations are started from $\beta = 1$.

A simple procedure enables us to generate much better initial estimates in such situations. At the solution, we must of course require that no mole fraction exceeds 1. Consider first a component i for which the K -factor exceeds unity. The condition $y_i \leq 1$ yields from eqn. (6)

$$1 - \beta + \beta K_i \geq K_i z_i \quad \text{or} \quad \beta \geq \frac{K_i z_i - 1}{K_i - 1} \quad (7)$$

For a component with a K -factor smaller than unity, we obtain similarly

$$1 - \beta + \beta K_i \geq z_i, \quad \text{yielding} \quad \beta \leq \frac{1 - z_i}{1 - K_i} \quad (8)$$

The largest positive value of β , calculated from eqn. (7), and the smallest positive value of β , calculated from eqn. (8), define an upper and a lower β -limit for our search. Within this β -range each mole fraction now has a value less than 1 in magnitude.

Finally, roundoff errors may corrupt the result if β is close to 1 and very heavy components are present, as digits are lost in the subtraction $1 - \beta$ in the denominator term $1 - \beta + \beta K_i$. In such cases it is preferable to use the liquid fraction $\beta_l = 1 - \beta$ as the independent variable, yielding the following form of eqn. (2)

$$g(\beta_l) = \sum_{i=1}^C z_i \frac{K_i - 1}{\beta_l + (1 - \beta_l) K_i}$$

A simple safeguard is to evaluate g at $\beta = 0.5$. If the value is negative, the desired root is located in the interval $(0, 0.5)$, and eqn. (2) should be used. In the opposite case the alternative form given above is chosen.

A 'model' Rachford-Rice routine could thus proceed as follows

- i. Check conditions (4) and (5) for existence of a solution. If both are satisfied, set $\beta_{min} = 0$ and $\beta_{max} = 1$. If not, terminate.
- ii. Test conditions (7) and (8) for, whether tighter bounds can be set. For all components with K -factors greater than 1, check whether eqn. (7) yields a positive value for β . If this is the case, set $\beta_{min} = \max_i(K_i z_i - 1)/(K_i - 1)$. In a similar way, eqn. (8) might provide a better value for β_{max} .

- iii. Calculate $\beta_{\text{ini}} = \frac{1}{2}(\beta_{\min} + \beta_{\max})$. If $g(\beta_{\text{ini}}) > 0$, set $\beta_{\min} = \beta_{\text{ini}}$, otherwise set $\beta_{\max} = \beta_{\text{ini}}$. In the latter case, it may also be advisable to change to the liquid fraction as the iteration variable.
- iv. At the current value of β , calculate $g(\beta)$ and $dg/d\beta$. If $g > 0$, set $\beta_{\min} = \beta$, if $g < 0$, set $\beta_{\max} = \beta$. Calculate the Newton step $\Delta\beta$ and set $\beta_{\text{new}} = \beta + \Delta\beta$.
- v. If $\beta_{\min} < \beta_{\text{new}} < \beta_{\max}$, set $\beta = \beta_{\text{new}}$, otherwise set $\beta = \frac{1}{2}(\beta_{\min} + \beta_{\max})$.
- vi. If the length of the Newton step is above the tolerance set for the solution, return to iv. Otherwise calculate the mole fraction of the equilibrium phases from eqn. (6) and terminate the calculation.

If a good initial estimate of the vapour fraction is available (as is the case in the successive substitution method), it may be a waste of time to converge the Rachford-Rice equation to a high tolerance. A solution satisfying the material balances exactly, regardless of whether $g = 0$, can be generated for any value of the vapour fraction using

$$l_i = \frac{(1 - \beta) z_i}{1 - \beta + \beta K_i}, \quad v_i = \frac{\beta K_i z_i}{1 - \beta + \beta K_i}$$

The *successive substitution method* is an extension of the ideal solution procedure to non-ideal mixtures. An initial estimate of the K -factors is used to generate phase composition estimates, which in turn enables us to calculate liquid and vapour fugacity coefficients and new K -factors. The process is repeated until the estimated K -factors agree with the values calculated from the fugacity coefficients.

2 Convergence analysis

As expected, the rate of convergence of successive substitution depends on the degree of non-ideality. In low pressure vapour-liquid equilibrium calculations the vapour phase is nearly ideal, and for hydrocarbon mixtures the deviation from ideality in the liquid phase is also modest, leading to convergence in a few iterations. At higher pressures deviation from ideality becomes pronounced in both phases, and in the vicinity of the mixture critical point convergence becomes intolerably slow.

In order to analyze the convergence properties of successive substitution we shall consider a Newton procedure for solving the flash equations, using

the full set of independent variables. The equilibrium equations are written in the form

$$g_i(\mathbf{v}) = \ln \hat{f}_i^v - \ln \hat{f}_i^l = 0 \quad (9)$$

taking as independent variables the vapour phase component amounts v_i and calculating the corresponding liquid amounts from the overall material balance, $l_i = z_i - v_i$. The Jacobian matrix for the set of C coupled equations, (9), is given by

$$J_{ij} = \frac{\partial g_i}{\partial v_j} = \frac{\partial \ln \hat{f}_i^v}{\partial v_j} - \frac{\partial \ln \hat{f}_i^l}{\partial v_j} = \frac{\partial \ln \hat{f}_i^v}{\partial v_j} + \frac{\partial \ln \hat{f}_i^l}{\partial l_j} \quad (10)$$

where we have utilised that $\frac{\partial l_j}{\partial v_j} = -1$.

In terms of fugacity coefficients we obtain

$$\ln \hat{f}_i^v = \ln y_i + \ln \hat{\varphi}_i^v + \ln P = \ln \frac{v_i}{V} + \ln \hat{\varphi}_i^v + \ln P$$

with $V(= \beta) = \sum_{i=1}^C v_i$, and for the derivatives,

$$\frac{\partial \ln \hat{f}_i^v}{\partial v_j} = \frac{1}{v_j} \delta_{ij} - \frac{1}{V} + \frac{\partial \ln \hat{\varphi}_i^v}{\partial v_j} = \frac{1}{\beta} \left(\frac{1}{y_i} \delta_{ij} - 1 + \bar{\Phi}_{ij} \right) \quad (11)$$

where the elements of $\bar{\Phi}$ for a phase of composition \mathbf{n} are given by

$$\bar{\Phi}_{ij} \doteq n_T \left(\frac{\partial \ln \hat{\varphi}_i}{\partial n_j} \right)_{T,P}, \quad n_T = \sum_{k=1}^C n_k \quad (12)$$

Expanding the liquid phase derivatives similarly, we arrive at the following expression for the Jacobian matrix

$$\begin{aligned} J_{ij} &= \frac{1}{\beta} \left(\frac{1}{y_i} \delta_{ij} - 1 + \bar{\Phi}_{ij}^v \right) + \frac{1}{1-\beta} \left(\frac{1}{x_i} \delta_{ij} - 1 + \bar{\Phi}_{ij}^l \right) \\ &= \frac{1}{\beta(1-\beta)} \left(\frac{z_i}{x_i y_i} \delta_{ij} - 1 + (1-\beta)\bar{\Phi}_{ij}^v + \beta\bar{\Phi}_{ij}^l \right) \end{aligned} \quad (13)$$

Rather than utilizing the full Jacobian matrix, we shall construct an iterative sequence based on the approximation used in the successive substitution method, i.e. that fugacity coefficients are composition independent. The analytic Jacobian given by eqn. (13) is then replaced by the approximate expression

$$J_{ij}^A = \frac{1}{\beta(1-\beta)} \left(\frac{z_i}{x_i y_i} \delta_{ij} - 1 \right) \quad (14)$$

and corrections to the vapour flows are found from

$$\Delta \mathbf{v} = -(\mathbf{J}^A)^{-1} \mathbf{g} \quad (15)$$

The simple structure of \mathbf{J}^A permits analytic inversion, yielding

$$\delta v_i = \beta(1 - \beta) s_i \left(\frac{\sum_j s_j g_j}{\sum_j s_j - 1} - g_i \right) \quad (16)$$

with $s_i = \frac{x_i y_i}{z_i}$.

The correction procedure based on eqn. (16) has convergence properties completely identical to the successive substitution method, as both are based on the same simplification, the assumption of composition independent fugacity coefficients. The rate of convergence for the iterative procedure is linear, with characteristics that can be derived as follows: Assume that the current iterate, \mathbf{v}^k , is close to the final solution, \mathbf{v}^∞ . The subsequent iterate, \mathbf{v}^{k+1} , can be found from eqn. (15), where we can replace \mathbf{J}^A with its value at \mathbf{v}^∞

$$\mathbf{v}^{k+1} = \mathbf{v}^k + \Delta \mathbf{v} = \mathbf{v}^k - (\mathbf{J}^A)^{-1} \mathbf{g}^k \quad (17)$$

Defining the error in the k 'th iteration by $\mathbf{e}^k = \mathbf{v}^k - \mathbf{v}^\infty$, we obtain

$$\mathbf{e}^{k+1} = \mathbf{e}^k - (\mathbf{J}^A)^{-1} \mathbf{g}^k \quad (18)$$

A Taylor series expansion of \mathbf{g} from \mathbf{v}^∞ yields

$$\mathbf{g}^k \approx \mathbf{g}^\infty + \mathbf{J}^E (\mathbf{v}^k - \mathbf{v}^\infty) = \mathbf{J}^E \mathbf{e}^k \quad (19)$$

where \mathbf{J}^E is the exact Jacobian, given by eqn. (13). Substitution of eqn. (19) into eqn. (18) thus yields

$$\mathbf{e}^{k+1} = \mathbf{e}^k - (\mathbf{J}^A)^{-1} \mathbf{J}^E \mathbf{e}^k = (\mathbf{J}^A)^{-1} (\mathbf{J}^A - \mathbf{J}^E) \mathbf{e}^k \quad (20)$$

or

$$\mathbf{e}^{k+1} = \mathbf{M} \mathbf{e}^k, \quad \mathbf{M} = (\mathbf{J}^A)^{-1} (\mathbf{J}^A - \mathbf{J}^E) \quad (21)$$

Let the normalised eigenvectors of \mathbf{M} be \mathbf{u}_i and the corresponding eigenvalues λ_i , and expand the error vector at step k on the set of eigenvectors, i.e.

$$\mathbf{e}^k = \sum_j c_j \mathbf{u}_j \quad (22)$$

The error vector at step $k + 1$ is then given by $\mathbf{e}^{k+1} = \sum_j c_j \lambda_j \mathbf{u}_j$ and that at step $k + m$ by

$$\mathbf{e}^{k+m} = \sum_j c_j \lambda_j^m \mathbf{u}_j \quad (23)$$

It is evident that a *necessary* condition for convergence of the iterative procedure is that all eigenvalues of \mathbf{M} must be smaller than unity in magnitude.

Let λ_1 be the eigenvalue of largest modulus. When m becomes sufficiently large, the term multiplying λ_1^m becomes dominant, and the error is given by

$$\mathbf{e}^{k+m} \simeq c_1 \lambda_1^m \mathbf{u}_1 \quad (24)$$

with that in the subsequent iteration given by

$$\mathbf{e}^{k+m+1} \simeq c_1 \lambda_1^{m+1} \mathbf{u}_1 = \lambda_1 \mathbf{e}^{k+m} \quad (25)$$

Convergence of the iterative procedure is thus linear, the convergence factor (the factor multiplying the error in each subsequent iteration) being equal to λ_1 , the eigenvalue of \mathbf{M} of largest modulus.

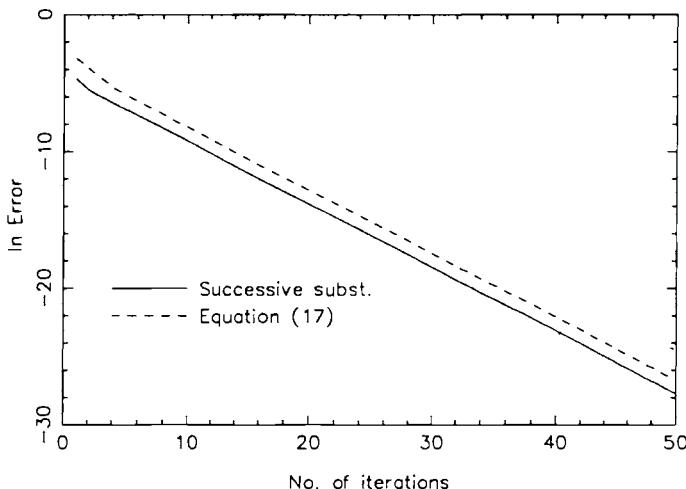


Figure 1: 7-Component mixture containing 94.3% C₁, 2.7% C₂, 0.74% C₃, 0.49% nC₄, 0.27% nC₅, 0.10% nC₆ and 1.4% N₂ at 200 K, 4.559 MPa.

Figure 1 shows the error in β vs. the iteration count for flash calculations on a 7-component mixture at $T = 200$ K, $P = 4.559$ MPa, using i) successive substitution and ii) eqn. (16). It is evident that the rates of convergence of the two methods are identical, both conforming to a value of 0.63 for λ_1 . The difference between \mathbf{J}^A and \mathbf{J}^E (see eqn. (21)) contains only terms related to the composition derivatives of the fugacity coefficients, and it is therefore evident that all eigenvalues of \mathbf{M} are close to zero, and convergence

thus rapid, for nearly ideal mixtures. For non-ideal mixtures the dominant eigenvalue λ_1 is almost invariably located in the interval $0 < \lambda_1 < 1$ and convergence to the desired solution will therefore occur monotonically.

It can be shown theoretically – and verified by computation – that two eigenvalues of \mathbf{M} approach unity when the specified values of T and P are close to the critical point of the feed mixture. In this situation successive substitution will eventually converge, but a very large number of iterations may be required. In Table 1 are listed the number of iterations required to converge the mixture of Figure 1 for a variety of conditions. The critical point for this mixture is $T_c = 203.13$ K, $P_c = 5.886$ MPa.

Table 1: Successive substitution iterations at 203 K to reduce error in the vapour fraction to 10^{-6} .

Pressure (MPa)	Iterations
2.03	3
3.04	6
4.05	12
5.07	26
5.27	33
5.47	41
5.67	85
5.77	154
5.83	264
5.87	1200

Compositions satisfying the condition of equal fugacities do not necessarily represent minima of the Gibbs energy surface. False ‘solutions’ representing stationary points ($\mathbf{g} = 0$) which are not minima can be detected by checking the full Jacobian matrix, eqn. (13), for positive definiteness. Fortunately, it is readily shown that successive substitution can only converge to stationary points that represent minima in G .

In theory it is possible that a stable solution could have a value of λ_1 below -1 , which would prevent convergence of successive substitution. This situation is, however, unlikely to occur, as it would correspond to very strong negative deviations from ideality, and in our experience eigenvalues below -0.1 are rarely observed. Practically relevant examples with an eigenvalue smaller than -1 do exist, however, e.g. in certain polymer mixtures and in solutions of strong electrolytes.

The popularity of successive substitution can be ascribed to two factors, the basic simplicity and ease of implementation for the method, and its robustness. Given tolerable initial estimates, the method will – eventually, and with the rare exceptions above – reach the correct solution. Successive substitution, when properly used, is thus a very safe, and in many instances quite efficient convergence procedure. Its main drawbacks are the inefficiency in particular in the near-critical region and the fact that inadequate initial estimates may well lead to the so-called 'trivial solution' with fluid phases of identical composition.

3 Initial estimates

If no advance knowledge about the solution is available, it is customary to employ as initial estimate Wilson's approximation for the K -factors,

$$\ln K_i = \ln \left(\frac{P_{c_i}}{P} \right) + 5.373 (1 + \omega_i) \left(1 - \frac{T_{c_i}}{T} \right) \quad (26)$$

where T_{c_i} , P_{c_i} and ω_i are critical temperature, critical pressure and acentric factor for component i . The Wilson K -factor approximation is actually a generalised vapour pressure correlation of the form $\ln P = A - B/T$, fixed at the pure component critical point and at a reduced temperature of 0.7, where $\log_{10} P_r = -1 - \omega$. The Wilson approximation is usually adequate for calculations on hydrocarbon mixtures, although the K -values predicted for supercritical components can be quite erroneous.

Early iterations may indicate that the mixture to be flashed will only form a single phase, as characterised by β -values below zero or above unity. If, for example, condition (4) is violated, the liquid phase composition is set to that of the feed, and a new vapour composition is calculated from

$$y_i = \frac{K_i z_i}{\sum_j K_j z_j} \quad (27)$$

New vapour phase fugacity coefficients are evaluated, and the process is repeated until

- a) A vapour fraction in the range $0 < \beta < 1$ is obtained,
- b) The vapour composition converges, while eqn. (4) is still violated, or
- c) The trivial solution $y = x$ is obtained.

Cases b) and c) indicate that the (P, T) -specification corresponds to a point in the single phase region.

This procedure may lead to failure (convergence to a single phase, where the proper result is two phases) in the vicinity of a critical point, but such failures are rare.

4 Accelerated direct substitution

During the last decades several attempts have been made to accelerate the convergence of successive substitution. A general feature of these acceleration procedures is that they manipulate the results of the basic successive substitution procedure with the purpose of extrapolating to the result that would be obtained after infinitely many steps. Consider for example successive substitution after k steps and assume that at this stage the error vector is dominated by a single contribution, i.e.

$$\mathbf{e}^k \simeq c_1 \mathbf{u}_1 \quad (28)$$

The two subsequent steps then become

$$\mathbf{e}^{k+1} \simeq c_1 \lambda_1 \mathbf{u}_1 \quad (29)$$

$$\mathbf{e}^{k+2} \simeq c_1 \lambda_1^2 \mathbf{u}_1 \quad (30)$$

Subtraction of eqn. (29) from eqn. (28), and eqn. (30) from eqn. (29) yields

$$\Delta^k = \mathbf{e}^{k+1} - \mathbf{e}^k = \mathbf{v}^{k+1} - \mathbf{v}^k \simeq (\lambda_1 - 1) c_1 \mathbf{u}_1 \quad (31)$$

$$\Delta^{k+1} = \mathbf{e}^{k+2} - \mathbf{e}^{k+1} = \mathbf{v}^{k+2} - \mathbf{v}^{k+1} \simeq \lambda_1 (\lambda_1 - 1) c_1 \mathbf{u}_1 \quad (32)$$

indicating that the difference Δ^k between iterates \mathbf{v}^{k+1} and \mathbf{v}^k should be proportional to the difference Δ^{k+1} between \mathbf{v}^{k+2} and \mathbf{v}^{k+1} , the proportionality factor being λ_1 . If vectors are indeed proportional, we can calculate the eigenvalue from

$$\lambda_1 = \frac{(\Delta^k)^T \Delta^{k+1}}{(\Delta^k)^T \Delta^k} \quad (33)$$

and $c_1 \mathbf{u}_1 = \frac{\Delta^k}{\lambda_1 - 1}$. Eqn. (30) then yields \mathbf{e}^{k+2} and hence the desired solution,

$$\mathbf{v}^\infty = \mathbf{v}^{k+2} - \mathbf{e}^{k+2} = \mathbf{v}^{k+2} + \lambda \frac{1}{1 - \lambda_1} \Delta^{k+1}$$

In practice, the vectors will not be exactly proportional, and λ_1 is determined by minimizing the norm of the vector $\Delta^{k+1} - \lambda_1 \Delta^k$. The extrapolation

to v^∞ in this case does not yield the exact solution but – hopefully – a much better estimate than that obtained from just continuing successive substitution. Iterations are therefore restarted using the extrapolated value as the new initial estimate, and after a sequence of successive substitution steps, extrapolation is again performed.

The acceleration method can be used equally well with the usual choice of the $\ln K_i$ as the independent variables, and this is normally preferable, as a better scaling of the variables is obtained.

Figure 2 shows the example of Figure 1, where the extrapolation is performed after every 5th step of successive substitution.

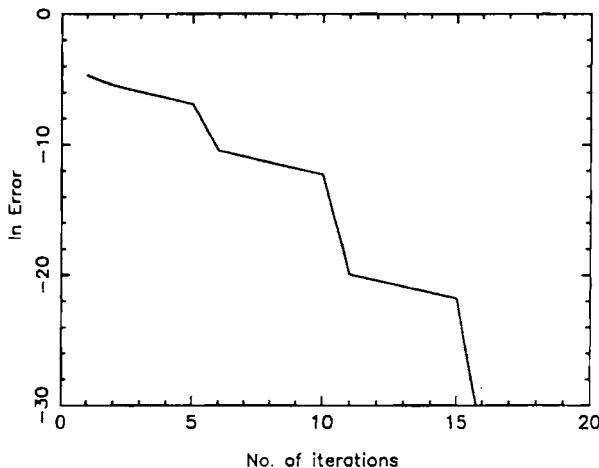


Figure 2: Example of Figure 1 with extrapolation after every 5 SS-steps.

The extrapolation method suggested here is essentially the Dominant Eigenvalue Method of Orbach and Crowe (1971). Its use is evidently not restricted to flash calculations. An efficient extrapolation requires that the λ_1 -term is the dominant contribution to the error vector, and in cases where the smaller eigenvalues are close to λ_1 in magnitude many successive substitution steps may be required to isolate the λ_1 -term. We noted earlier that as a critical point is approached, 2 eigenvalues of M become close to unity in magnitude, and the single term extrapolation might therefore be inefficient.

The Dominant Eigenvalue method is easily extended to handle several components of the error vector simultaneously. Assuming that the error vec-

tor at the current iteration is confined to a subspace spanned by 2 eigenvectors of \mathbf{M} , constants a and b are determined such that the norm of a linear combination of the delta-vectors, is minimised. Determination of a and b subsequently are used to calculate an extrapolated value for \mathbf{v} , as described by Crowe and Nishio (1975).

Our computational experience is that inclusion of 2 terms is slightly superior to using one term only, whereas no additional benefits result from including more than 2 terms. Using 2 terms, about 5 successive substitution steps are recommended between extrapolations.

The use of extrapolation procedures can have a profound influence on the rate of convergence of successive substitution, in particular at higher pressures. This improvement in performance is obtained at a cost: The basic stability of successive substitution is lost. The reason for this is that the extrapolation frequently involves substantial magnification of Δ^k . A value of λ_1 of e.g. 0.95 corresponds to multiplying the steplength by a factor of 20. If, however, λ_1 is incorrectly estimated to be 0.98, the extrapolation 'overshoots' the target, and an estimated λ_1 -value above unity should not be used at all for extrapolation, as it leads to a step in the wrong direction. A mandatory precaution is therefore to check the mixture Gibbs energy after each extrapolation step. If an increase in G is observed, the extrapolation should be discarded, and additional steps of successive substitution performed.

An illustration of the problems that can be encountered with extrapolation methods is given in Figure 3, a flash calculation for the mixture of Figure 1 under near-critical conditions ($T = 204.94$ K, $P = 6.08$ MPa), where the dominant eigenvalue, calculated from eqn. (33), is plotted against the iteration count. The final value of λ_1 is 0.98, but it is evident that strong variations in the eigenvalue is observed initially, making early extrapolations inaccurate or even leading to steps in the wrong direction.

5 Gibbs energy minimization by second order methods

The efficiency of successive substitution decreases when eigenvalues are close to unity, where 'overshooting' makes frequent use of successive substitution steps necessary. Methods that directly take into account their composition derivatives of the fugacity coefficients are preferable under these conditions. Rather than applying Newton's method directly, it is advantageous to treat the flash calculation as a minimization problem, using as objective function G/RT and the vapour amounts v_i as the independent variables. The gradient

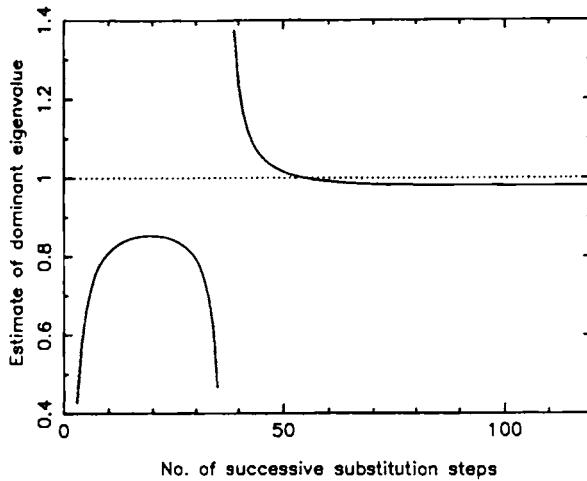


Figure 3: Estimate of Dominant Eigenvalue vs. iteration count.

vector is obtained from (cf. eqn. (9))

$$\frac{\partial}{\partial v_i} \left(\frac{G}{RT} \right) = g_i = \ln \hat{f}_i^v - \ln \hat{f}_i^l \quad (34)$$

and the Hessian matrix, $H_{ij} = \frac{\partial g_i}{\partial v_j}$ is identical to the Jacobian matrix derived in eqn. (9).

Newton's method for solving the minimization problem calculates the correction vector from

$$\mathbf{H} \Delta \mathbf{v} + \mathbf{g} = \mathbf{0} \quad (35)$$

and is thus identical to the Newton-Raphson method for solving the flash as a set of algebraic equations. If the current estimate is sufficiently close to the solution, the Hessian matrix is positive definite, and second order convergence is obtained.

In the critical region, however, Newton's method faces the same problems as accelerated direct substitution. The determinant of \mathbf{H} will be close to zero, and the correction vector may overshoot the target. Step length adjustment, e.g. by performing a search along the direction defined by the correction vector, may reduce these problems but does not guarantee convergence, as Newton's method may fail if \mathbf{H} is not positive definite, which is frequently

the case in early iterations. In order to guarantee convergence it is necessary to modify \mathbf{H} , solving instead

$$\hat{\mathbf{H}} \Delta \mathbf{v} + \mathbf{g} = \mathbf{0} \quad (36)$$

where the modified matrix $\hat{\mathbf{H}}$ is positive definite. The algorithm presented earlier, where composition derivatives of the fugacity coefficients were neglected in the Jacobian, actually represent such a modification. The correction vector calculated from eqn. (36) always defines a descent direction, which explains the stability of successive substitution.

Any modification of \mathbf{H} , however, has an adverse effect on the rate of convergence, and the modified matrix should therefore only be used when \mathbf{H} is indefinite or nearly singular.

In the method of Murray, suggested for use in flash calculations by Michelsen (1982b), the modification of \mathbf{H} consists of a correction of the diagonal elements during the factorization, provided it is indicated that \mathbf{H} has negative or very small eigenvalues. The main advantage of this method is that an indefinite Hessian does not require refactorization. While providing a descent direction, the Murray correction necessitates a subsequent line search, and the direction generated is frequently suboptimal, since the essentially empirical modification of \mathbf{H} affects the scaling of the problem.

A preferable approach, in our opinion, is the use of a 'restricted step' method. A diagonal correction term, multiplied by a factor, unspecified for the moment, is added to the Hessian, i.e.

$$\hat{\mathbf{H}} = \mathbf{H} + \alpha \mathbf{s} \quad (37)$$

where the factor α is chosen such that the length of the resulting correction is restricted to a prespecified maximum size. The modification is only used, if the step calculated with the unmodified Hessian exceeds this maximum size, and the final quadratic convergence of the procedure is therefore unaffected. The value of the maximum stepsize is adjusted during the course of iteration by means of the match between expected (from the second order expansion) and the actually calculated value of the objective function. If the calculated improvement exceeds or is close to the expected improvement, larger steps are permitted, and vice versa.

The iterative determination of the α -parameter involves additional work, but in our experience the restricted step procedure is capable of converging difficult flash problems significantly faster than Murray's algorithm. As the correction term we use the diagonal from the approximate Jacobian of eqn. (14), i.e.

$$s_i = \frac{z_i}{x_i y_i} \quad (38)$$

It should be kept in mind that situations requiring modification of the Hessian matrix are rare. Even in the critical region the Newton-Raphson method works quite well, and failures are rare. Michelsen (1982b) suggested, somewhat optimistically, that judicious selection of initial estimates (based on stability analysis) combined with the Newton-Raphson method would be adequate for all two-phase calculations. Since the precautions required to enhance robustness are easily implemented and do not affect efficiency, there is, however, no reason to prefer the equation based Newton-Raphson method to the minimization approach.

One drawback of second order methods is the requirement for the composition derivatives of the fugacity coefficients. These derivatives can normally be coded quite efficiently, the additional cost typically being less than 2 times that required for fugacity coefficients alone, an effort easily compensated by the reduction in the number of iterations.

As most flash problems are readily converged using accelerated successive substitution, our preference is to use this approach initially. Two or three accelerations, each using the General Dominant Eigenvalue Method with 2 terms after 5 steps of successive substitution, are performed. If convergence has not been obtained at this stage, we switch to the second order minimization.

6 Strategy for a flash algorithm

The traditional approach in two-phase flash calculations is based on the implicit assumption that two phases will be present at equilibrium. An initial estimate of the phase compositions is used to initiate calculations, and the iterative process is continued to convergence provided two phases are found in all iterations. The vanishing of a phase is taken as indication of the specification corresponding to a single phase. The alternative approach is to start with stability analysis and to utilise the outcome to generate initial estimates for the flash calculation, provided the feed mixture is unstable.

Both methods have their advantages and their disadvantages. Starting directly with phase split calculations 'saves' the stability analysis in cases where the correct equilibrium distribution is two phases but leads to wasted calculations for single phase specifications. In addition, the traditional approach is more sensitive to the quality of the initial estimate and may lead to incorrect results when intermediate iterations indicate single phase behaviour. Our suggestion is to try to combine the best of both approaches, initiating calculations with the assumption of two phases being present but reverting to stability analysis at a very early stage if instability of the single

phase has not been verified. Therefore, we proceed as follows:

Start with 3 steps of successive substitution, using the Wilson K -factor approximation as the initial guess.

The following conditions may occur:

- a) The total Gibbs energy of the resulting vapour and liquid is lower than that of the feed. This verifies the presence of (at least) two equilibrium phases, and as our algorithm requires that the Gibbs energy decreases at each step, convergence to the ‘trivial’ solution can never take place. Continue with accelerated successive substitution and, if necessary, the second order minimization.

$$\frac{\Delta G}{RT} = (1 - \beta) \sum_i x_i (\ln x_i + \ln \hat{\varphi}_i^l) + \beta \sum_i y_i (\ln y_i + \ln \hat{\varphi}_i^v) - \sum_i z_i (\ln z_i + \ln \hat{\varphi}_i^z) \quad (39)$$

is the difference in Gibbs energy between the split phases and the feed.

Using the material balance, $z_i = \beta y_i + (1 - \beta) x_i$, this relation can be written

$$\frac{\Delta G}{RT} = (1 - \beta) \sum_i x_i (\ln x_i + \ln \hat{\varphi}_i^l - \ln z_i - \ln \hat{\varphi}_i^z) + \beta \sum_i y_i (\ln y_i + \ln \hat{\varphi}_i^v - \ln z_i - \ln \hat{\varphi}_i^z) \quad (40)$$

or

$$\frac{\Delta G}{RT} = (1 - \beta) tpd_x + \beta tpd_y \quad (41)$$

where tpd_x and tpd_y are reduced tangent plane distances for the feed composition, using the current liquid and vapour composition as trial phases.

- b) Even if $\Delta G/(RT)$ is positive, it is possible that either tpd_x or tpd_y is negative, in which case we also know that the feed is unstable. Assume for example that tpd_y is negative. We then select $\ln K_i$ for the subsequent iteration as $\ln K_i = \ln \hat{\varphi}_i^z - \ln \hat{\varphi}_i^y$, perform one step of successive substitution (guaranteed to lead to a negative ΔG) and continue as in a). With a negative tpd_x we select instead $\ln K_i = \ln \hat{\varphi}_i^x - \ln \hat{\varphi}_i^z$.
- c) If neither event has occurred after 3 iterations, we continue with tangent plane stability analysis.

- d) If β exceeds its bounds, it is very likely that the specification corresponds to a single phase. As no guarantee can be given, we prefer to continue with stability analysis also in this situation.

It may be argued that this procedure is very conservative, as stability analysis is always performed in 'questionable' situations. In the majority of cases the stability analysis will verify the expected result of the feed being stable. The 'optimal' algorithm always has to balance efficiency against reliability, and if one is willing to accept occasional (infrequent) errors in the phase identification, less stringent procedures can be used with a corresponding reduction in computational cost.

7 Tangent plane analysis

As outlined above tangent plane stability analysis is invoked when 3 steps of successive substitution are inconclusive. The initial calculations indicate that only a single phase is present at the specified (T, P) , but a verification is desired. On the other hand, if the stability analysis reveals that the feed is unstable, we need to generate an improved K -factor estimate for the subsequent phase split calculation. Tangent plane analysis serves both purposes.

The tangent plane criterion for stability, eqn. (9), can be formulated as follows: The phase of composition \mathbf{z} is stable at the specified (T, P) if and only if

$$tpd(\mathbf{w}) = \sum_i w_i (\ln w_i + \ln \hat{\varphi}_i(\mathbf{w}) - \ln z_i - \ln \hat{\varphi}_i(\mathbf{z})) \geq 0 \quad (42)$$

for any trial phase composition \mathbf{w} , or, for brevity,

$$tpd(\mathbf{w}) = \sum_i w_i (\ln w_i + \ln \hat{\varphi}_i(\mathbf{w}) - d_i) \geq 0 \quad (43)$$

with $d_i = \ln z_i + \ln \hat{\varphi}_i(\mathbf{w})$.

In practice, we prefer to use the *modified tangent plane distance* introduced in Chapter 9, where the elements of \mathbf{W} are formally treated as *mole numbers*,

$$tm(\mathbf{W}) = 1 + \sum_i W_i (\ln W_i + \ln \hat{\varphi}_i(\mathbf{W}) - d_i - 1) \quad (44)$$

The stationary points of tm are given by

$$\frac{\partial tm}{\partial W_j} = 0, \quad j = 1, 2, \dots, C \quad (45)$$

or

$$\ln W_j + \ln \hat{\varphi}_j(\mathbf{W}) - d_j = 0 \quad (46)$$

with the corresponding stationary value being

$$tm^{SP} = 1 - \sum_i W_i \quad (47)$$

8 Locating the minima of tm

The location of one stationary point of tm is immediately evident, the ‘trivial’ solution, $\mathbf{W} = \mathbf{z}$. The trivial solution is also a minimum of tm provided the Hessian, evaluated at \mathbf{z} ,

$$H_{ij} = \frac{\partial^2 tm}{\partial W_i \partial W_j} = \left(\frac{1}{W_i} \delta_{ij} + \frac{\partial \ln \hat{\varphi}_i}{\partial W_j} \right)_{\mathbf{W}=\mathbf{z}} \quad (48)$$

is at least positive semidefinite, i.e., all eigenvalues of \mathbf{H} must be non-negative. If any eigenvalue of \mathbf{H} is negative, the mixture is unstable since the tangent plane criterion is violated in the immediate vicinity of \mathbf{z} along the direction of the eigenvector with negative eigenvalue. If \mathbf{H} has negative eigenvalues, the mixture of composition \mathbf{z} is called *intrinsically unstable*.

When the smallest eigenvalue of \mathbf{H} is exactly zero, the mixture is at the *limit of intrinsic instability* (the *spinodal curve*). As we shall see later, a critical mixture is located on the intrinsically unstable locus. If \mathbf{H} is positive definite, the mixture is either stable (tm being non-negative anywhere) or metastable (with tm negative at a non-zero distance from \mathbf{z}).

Intrinsic instability is easily detected numerically, and we shall therefore concentrate on the more interesting case of the trivial solution representing a minimum in tm . In this situation, instability requires the existence of additional minima with negative tm .

In cases where the feed of composition \mathbf{z} can be unambiguously identified as a ‘liquid’ or as a ‘vapour’, the search is relatively simple. For a liquid feed, we shall search for a ‘vapour-like’ trial phase which minimises tm , and for a vapour feed the search is for a ‘liquid-like’ trial phase. Unfortunately, at high pressures it is not possible to make a unique phase identification based on the properties of the feed \mathbf{z} only, and it is therefore necessary to investigate both possibilities. We shall again utilise the Wilson K -factors for constructing ‘vapour-like’ and ‘liquid-like’ trial phases of compositions

$$W_i = K_i z_i \quad (\text{'vapour' trial phase}) \quad (49)$$

and

$$W_i = \frac{z_i}{K_i} \quad (\text{'liquid' trial phase}) \quad (50)$$

respectively.

9 Procedures for minimizing tm

Given an initial estimate for \mathbf{W} our aim is to determine the solution of eqn. (46). As discussed in Chapter 9, successive substitution

$$\ln W_i^{k+1} = d_i - \ln \varphi_i(\mathbf{W}^k) \quad (51)$$

is an obvious possibility. Convergence analysis can be performed in a similar manner as for the flash calculation, and it is readily shown that \mathbf{W} can only converge to a minimum of tm . The matrix \mathbf{M} determining the rate of convergence is given by

$$M_{ij} = -\bar{\Phi}_{ij} w_j \quad (52)$$

and exactly one eigenvalue of \mathbf{M} approaches unity for a near-critical minimum. Acceleration can be used as for the flash calculation, and a dominant eigenvalue approach with one term is adequate.

If rapid convergence does not occur, use of a second order minimiser should be considered. As suggested in Chapter 9 we apply the variable transformation

$$\alpha_i = 2\sqrt{W_i} \quad (53)$$

yielding the gradient vector

$$g_i = \frac{\partial tm}{\partial \alpha_i} = \sqrt{W_i} (\ln W_i + \ln \varphi_i(\mathbf{W}) - d_i) \quad (54)$$

and the Hessian matrix

$$H_{ij} = \frac{\partial^2 tm}{\partial \alpha_i \partial \alpha_j} = \delta_{ij} \left(1 + \frac{g_i}{\alpha_i} \right) + \sqrt{w_i w_j} \bar{\Phi}_{ij} \approx \delta_{ij} + \sqrt{w_i w_j} \bar{\Phi}_{ij} \quad (55)$$

A restricted step procedure is recommended, where step length control is accomplished by addition of a constant term to the diagonal of \mathbf{H} . Stability analysis results in one of the following two possibilities:

- i) We locate a composition \mathbf{W} where tm is negative, based on at least one of the initial estimates given by eqns. (49) and (50). In this case we continue with flash calculations, \mathbf{W} providing a composition estimate for the incipient phase.
- ii) Both initial estimates result in convergence to either the trivial solution or to a positive minimum of tm , leading to the conclusion that the feed \mathbf{z} is stable. Convergence to a positive minimum usually indicates that the feed corresponds to a point in the single phase region fairly close to the phase boundary, with \mathbf{W} being a good approximation for the composition of the incipient phase at the phase boundary.

The procedure suggested here for stability analysis is very conservative in the sense that it attempts to minimise the risk of missing a two-phase solution. In most cases, converging stability analysis twice, with initial estimates from both eqns. (49) and (50) represents wasted effort, as at least one of these estimates is very likely to converge to the trivial solution. If a phase identification for the feed can be made with confidence (as 'liquid-like' or as 'vapour-like'), a one-sided stability analysis is adequate. Such a phase identification is, however, difficult to perform in the critical region, and if emphasis is on safety the two-sided approach is the only 'guarantee' against misinterpreting the phase distribution.

10 Hybrid models

Our considerations so far are related to flash calculations based on the use of the same equation of state for modelling both phases. When different phase models are used (e.g. a g^E -model for the liquid phase and the virial equation for the vapour), life becomes much easier. The use of hybrid models implies that critical points are absent, and more rapid convergence of the flash calculations can be expected. More important, the feed can now unambiguously be identified as either a liquid or as a vapour, by selection of the phase type with the smaller Gibbs energy.

11 Liquid-liquid equilibrium

Two factors complicate the calculation of liquid-liquid equilibrium. Although the methods described above for vapour-liquid equilibrium can be used, conditions are very frequently 'near-critical', and it is therefore much more often necessary to resort to second order procedures. Second no 'natural' K -factor estimate is available, and verification of stability by means of tangent plane analysis becomes much more involved and requires repeated calculations using many different initial estimates. Calculation of LLE shares many of the characteristics of multiphase calculations, and the procedures for selection of initial estimates for the stability analysis essentially follows the guidelines for multiphase stability analysis, to be discussed in the following chapter.

12 When speed counts

The computational requirements for solving the PT -flash using the methodology given in this chapter is modest, and usually of the order of a fraction of a millisecond for a mixture containing 10-20 components. Therefore, in most applications requiring up to a few thousands of calculations robustness and reliability are much more important than speed.

In the modeling and simulation of unsteady state multiphase flow, however, phase equilibrium is normally applied as a constraint for the phases in contact. Such simulations incorporate a discretisation in time and in up to 3 spatial dimensions and consequently a request for a very large number of equilibrium calculations. In 3D-simulations a total of one million discretization points (grid blocks) are not unusual, and the time integration can easily involve around 1000 time steps. With a total demand for more than 10^9 flash calculations a computation time of 10^{-3} seconds for each suddenly becomes prohibitive instead of insignificant.

Utilizing previous history

Fortunately, the conditions under which these calculations have to be performed differ from the usual situation in that the calculations are no longer isolated. The overall composition, as well as that of the equilibrium phases, will resemble those at neighbouring points in space as well as in time. In particular, conditions in any given gridblock will be closely related to those in the same gridblock at the previous time step, in particular when the timesteps are small. The way this information is utilised depends on the outcome of the previous calculation, and we may here distinguish between 3 different situations:

1. The calculation resulted in two equilibrium phases.
2. The mixture is in the single phase region, but a positive minimum of the tangent plane condition was found.
3. The mixture is in the single phase region and only the trivial minimum of the tangent plane distance was found.

These different outcomes are best illustrated by means of a graphical representation. Figure 4 shows a phase diagram for a typical oil, with properties and composition as specified in Table 2. Only the binary interaction coefficients between carbon dioxide and the other mixture components are nonzero.

We may encounter the following situations:

1. At point A two equilibrium phases exist. Most likely, the calculation in the next timestep, with slightly changed temperature, pressure and mixture composition, will also lead to two equilibrium phases.
2. At point C, only one phase exists at equilibrium. However, the tangent plane distance minimization has located a nontrivial minimum with a positive value of the tangent plane distance. The phase boundary, point

Table 2: The pure-component parameters, the binary interaction coefficients and the composition of the oil.

Component	T_c (K)	P_c (Atm)	ω	k_{1j}	Mole pct
CO ₂	304.2	72.9	0.2280	0.00	2.13
C ₁	190.6	45.4	0.0080	0.12	31.28
C ₂	305.4	48.2	0.0980	0.15	7.51
C ₃	369.8	41.9	0.1520	0.15	6.93
<i>i</i> C ₄ - <i>n</i> C ₄	424.5	37.4	0.1923	0.15	6.26
<i>i</i> C ₅ - <i>n</i> C ₅	467.7	33.3	0.2461	0.15	4.74
C ₆	507.4	29.3	0.2960	0.15	4.37
C ₇ -C ₁₁	632.3	28.8	0.2323	0.15	18.75
C ₁₂ -C ₁₆	662.9	22.7	0.5192	0.15	8.93
C ₁₇ -C ₂₉	723.2	18.0	0.9837	0.15	6.03
C ₃₀ -C ₈₀	885.8	14.5	1.3391	0.15	3.07

Phase Envelope and Shadow Region

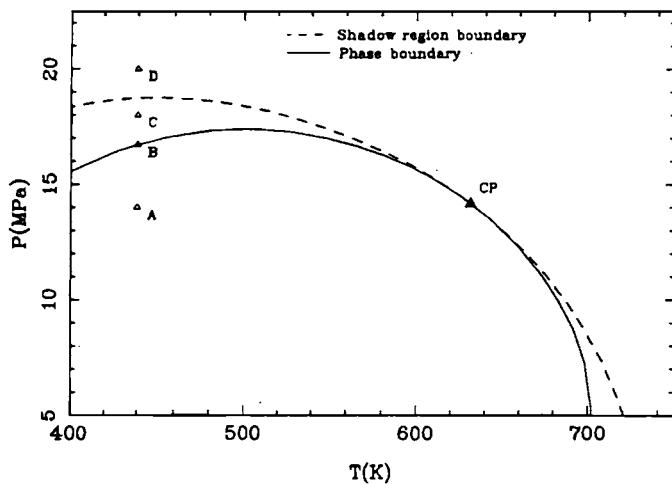


Figure 4: Phase envelope and shadow region.

B, represents the borderline case, where the value of the nontrivial minimum is exactly zero. The most likely outcome in the following timestep is a new nontrivial, positive minimum.

3. At point D we are in the single phase region, and tangent plane minimization has the trivial solution as outcome, regardless of the initial estimate. There is a high probability that the conditions in the next time step also corresponds to a single phase.

We shall subsequently consider in more detail how each of these outcomes are treated.

The two-phase case

Here, our working assumption is that the subsequent calculation is also going to yield two phases. Also, the phase compositions at current conditions are assumed to provide an excellent initial estimate for the new calculation. We utilise the vapour split factors, defined by

$$\theta_i = \frac{v_i}{v_i + l_i}$$

to create initial estimates of the vapour flows from:

$$v_i^{\text{new}} = \theta_i z_i^{\text{new}} \theta_i$$

With this estimate we proceed directly to solve eqn. (9) by Newton's method, using the full Jacobian of eqn. (16). We expect to be able to solve the equations in at most 3 iterations, and the solution attempt is terminated if any of following events occur:

- The Jacobian is not positive definite.
- The correction results in negative flows (indicating removal of a phase)
- The maximum iteration count (normally 3) is exceeded.

In the case termination occurs for any of the above reasons we revert to the 'safe' approach escribed earlier, with successive substitution, Gibbs energy minimization and full stability analysis.

The raw Newton approach without any safeguards may well fail, even in many cases where a more cautious approach would have converged. The failures are, however, rare enough that their cost is easily outweighed by the speed gains of the very simple convergence approach. Note that the Rachford-Rice procedure is not used at all.

The shadow region

We shall denote the part of the single phase region, where a non-trivial positive minimum of the tangent plane distance exists, as *the shadow region*. Here, we converge and subsequently store the minimizing composition even though this might not be needed in order to resolve the stability question. The phase with this composition is called *the shadow phase*.

The subsequent calculation is assumed also to lead to a positive minimum in the tangent plane distance, and the determination of this minimum is performed directly, with the second order method using eqns. (53)-(55). The potential outcomes are

- A new positive minimum is found.
- A negative minimum is found. We then continue with the conventional flash calculation. This event occurs at some stage (close to B) if conditions move gradually from point C to point A. At point B, the composition of the shadow phase equals that of the incipient phase.
- The non-trivial minimum ceases to exist. This occurs when we pass the outer boundary on the shadow region, on the move towards point D. On the outer region of the phase boundary the shadow phase is at its limit of intrinsic stability.

Outside the shadow region

Finally, we shall frequently encounter the case where only the trivial solution is found in the tangent plane minimization. Current conditions are in the single phase region and, unless we are close to the critical point, we are also at some distance from the phase boundary, as is the case for point D. This implies that modest changes in conditions for the next timestep will also with high probability lead to a point in the single phase region, and it may be safe to skip stability investigations entirely if the changes in conditions (temperature, pressure and overall composition) are small enough. Clearly, this implies substantial savings in computing time.

Close to the critical point, however, the shadow region that acts like a buffer zone is very narrow, and there is a danger that a small change in conditions might move us directly from the outer part of the single phase region into the two-phase region and here stability analysis may be called for at each time step.

Obviously, a measure of the distance from the critical point is useful, as it allows us to judge whether a given change in compositions requires renewed stability analysis. Based on Michelsen's analysis of phase equilibrium in the

critical region (Michelsen, 1984), Rasmussen et al. (2006) used the minimum eigenvalue, λ_1 , of the scaled Hessian, eqn. (55), as such a measure.

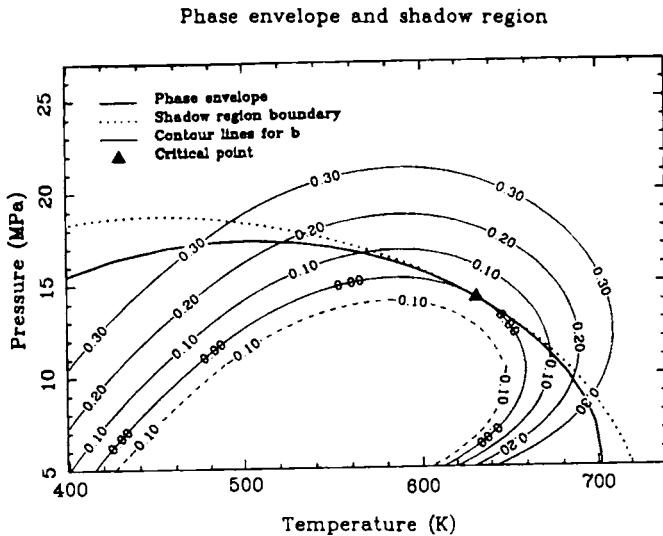


Figure 5: Phase envelope and shadow region.

Figure 5 shows the phase diagram with contour lines of constant λ_1 . One can show that the width of the shadow region is, to a first approximation, proportional to the value of λ_1 at the outer boundary of the shadow region, and λ_1 can therefore be used to regulate the size of the changes in composition that is permitted before renewed stability analysis is performed. Rasmussen et al. (2006) suggested the following procedure:

- When stability analysis is required in a given time step and results in the trivial minimum only, calculate and store the value of λ_1 , together with the mixture temperature, T^* , pressure P^* and composition \mathbf{z}^* .
- In subsequent timesteps, check whether the conditions

$$|z_i - z_i^*| < 0.1\lambda_1, \quad |T - T^*| < 10\lambda_1(K), \quad |P - P^*| < 0.1P\lambda_1$$

are all satisfied. If this is the case, skip stability analysis. If not, redo the stability calculation.

The numerical coefficients used in the above comparison were determined empirically from a large number of simulations. It is likely that a relative

critierion for the composition change would be superior to the absolute change applied above and that other numerical values would provide a better balance between safety and speed for other mixtures than those used by Rasmussen et al. (2006), but the overall effect of all these modifications, relative to the time consumption by use of the standard approach for flash calculations, was a reudction in computing time by about a factor of 10, without the result of the simulations being affected.

Other factors

In addition to the speedup that can be accomplished by taking advantage of the results from previous time step, much can also frequently be gained by tuning the code to avoid unnecessary and expensive operations. In particular, transcendentals are very expensive, with a cost of up to 100 additions or multiplications. The direct Newton approach used in the phase split calculation, for example, only needs the evaluation of one logarithm per component in order to calculate the gradient vector (eqn. (9)), since

$$g_i = \ln \hat{f}_i^v - \ln \hat{f}_i^l = \ln \frac{y_i}{x_i} + \ln \hat{\varphi}_i^v - \ln \hat{\varphi}_i^l$$

where the thermodynamic property routine directly provides the logarithms of the fugacity coefficients. Evaluation of the objective function, however, requires the molar Gibbs energy of vapour as well as of liquid, and this requires twice the number of logartihm evaluations.

Also divisions, however, are much more expensive than additions or multiplications, and as a consequence the Rachford-Rice solution procedure is far from being as inexpensive computationally as normally believed. Each iteration requires as many divisions as the number of components in the mixture, and additional divisions are needed for the final calculation of mole fractions.

Conditional instructions can also incur an unexpected cost. Modern computers are pipelined, meaning that many instructions are processed simultaneously, with the computer attempting to predict ahead of the actual evaluation which way a condition will turn out. If the wrong assumption is made, the work done on instructions in the pipeline are lost. It is therefore rarely beneficial to test for whether e.g. binary interaction coefficients are equal to zero (in order to save an operation) as the cost of the test may exceed the potential savings.

Finally one may often arrange calculations such that instructions are independent and can be executed in parallel. A typical example is the loops involved in the calcualtion of the composition derivatives of the a -parameter

in cubic Equations of State,

$$s_i = \frac{\partial n^2 a}{\partial n_i} = 2 \sum_j \sqrt{a_i a_j} (1 - k_{ij}) n_j = r_{ij} n_j, \quad r_{ij} = 2 \sqrt{a_i a_j} (1 - k_{ij})$$

where the r_{ij} are of course precalculated since they are constant throughout the flash calculation. We may here note that the sums for each value of the index i can be evaluated independent of each other, and we may therefore with advantage calculate the sums in parallel, e.g.

```

do i=1,nc,3
  s(i)=0.; s(i+1)=0.; s(i+2)=0.
  do j=1,nc
    s(i) = s(i) + n(j)*r(j,i)
    s(i+1) = s(i+1) + n(j)*r(j,i+1)
    s(i+2) = s(i+2) + n(j)*r(j,i+2)
  enddo
enddo

```

Unfortunately computer architectures change rapidly, and optimizing for today's generation is no guarantee of efficiency with tomorrow's.

References

Before 1980, successive substitution combined with Newton's method for solving the Rachford-Rice equation was the dominant approach for solving the two-phase flash (Prausnitz et al., 1980). At that time equation of state models were less widely used and problems with near-critical mixtures and convergence to the trivial solution therefore less frequent. An additional reason for the unpopularity of higher order methods is that partial composition derivatives of thermodynamic properties were considered unavailable, and Newton-based methods therefore were expensive as they required numerical differentiation. Starting with the important work of Boston and Britt (1978) quasi-Newton methods gained considerable popularity, see e.g. Ammar and Renon (1987); Mehra et al. (1983) and Lucia (1985) who included elements of the thermodynamic structure in the update method. Among the derivative-free methods variants of the Dominant Eigenvalue Method of Orbach and Crowe (1971) have also been popular (Michelsen, 1982a,b). Minimization-based methods have also been investigated (Castillo and Grossmann, 1981; Gautam and Seider, 1979a,b) but did not find widespread use before the coupling to stability analysis.

Michelsen and Mollerup (1986) and Mollerup and Michelsen (1992) demonstrated that the cost of evaluating derivatives was much less than normally expected, and recent results (Michelsen, 1998) indicate a clear superiority to second order based methods, in particular for near-critical mixtures.

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Chapter 11

The Multiphase Isothermal Flash

Introduction

Two different types of multiphase PT -flash calculations are encountered in practice. The first is characterised by the presence of a vapour phase, a liquid phase and one or more phases that essentially consist of a pure component, e.g. solids or water in a hydrocarbon mixture. The second problem type is characterised by the potential presence of two or more liquid phases, in which more than one component is present in substantial amounts. The first type of multiphase calculation has much in common with the simple VLE-calculation, as the potential presence of pure phases can be detected by simple (explicit) tests. The second type is frequently much more demanding, requiring extensive stability analysis calculations and being in general fairly difficult to converge with successive substitution and its variants.

1 Successive substitution

Although a large number of iterations may be required in order to obtain convergence in multiphase calculations, successive substitution for many reasons remains a very useful procedure, in particular during early iterations. The basis for successive substitution is still the implicit assumption of composition independent fugacity coefficients, with the iterative procedure alternating between determining the phase distribution corresponding to the current estimate of the physical properties, and a re-evaluation of the fugacity coefficients at the current composition estimate.

Solution for phase amounts and phase compositions is performed by means of a modified Rachford-Rice procedure which for an F -phase mixture can be formulated as a set of $F - 1$ equations in the $F - 1$ unknown phase fractions. Phase F is selected as a 'reference' phase, and denoting composition and

fugacity coefficients in phase j by y_{ij} and $\hat{\varphi}_{ij}$, respectively, the equilibrium equations become

$$y_{ij} \hat{\varphi}_{ij} = y_{iF} \hat{\varphi}_{iF}, \quad i = 1, 2, \dots, C, \quad j = 1, 2, \dots, F - 1 \quad (1)$$

The material balance equation for component i is

$$\sum_{j=1}^F \beta_j y_{ij} = z_i, \quad i = 1, 2, \dots, C \quad (2)$$

or, utilizing

$$\begin{aligned} \beta_F &= 1 - \sum_{j=1}^{F-1} \beta_j \\ y_{iF} + \sum_{j=1}^{F-1} \beta_j (y_{ij} - y_{iF}) &= z_i \end{aligned} \quad (3)$$

Finally, $F - 1$ independent summation of mole fraction conditions must be satisfied. These are conventionally written in the form

$$\sum_{i=1}^C (y_{ij} - y_{iF}) = 0, \quad j = 1, 2, \dots, F - 1 \quad (4)$$

Defining equilibrium factors by

$$K_{ij} = \frac{y_{ij}}{y_{iF}} \quad \left(= \frac{\hat{\varphi}_{iF}}{\hat{\varphi}_{ij}} \right) \quad (5)$$

mole fractions in the reference phase can be found from the phase fractions β_j and the equilibrium factors, by substituting eqn. (5) into the material balance, eqn. (3), i.e.

$$y_{iF} \left(1 + \sum_{l=1}^{F-1} \beta_l (K_{il} - 1) \right) = z_i \quad (6)$$

from which

$$y_{iF} = \frac{z_i}{1 + \sum_{l=1}^{F-1} \beta_l (K_{il} - 1)} \quad (7)$$

and

$$y_{ij} = \frac{z_i K_{ij}}{1 + \sum_{l=1}^{F-1} \beta_l (K_{il} - 1)} \quad (8)$$

Substitution of these expressions into the summation of mole fraction equations finally yields the desired set of $F - 1$ equations in the $F - 1$ unknown, β_j ,

$$\sum_{i=1}^C z_i \frac{K_{ij} - 1}{1 + \sum_{l=1}^{F-1} \beta_l (K_{il} - 1)} = 0, \quad j = 1, 2, \dots, F - 1 \quad (9)$$

Given the fugacity coefficients, the K -factors are calculated from eqn. (5). Next, phase fractions are determined, solving the set of equations (9), and new phase compositions are determined from eqns. (7) and (8). These new compositions are used for re-evaluation of the fugacity coefficients, and the process is repeated until convergence.

The set of equations (9) is normally easily solved using Newton's method, but some situations require precautions. In particular, phase fractions may become negative, indicating that the actual number of phases present at equilibrium is smaller than currently assumed. If this happens, the corresponding phase is deleted from the set of equations, which are subsequently solved for the remaining phase fractions. At the solution, the sum of mole fractions is evaluated for the 'deleted' phase, using eqn. (8). If the sum of mole fractions exceeds unity, the phase is 'reintroduced' and iterations are continued. In case the phase fraction for the reference phase becomes negative, it is necessary to select a new reference phase, preferably the phase present in the largest amount.

Convergence can be safeguarded and the administrative task of keeping track of 'deleted' phases facilitated by an alternative formulation of the equilibrium calculation. Consider the function

$$Q(\beta) = \sum_{j=1}^F \beta_j - \sum_{i=1}^C z_i \ln E_i \quad (10)$$

with

$$E_i = \sum_{k=1}^F \frac{\beta_k}{\hat{\varphi}_{ik}} \quad (11)$$

We shall show that the phase fractions β minimise Q , subject to the constraints $\beta_j \geq 0$. The minimum of Q , subject to these constraints, is given by

$$\frac{\partial Q}{\partial \beta_j} = 0, \quad \beta_j \geq 0, \quad \text{or} \quad \frac{\partial Q}{\partial \beta_j} > 0, \quad \beta_j = 0 \quad (12)$$

The gradient of Q is

$$g_j = \frac{\partial Q}{\partial \beta_j} = 1 - \sum_{i=1}^C \frac{z_i}{E_i} \frac{1}{\hat{\varphi}_{ij}} \quad (13)$$

and at the solution it is readily verified that the mole fractions in each phase are given by

$$y_{ij} = \frac{z_i}{E_i} \frac{1}{\hat{\varphi}_{ij}} \quad (14)$$

To show this, we notice that eqn. (14) implies that

$$y_{i1}\hat{\varphi}_{i1} = y_{i2}\hat{\varphi}_{i2} = \cdots = y_{iF}\hat{\varphi}_{iF} \quad \left(= \frac{z_i}{E_i} \right) \quad (15)$$

thus satisfying the phase equilibrium conditions, and that in addition

$$\sum_{j=1}^F \beta_j y_{ij} = \frac{z_i}{E_i} \sum_{j=1}^F \frac{\beta_j}{\hat{\varphi}_{ij}} = z_i \quad (16)$$

which shows that the overall material balance is satisfied. The conditions (eqn. (12)) thus state that mole fractions for a phase present in non-zero amounts must sum to 1 and that 'mole fractions' in a phase absent at equilibrium has a sum below 1.

The Hessian matrix is found from

$$H_{jk} = \frac{\partial g_j}{\partial \beta_k} = \sum_{i=1}^C \frac{z_i}{E_i^2 \hat{\varphi}_{ij} \hat{\varphi}_{ik}} \quad (17)$$

The Hessian is at least *positive semidefinite* since for any vector \mathbf{u} the quadratic form

$$\mathbf{u}^T \mathbf{H} \mathbf{u} = \sum_j \sum_k u_j u_k H_{jk} = \sum_i \frac{z_i}{E_i^2} \left(\sum_k \frac{u_k}{\hat{\varphi}_{ik}} \right)^2 \geq 0$$

The Hessian is *positive definite* except for the case where the number of phases exceeds the number of components, which makes the Hessian singular. Positive definiteness guarantees a unique solution, and Newton's method, combined with a line search, is an efficient, as well as an extremely robust solution procedure. However, the solution procedure is more complex than for the two-phase Rachford-Rice equation, since it may be necessary to add or remove phases during the iterative solution. The main steps in a solution procedure are outlined below:

- i. Based on the initial estimate for the phase fractions, evaluate $Q(\beta_{ini}) = Q_{old}$ using eqn. (10).
- ii. Calculate the gradient vector and the Hessian matrix from eqns. (13) and (17). Solve for the Newton correction $\mathbf{H}\Delta\beta + \mathbf{g} = 0$. Select the ‘step length modifier’ $\alpha = 1$. To avoid breakdown in the case where we may have more phases than components (yes, this does occur in practice!), add 10^{-10} to the Hessian diagonal.
- iii. Calculate a new phase fractions, $\beta_{new} = \beta_{old} + \alpha\Delta\beta$. If any of the new phase fractions become negative, choose $\alpha < 1$ such that *exactly* one phase fraction becomes zero and the remaining are positive.
- iv. Evaluate $Q_{new} = Q(\beta_{new})$. If a reduction is observed, set $Q_{old} = Q_{new}$, $\beta_{old} = \beta_{new}$ and, after checking for convergence, return to ii. If any phase fractions in these steps are set to zero, the corresponding phases are marked as ‘inactive’ and not updated in the subsequent steps. The easiest way of doing this is just to replace the corresponding element of the gradient vector, and the corresponding row and column in the Hessian with zeroes, with 1 on the Hessian diagonal.
If an increase in the objective function was observed, set $\alpha = \alpha/2$ and try the reduced step. Continue until a reduction of Q is obtained.
- v. When the set of equations is converged, it is necessary to check the status of any ‘deactivated’ phase, i.e. any phase j for which $\beta_j = 0$. We do that by calculating the gradient g_j . If the gradient is *negative*, the phase is ‘re-activated’, and we return to step ii. It is not advisable to reactivate more than one phase at a time.
- vi. When all phases are converged, eqn. (14) yields the final phase compositions. These are, in a successive substitution procedure, in turn used to evaluate new fugacity coefficients. It is also here worthwhile noticing that tight convergence of the multiphase Rachford-Rice equations might not be necessary. It is always possible to generate an approximate solution that satisfies the material balances, from

$$n_{ik} = \frac{z_i \beta_k}{E_i \hat{\varphi}_{ik}}$$

Solution methods based on eqn. (10) offer no advantage over the conventional Rachford-Rice procedure for two-phase problems and involve solution of a set of F rather than $F - 1$ equations for multiphase problems. The additional cost, however, is marginal as the number of phases is usually modest,

and the additional safety of a minimization approach and the ease of handling vanishing phases makes it our preferred choice for multiphase calculation.

As for the two-phase Rachford-Rice equation it may be possible to set bounds for the phase fractions. Assume that the phase indices for component i are ordered such that

$$\hat{\varphi}_{im} \leq \hat{\varphi}_{im^*} \leq \dots$$

i.e. the lowest value of the fugacity coefficient for the component i is found in phase m , the second lowest in phase m^* , etc. The condition that mole fractions cannot exceed 1 then yields

$$\sum_j \frac{\beta_j}{\hat{\varphi}_{ij}} \geq \frac{z_i}{\hat{\varphi}_{im}}$$

or

$$\sum_j \frac{\beta_j}{\hat{\varphi}_{ij}} = \frac{\beta_m}{\hat{\varphi}_{im}} + \sum_{j \neq m} \frac{\beta_j}{\hat{\varphi}_{ij}} \geq \frac{z_i}{\hat{\varphi}_{im}}$$

Now,

$$\frac{\beta_m}{\hat{\varphi}_{im}} + \sum_{j \neq m} \frac{\beta_j}{\hat{\varphi}_{im^*}} \geq \frac{\beta_m}{\hat{\varphi}_{im}} + \sum_{j \neq m} \frac{\beta_j}{\hat{\varphi}_{ij}} \geq \frac{z_i}{\hat{\varphi}_{im}}$$

Using $\sum_{j \neq m} \beta_j = 1 - \beta_m$ we finally arrive at

$$\beta_m \geq \frac{z_i \hat{\varphi}_{im^*} - \hat{\varphi}_{im}}{\hat{\varphi}_{im^*} - \hat{\varphi}_{im}}$$

which is of use in case the limit thus obtained is positive.

2 Pure phases and solids

At low temperatures solid phases consisting of pure components may also form. The multiphase calculation based on composition independent fugacity coefficients is particularly simple for such phases, as we shall derive below.

We first consider the case of a single solid. The solid forming component (e.g. carbon dioxide) is capable of distributing in the fluid phases, but the solid phase s can only contain component s , corresponding to

$$\hat{\varphi}_{is} = \infty, \quad i \neq s \tag{18}$$

The gradient of the objective function with respect to β_s is

$$\frac{\partial Q}{\partial \beta_s} = 1 - \sum_{i=1}^C \frac{z_i}{E_i} \frac{1}{\hat{\varphi}_{is}} = 1 - \frac{z_s}{E_s} \frac{1}{\hat{\varphi}_{ss}} \tag{19}$$

and formation of the solid phase thus requires that

$$\frac{\partial Q}{\partial \beta_s} = 0 \Rightarrow E_s \hat{\varphi}_{ss} = z_s \quad (20)$$

Substituting eqn. (11) for E_s , eqn. (19) yields

$$\beta_s = z_s - \sum_{\substack{k=1 \\ k \neq s}}^F \beta_k \frac{\varphi_{ss}}{\varphi_{sk}} \quad (21)$$

which enables us to calculate β_s , given the phase fractions for the fluid phases. If the value of β_s , calculated from eqn. (21), is negative, the solid is not formed and component s is treated as an 'ordinary' distributing component. If the value is positive, the objective function is modified, substituting eqn. (21) for the solid phase fraction, i.e.

$$\begin{aligned} Q(\beta) &= \beta_s - z_s \ln E_s + \sum_{\substack{j=1 \\ j \neq s}}^F \beta_j - \sum_{\substack{i=1 \\ i \neq s}}^C z_i \ln E_i \\ &= z_s - z_s \ln \frac{z_s}{\hat{\varphi}_{ss}} + \sum_{j=1}^F \beta_j \left(1 - \frac{\hat{\varphi}_{ss}}{\hat{\varphi}_{sj}} \right) - \sum_{\substack{i=1 \\ i \neq s}}^C z_i \ln E_i \end{aligned} \quad (22)$$

where the E_i for $i \neq s$ are unaffected by β_s since $\frac{1}{\hat{\varphi}_{is}} = 0$ for $i \neq s$.

To generalise to the multi-solid case we mark the fluid phases by index f and the solid phases by index s , corresponding to the component that forms the solid. We assume that the fugacity coefficient of all components in all phases are given, $\hat{\varphi}_{if}$ being the fugacity of component i in phase f , and $\hat{\varphi}_{ss}$ that of pure solid s . In addition, an estimate of the phase fractions β_f of the fluid phases are given.

We proceed as follows: For each (potential) solid forming component, calculate

$$\beta_s = z_s - \sum_f \beta_f \frac{\hat{\varphi}_{ss}}{\hat{\varphi}_{sf}} \quad (23)$$

If β_f is positive, component s is included in the set, S , of solid-formers.

The objective function to be minimised wrt. the fluid phase phase frac-

tions is

$$Q(\beta) = \sum_{s \in S} z_s \left(1 - \ln \frac{z_s}{\hat{\varphi}_{ss}} \right) - \sum_{s \in S} \sum_f \beta_f \frac{\hat{\varphi}_{ss}}{\hat{\varphi}_{sf}} + \sum_f \beta_f - \sum_{i \notin S} z_i \ln E_i \quad (24)$$

where

$$E_i = \sum_f \frac{\beta_f}{\hat{\varphi}_{if}}$$

The gradient is given by

$$\frac{\partial Q}{\partial \beta_f} = 1 - \sum_{s \in S} \frac{\hat{\varphi}_{ss}}{\hat{\varphi}_{sf}} - \sum_{i \notin S} \frac{z_i}{\hat{\varphi}_{if} E_i} \quad (25)$$

and the Hessian,

$$\frac{\partial^2 Q}{\partial \beta_f \partial \beta_k} = \sum_{i \notin S} \frac{z_i}{E_i^2 \hat{\varphi}_{if} \hat{\varphi}_{ik}} \quad (26)$$

The procedure for solving the equations is then:

- i. Calculate the solid formers and the solid amounts from eqn. (23). Evaluate the objective function from eqn. (24)
- ii. Calculate gradient and Hessian from eqns. (25) and (26).
- iii. Calculate the Newton step and new β -values. If any of these becomes negative, calculate a 'reduction factor' used to multiply the step such that exactly one β -value becomes zero.
- iv. At the new β -values, re-evaluate the amounts of solids and the objective function. If the objective function is decreased, accept the step and continue iterations. Phase amounts that became zero during the iteration is, for the time being, removed from the set. If not, further reduce the step by a factor of 2, and try again.
- v. When a converged solution is reached, check whether any of the fluid phase β -values are equal to zero (since they were removed earlier). Calculate the corresponding element of the gradient vector. If this is negative, re-introduce the phase, and continue the calculation. Convergence is obtained when the gradient vector is zero for all the fluid phases

present, and positive for all those that are absent. The converged mole fractions in the fluid phases are given by

$$y_{if} = \frac{z_i}{E_i \hat{\varphi}_{if}}, \quad i \notin S, \quad y_{sf} = \frac{\hat{\varphi}_{ss}}{\hat{\varphi}_{sf}}, \quad s \in S$$

3 Acceleration of successive substitution

The acceleration methods discussed earlier for two-phase calculations are readily adapted to the multiphase case. Unfortunately, they are likely to be less efficient, and a check for a decrease in the Gibbs energy after each extrapolation step is mandatory. In particular, difficulties are observed when more than one liquid phase is present, since liquid-liquid equilibrium has 'near-critical' character under a much wider range of conditions. For multiphase calculations involving a vapour, a single liquid and an arbitrary number of pure phases the extrapolation procedures are, however, as efficient as for the two-phase calculations. It is also worthwhile to notice that highly immiscible liquid phases, like hydrocarbon-water mixtures, do not create convergence problems, as such mixtures are usually far from being critical. The general dominant eigenvalue method of order 2 remains our preferred choice, with about 3 acceleration cycles, each consisting of 5 successive substitution steps. The subsequent switch to second order methods is required much more frequently than for two-phase mixtures.

4 Gibbs energy minimization by second order methods

In terms of component fugacities the objective function for Gibbs energy minimization can be formulated

$$Q = \sum_{k=1}^F \sum_{i=1}^C n_{ik} \ln \hat{f}_{ik} \quad (27)$$

A straightforward approach is to use the molar amounts in phases 1 to $F-1$ as the independent variables, eliminating the n_{iF} by means of the overall material balance, i.e.,

$$n_{iF} = z_i - \sum_{k=1}^{F-1} n_{ik} \quad (28)$$

The gradient and the Hessian are then given by

$$\frac{\partial Q}{\partial n_{ij}} = \ln \hat{f}_{ij} - \ln \hat{f}_{iF} \quad (29)$$

and

$$\frac{\partial^2 Q}{\partial n_{ij} \partial n_{im}} = \frac{\partial \ln \hat{f}_{ij}}{\partial n_{ij}} \delta_{jm} + \frac{\partial \ln \hat{f}_{iF}}{\partial n_{iF}} \quad (30)$$

This choice of independent variables may, however, create problems when specific components in phase F are present in very small amounts since the calculation of the n_{iF} from eqn. (28) will be sensitive to roundoff errors. In addition, the ideal solution contribution to the Hessian matrix introduces large off-diagonal elements ($1/n_{iF}$), making the set of linear equations, that must be solved for the correction vector, ill-conditioned. For this reason, Michelsen (1982b) suggested to use individual 'dependent' variables for each component, selecting

$$n_{iM} = z_i - \sum_{k \neq M}^F n_{ik} \quad (31)$$

where M specifies the phase in which component i is present in the largest amount. Michelsen also chose to use scaled independent variables, given by

$$\theta_{ij} = \frac{n_{ij}}{z_i} \quad (32)$$

and suggested to use the Murray factorization of the Hessian to ensure a positive definite approximation to this matrix.

The approach of Michelsen appears to work adequately in practice, but it is by no means guaranteed to be the most efficient approach. As mentioned earlier the method of Murray involves essentially empirical modification of the Hessian, with a potentially adverse effect on the rate of convergence. An alternative possibility worthwhile considering is the restricted step method, which works very well for the two-phase problem, but no natural diagonal correction term to the Hessian in the cases where modifications are needed seems evident. In spite of its drawbacks the Murray method is robust and capable of converging near-critical mixtures more efficiently than accelerated successive substitution. New and more efficient algorithms may well appear, but drastic gains are not likely to be found.

5 Stability analysis

Stability analysis represents the most challenging problem associated with multiphase flash calculations. The phase split calculation, which given the number of phases leads to locating an unconstrained local minimum, is essentially a purely technical problem, where the choice of solution procedure affects speed rather than reliability. The stability analysis, in contrast, requires the determination of a global minimum, with no advance information

on the location of this minimum. Any practical implementation of multiphase stability analysis has to balance speed of execution against reliability, the more extensive, and thus more costly, search being less likely to overlook indications of instability. Previous algorithms have mostly been based on partly empirical observations relating to the characteristics of multiphase equilibrium, selecting trial phase compositions in the manner most likely to yield conclusive information. Currently, 'safe' algorithms that are guaranteed to resolve the stability question are under active investigation by many groups. The techniques used comprise global optimization methods and interval analysis, and currently the time expenditure for the calculations appear prohibitive for more complex problems.

The essential difference between stability analysis for two-phase (vapour / liquid) and multiphase problems is that selection of two trial phase compositions (with subsequent local minimization) is adequate – and feasible – in the first case, whereas even selection of as many trial phases as the number of components in the mixture may not be sufficient in the latter. For mixtures containing 10 or more components, converging the tangent plane distance minimization for a large number of individual initial estimates represents a substantial effort, and we therefore suggest the use of a screening procedure rather than a full search. The outcome of the screening procedure then decides which of the trial phases to investigate further.

6 Selection of initial estimates for stability analysis

Assume that the current status of a multiphase equilibrium calculation is that a local minimum in the Gibbs energy corresponding to F phases has been determined, i.e.

$$\ln \hat{f}_{i1} = \ln \hat{f}_{i2} = \dots = \ln \hat{f}_{iF} \quad (= \ln \hat{f}_i^*) \quad (33)$$

where each of the F phases

$$\mathbf{n}^1, \mathbf{n}^2, \dots, \mathbf{n}^F$$

are intrinsically stable.

The tangent plane distance for a trial phase of composition \mathbf{w} is given by

$$tpd(\mathbf{w}) = \sum_i w_i (\ln f_i(\mathbf{w}) - \ln \hat{f}_i^*) = \sum_i w_i (\ln w_i + \ln \varphi_i(\mathbf{w}) - d_i) \quad (34)$$

with $d_i = \ln (\hat{f}_i^*/P)$, and if $tpd(\mathbf{w})$ is non-negative for all \mathbf{w} the equilibrium phase distribution is stable and no further calculation is required. If, on the

other hand, a composition w with a negative tangent plane distance can be located, the phase distribution is unstable and the composition w can be utilised for generating initial estimates for an $F+1$ -phase calculation, as we know that the mixture Gibbs energy can be reduced by introducing a small amount of a phase with this composition.

In practice we shall test a sequence of composition estimates w for negative tangent plane distances. If none of the trial phases verify instability, the mixture is assumed to be stable. One of the objectives is to select and evaluate the set of trial phase compositions most likely to indicate instability and thus to form new phases. Another objective is to perform the evaluation for a given test phase as economically as possible.

When a trial phase has been chosen, refinement is performed by means of successive substitution, as for the two-phase flash. Continuation of successive substitution until convergence will locate either a non-trivial minimum, i.e. a minimum with a composition different from that of any of the equilibrium phases, or a trivial solution. The aim of the screening procedure is to decide at an early stage whether convergence to a trivial solution is likely to occur, in which case further iteration on the chosen trial phase can be abandoned. Obviously, increasing the number of successive substitution steps increases the reliability of the screening procedure, as well as the associated cost.

Convergence to a trivial solution ultimately occurs along the direction of the eigenvector corresponding to the minimum eigenvalue for the Hessian of the tangent plane distance, with subsequent iterates being almost co-linear. The objective function (the tangent plane distance) will in the limit be proportional to the square of the distance s in composition space between the trivial solution composition and that of the current iterate, $tm = a s^2$. The gradient along the vector joining the two points will be proportional to s , $g = dtm/ds = 2a s$. tm , as well as g , can be evaluated from the fugacity coefficients at the current trial phase composition. In the limit, the ratio $U = 2tm/(sg)$ will approach 1 when a trivial solution is approached. If a non-trivial minimum is located between the current iterate and the equilibrium phase composition used for the evaluation of s , the variation of U will depend on the value of tm at this minimum. A positive value results in increasing values of U (tm positive, but g tending towards zero) whereas a negative value at the minimum leads to decreasing values of U (tm decreases more rapidly than g). If negative values are encountered during the search, instability has of course been verified, and further investigation is unnecessary.

In the procedure of Michelsen, 2–4 steps of successive substitution are performed in parallel for each trial phase. If instability (negative tm) is not

encountered during these steps, only the trial phase composition with the smaller, decreasing U -value is converged. The screening procedure is evidently empirical and cannot be guaranteed to succeed, but practical experience indicates that with proper selection of the initial phase composition the approach represents a reasonable compromise between reliability and cost.

7 Selection of trial phase compositions

In the absence of any advance knowledge about the nature of the mixture to be flashed, at least $C + 1$ different initial trial phases are required. One of these is used to search for a vapour (fortunately, equilibrium comprises at most one vapour phase), and the remaining C trial phases cater for the possibility of formation of a liquid phase rich in the corresponding mixture component.

The initial composition of the vapour phase is calculated as $W_i = \exp(d_i)$, based on the assumption that the trial phase is an ideal vapour (with a fugacity coefficient of 1), and in all subsequent iterations properties of this trial phases are calculated using the vapour density, if the equation of state has multiple roots.

The additional C trial phases are initiated as the respective pure components, properties of the trial phase being calculated with the liquid density, as the purpose of this search is to reveal the potential formation of new liquid-like phases. Starting from each 'corner' of the composition space aims at ensuring that the search will cover the entire region as well as possible. The use of pure trial phases also ensures rapid detection of instability with highly immiscible components.

Unfortunately, even converging all $C + 1$ trial phase compositions does not guarantee that the global minimum of the tangent plane distance will be located, and many practically important exceptions are found. These are characterised by the existence of a liquid phase dominated by a light component, e.g. methane or carbon dioxide, under conditions where this component is unable to exist as a pure liquid. As a consequence the pure component initialization is incapable of creating the liquid phase rich in this particular component, and there is no certainty that the alternative initializations, which start far from the desired minimum, will converge to this solution. In practice, the problem can be overcome by evaluating the properties of the pure liquid at a pressure slightly higher (say 20%) than the actual.

A simple example of a 'shielded' liquid phase is shown on Figure 1, a Gibbs energy of mixing plot for a binary mixture of CH_4 and H_2S at 190 K, 4.052 MPa. A flash calculation for this mixture is likely to yield a vapour-liquid two-

phase equilibrium, and subsequent stability analysis might well have problems in locating the methane rich liquid phase. Correct identification of this phase ultimately leads to a liquid-liquid equilibrium. The selection of all C mixture

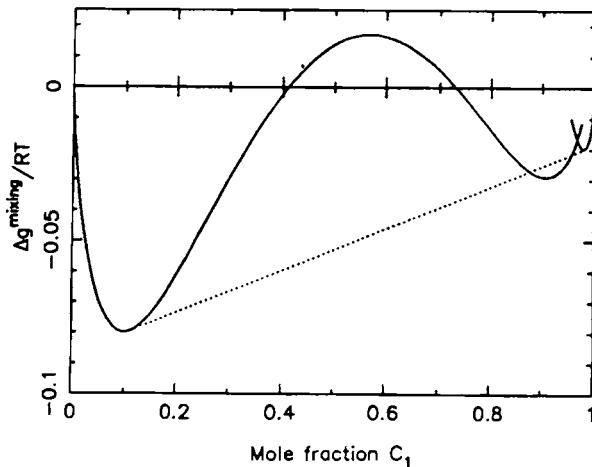


Figure 1: Excess Gibbs energy of mixing for mixture of methane and hydrogen sulphide at 190 K, 4.052 MPa.

components as initial trial phases is not always necessary. When many similar components are present, e.g. the members of a homologous series, it is often sufficient to select only the lightest and the heaviest member of such a series. As many mixtures of practical importance are dominated by hydrocarbons, the reduction in effort by including only two of these can be considerable.

Stability analysis is much simpler, as well as much safer, when the approximate composition of the potential equilibrium phases are known in advance. In such situations the number and the composition of the trial phases can be selected in advance, and converging each of these trial phases is no longer infeasible.

8 Near-critical phases

The screening procedure is most likely to fail when one or more of the equilibrium phases are nearly critical. The Hessian matrix for t_m is nearly singular in such cases, and successive substitution only makes slow progress. This implies that the trial phase composition after the first 2 – 4 iterations is

located at a substantial distance from the potential trivial solution, and it becomes difficult to assess whether a non-trivial minimum is located close to the equilibrium composition.

Improved reliability in such situations can be obtained by calculating the minimum eigenvalue and the corresponding eigenvector for each of the equilibrium phases. This calculation is quite inexpensive when performed in conjunction with the test for intrinsic stability (i.e. positive definiteness of the Hessian). If the eigenvalue is close to zero, a supplementary search can be performed along the direction of the corresponding eigenvector.

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The multiphase equilibrium calculation at constant temperature and pressure has understandably received much less attention than the two-phase calculation, a major obstacle being the lack of tools for stability analysis. An early noteworthy attempt is that of Gautam and Seider (1979) who introduced a 'phase-splitting' algorithm based on the magnitude of component activities. The systematic application of tangent plane analysis by Michelsen (1982a,b) followed the revival of the Gibbs tangent plane criterion. Stability analysis in some form has been utilised in most later work, e.g. Gupta et al. (1991). Recently much emphasis has been concentrated on developing global minimization methods for the stability calculation, e.g. McDonald and Floudas (1996).

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Chapter 12

Saturation Points and Phase Envelopes

Introduction

Phase equilibrium calculations with specified value of the vapour fraction β and either the temperature or the pressure have many characteristics in common. The most important cases are $\beta = 0$ (bubble points) and $\beta = 1$ (dew points). Traditionally, a determination of the bubble point and the dew point for a mixture have been used to initiate flash calculations in order to ensure that the specification for the flash was in the two-phase region. In the case where different models are used for the fluid phases or where the equilibrium pressure is low to moderate, the determination of the bubble and dew points is relatively straightforward. With equation of state based models, however, calculations of the bubble- or dew point at elevated pressures are much more difficult to perform than the flash calculation. Two factors contribute to this. First, the number of solutions to the saturation point calculation is not known in advance. It may even be that the saturation point does not exist at the prescribed conditions, as is the case for a prescribed pressure (or temperature) above the maximum pressure (temperature) at which two phases can coexist. Second, the *trivial solution* as a false solution to the specified conditions is a severe problem, since the trivial solution can exist for a wide range of values of the missing primary variable (i.e. T when P is specified, or P when T is specified).

Stability analysis cannot be used in the same manner as for PT -flash calculations to verify that the trivial solution is in fact the ‘true solution’, i.e. that a saturation point at the prescribed conditions does not exist. While we are able to verify that a current pair (T, P) is located in the one-phase region

this does not exclude the possibility that other values of the missing primary variable can represent a point on the phase boundary or in the two-phase region.

Currently, no entirely satisfactory method exists for 'blind' (i.e. in the absence of initial estimates) calculation of saturation points at arbitrary conditions. The most reliable procedure for locating *all solutions* to a given set of specifications seems to be construction of the entire phase boundary.

1 Ideal solution based methods

If fugacity coefficients are composition independent, the saturation point calculation reduces to solving a single equation for T or P . At the bubble point ($\beta = 0$) we have $x_i = z_i$, $y_i = K_i x_i = K_i z_i$, leading to the single equation

$$f = \sum_{i=1}^C z_i K_i(T, P) - 1 = 0 \quad (1)$$

with $K_i = \hat{\varphi}_i^l(T, P)/\hat{\varphi}_i^v(T, P)$. The equation is solved for T (pressure specified) or P (temperature specified). Initial estimates can be generated from the Wilson K -factor approximation,

$$\ln K_i = \ln \left(\frac{P_{ci}}{P} \right) + 5.373 (1 + \omega_i) \left(1 - \frac{T_{ci}}{T} \right) \quad (2)$$

If T is specified, the Wilson equation enables explicit solution of eqn. (1) for P . When P is specified, the K -factors from the Wilson equation increase monotonically with temperature, ensuring a unique solution.

The ideal solution approximation is excellent for bubble point calculations at low pressures ($P < 1$ MPa), where the vapour phase, for which the composition is unknown, is nearly ideal. Non-ideal behaviour of the liquid phase is immaterial since the composition of the liquid phase is fixed at the feed composition. At higher pressures the composition dependence of the vapour phase fugacity coefficients can be accounted for by means of a successive substitution approach. Initial estimates of T (or P) and the vapour phase composition y are generated from the Wilson K -factor approximation, and subsequent approximations are generated using Newton's method on eqn. (1), assuming composition independent K -factors in the derivative of f . At

specified pressure the iteration scheme becomes

$$\ln K_i^{(k)} = \ln \hat{\varphi}_i^l(\mathbf{z}, T^{(k)}) - \ln \hat{\varphi}_i^v(\mathbf{y}^{(k)}, T^{(k)})$$

$$f^{(k)} = \sum_{i=1}^C z_i K_i^{(k)} - 1$$

$$\frac{df^{(k)}}{dT} = \sum_{i=1}^C z_i K_i \left(\frac{\partial \ln \hat{\varphi}_i^l}{\partial T} - \frac{\partial \ln \hat{\varphi}_i^v}{\partial T} \right) \quad (3)$$

$$T^{(k+1)} = T^{(k)} - f^{(k)} / \frac{df^{(k)}}{dT}$$

$$y_i^{(k+1)} = z_i K_i^{(k)}$$

A similar approach is applicable for dew point calculations. Here, the rate of convergence is determined by the non-ideality of the incipient liquid which may, however, be pronounced even at low pressures. The rate of convergence is linear and follows the same pattern as that observed for successive substitution for stability analysis, i.e., the rate is determined by the numerically largest eigenvalue, λ_1 , of the matrix \mathbf{M} given by

$$M_{ij} = - \frac{\partial \ln \hat{\varphi}_i^v}{\partial y_j} y_j \quad (4)$$

where the vapour phase mole fractions are formally assumed independent in the differentiation. At the mixture critical point the dominant eigenvalue approaches 1 and convergence becomes very slow. In addition, the quality of the initial estimates generated from the Wilson approximation deteriorate at elevated temperatures, and divergence or convergence to the trivial solution may well occur at pressures (temperatures) below the critical.

The phase envelope for the 7-component natural gas mixture investigated earlier is shown in Figure 1. The convergence behaviour for this mixture for a bubble point calculation at 5.065 MPa is shown in Figure 2.

The error in composition, calculated as $|1 - y_1^{(k)}/y_1^{sat}|$, exhibits the expected behaviour, whereas the corresponding error in temperature, $|1 - T^{(k)}/T^{sat}|$ decreases at a much faster rate, the slope of the T -line being twice the slope of the y -line. This apparently peculiar behaviour can be explained as follows, where we use a binary mixture to exemplify:

Assume that at the specified pressure, P^{spec} , the saturation temperature is T^* and that the composition of the incipient phase is y^* . A stability analysis of the feed mixture at (T^*, P^{spec}) will result in a tangent plane distance

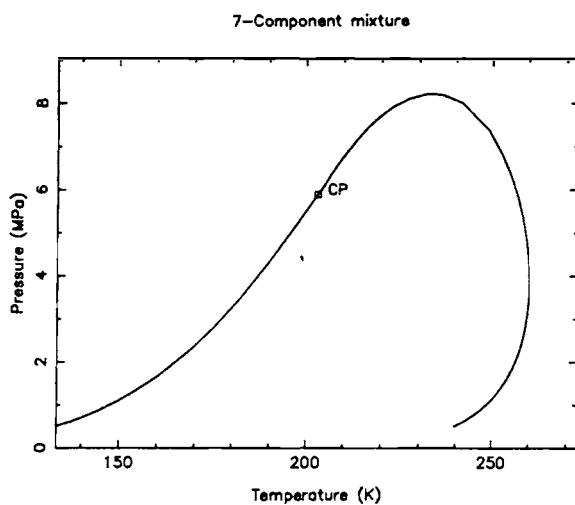


Figure 1: Phase boundary for natural gas mixture containing 94.3% C₁, 2.7% C₂, 0.74% C₃, 0.49% nC₄, 0.27% nC₅, 0.10% nC₆ and 1.4% N₂.

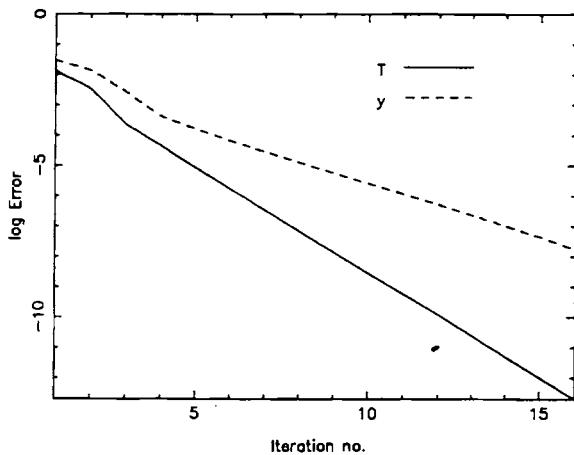


Figure 2: Error in composition and temperature for 7-component mixture containing 94.3% C₁, 2.7% C₂, 0.74% C₃, 0.49% nC₄, 0.27% nC₅, 0.10% nC₆ and 1.4% N₂.

function with a minimum at y^* , the minimum value being identically 0. In the vicinity of (y^*, T^*) the tangent plane distance function is approximated by

$$tpd(y, T) \approx a(y - y^*)^2 + b(T - T^*) \quad (5)$$

where a is positive and b is negative (assuming that a temperature increase leads to a point in the two-phase region).

Next, assume that an approximation, $y^{approx} = y^* + \epsilon$, for the composition of the incipient phase at the saturation point is available. If an approximate saturation temperature is determined by solving the equation

$$tpd(y^{approx}, T) = 0 \quad (6)$$

for T , we obtain

$$T = T^* - \frac{a}{b} \epsilon^2 \quad (7)$$

that is, the approximate saturation temperature is determined with an error proportional to ϵ^2 , rather than to ϵ . In other words, a 'first order' error in the incipient phase composition leads to a 'second order' error in the saturation temperature. This is exactly what is observed in the partial Newton's method for determining the saturation temperature. The compositions are updated by successive substitution and converge 'slowly', whereas the temperatures are relatively insensitive to the composition error.

The results obtained above can be utilised in many different manners. From the first order insensitivity of the tangent plane distance to the incipient phase composition we can derive the following expression for the slope of the phase boundary (the vapour pressure curve)

$$\frac{dP}{dT} = -\frac{\left(\frac{\partial tpd}{\partial T}\right)_{P,y}}{\left(\frac{\partial tpd}{\partial P}\right)_{T,y}} = -\frac{\sum_{i=1}^C y_i \left(\frac{\partial \ln \hat{\varphi}_i(y)}{\partial T} - \frac{\partial \ln \hat{\varphi}_i(z)}{\partial T}\right)}{\sum_{i=1}^C y_i \left(\frac{\partial \ln \hat{\varphi}_i(y)}{\partial P} - \frac{\partial \ln \hat{\varphi}_i(z)}{\partial P}\right)} \quad (8)$$

where y is the composition of the incipient phase. From this expression we can immediately deduce the conditions that must apply at the maximum pressure on the phase boundary,

$$\frac{dP}{dT} = 0 \Rightarrow \sum_{i=1}^C y_i \left(\frac{\partial \ln \hat{\varphi}_i(y)}{\partial T} - \frac{\partial \ln \hat{\varphi}_i(z)}{\partial T}\right) = 0 \quad (9)$$

and similarly for the maximum temperature,

$$\frac{dT}{dP} = 0 \Rightarrow \sum_{i=1}^C y_i \left(\frac{\partial \ln \hat{\varphi}_i(y)}{\partial P} - \frac{\partial \ln \hat{\varphi}_i(z)}{\partial P}\right) = 0 \quad (10)$$

It is readily seen that eqn. (8) can be reduced to the familiar form,

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \quad (11)$$

where ΔV and ΔS are the volume and entropy changes associated with the phase transition. This form, *the multicomponent Clapeyron equation*, is remarkably absent from current textbooks on thermodynamics in spite of its formal identity with the pure component version. A number of related results easily derived from this equation, e.g. that the isochore for multicomponent mixtures that passes through the maximum temperature point on the phase boundary does not change its slope when passing from the two-phase region to the single phase region, with a similar result applying for isenthalps and isentropes through the point of maximum pressure, have also recently been 'rediscovered'.

2 Constructing the phase envelope

For our natural gas mixture the critical point is at (203.1 K, 5.89 MPa), and the maximum pressure on the phase envelope is found at (233 K, 8.22 MPa). The successive substitution approach is able to determine bubble point temperatures up to a pressure of about 5.6 MPa and to determine the high temperature dew point almost up to the maximum pressure even though the temperature estimates generated by the Wilson approximation is considerably in error for the high pressure dew points. The low temperature (i.e. retrograde) part of the dew point branch, however, cannot be calculated, and calculations in the vicinity of the critical point are in general very difficult to perform. A Newton approach that accounts explicitly for the composition derivatives of the fugacity coefficients in the incipient phase is only a partial solution that remedies the slow rate of convergence but is unable to overcome the need for very accurate initial estimates.

As an alternative to isolated calculation of specific saturation points a sequential construction of the entire phase boundary is suggested. The individual points on this curve are generated using a full Newton's method, and initial estimates for subsequent calculations are obtained from information generated in earlier steps.

We start by specifying the vapour fraction, which here can take any value between zero and 1, and as the vector of independent variables, X , are chosen the $\ln K_i$, $\ln T$ and $\ln P$. The following set of $C + 1$ equations relate these

$C + 2$ variables

$$\begin{aligned} f_i &= \ln K_i + \ln \hat{\varphi}_i(T, P, \mathbf{y}) - \ln \hat{\varphi}_i(T, P, \mathbf{x}) = 0 \\ f_{C+1} &= \sum_{i=1}^C (y_i - x_i) = 0 \end{aligned} \quad (12)$$

where the mole fractions in the liquid and the vapour are given by

$$x_i = \frac{z_i}{1 - \beta + \beta K_i}, \quad y_i = \frac{K_i z_i}{1 - \beta + \beta K_i} \quad (13)$$

To complete the set of equations to be solved, we introduce an additional equation, the *specification equation*. This equation has the general form

$$f_{C+2} = X_s - S = 0 \quad (14)$$

where s is the index for the variable to be specified, and S is the desired value of this variable. The complete set of $C + 2$ equations can be written in the form

$$\mathbf{f}(\mathbf{X}) = \mathbf{0} \quad (15)$$

The sequence of calculations is started using a specification for which convergence is easily obtained and for which reasonable initial estimates can be generated, typically a low pressure bubble point, e.g. $P^{spec} = 0.5$ MPa. We thus take $s = C + 2$ and $S = \ln 0.5$ and generate initial estimates by first the Wilson approximation and subsequently a few steps of the successive substitution approach. Newton's method is used for final convergence of the initial point. Once the initial point has been generated subsequent points are calculated using a full Newton's method with initial estimates obtained from the previous points. For this purpose, the *sensitivities* of the independent variables with respect to the value of S are evaluated. Differentiation of eqn. (15) with respect to S and use of the chain rule yields

$$\frac{\partial \mathbf{f}}{\partial \mathbf{X}} \frac{\partial \mathbf{X}}{\partial S} + \frac{\partial \mathbf{f}}{\partial S} = \mathbf{0} \quad (16)$$

and the *sensitivity vector* $\partial \mathbf{X} / \partial S$ is obtainable as the solution to a set of linear equations for which the matrix of coefficients $\partial \mathbf{f} / \partial \mathbf{X}$ is the Jacobian matrix for the system of equations and hence available since Newton's method is used for solving the equations. The RHS vector is very simple, since only f_{C+2} depends on S . We obtain

$$-\frac{\partial \mathbf{f}}{\partial S} = (0, 0, \dots, 0, 1)^T$$

We can now estimate the location of a new point on the phase boundary from

$$\mathbf{X}(S + \Delta S) \approx \mathbf{X}(S) + \frac{\partial \mathbf{X}}{\partial S} \Delta S \quad (17)$$

If, for example, the next point is calculated at a pressure of 1.0 MPa, we get $\Delta S = \ln 1.0 - \ln 0.5 = \ln 2$, and an initial estimate can be calculated from eqn. (17). For the following points on the phase boundary, a refined generation of initial estimates is used. \mathbf{X} and its derivatives with respect to S is now available at two points, and this information is used to generate a polynomial expansion for each of the X -elements of the following form

$$X_i = \sum_{j=0}^3 C_{ij} S^j$$

The approximation by a 3rd degree polynomium enables us to calculate very accurate interpolations of the points on the phase boundary as well as quite accurate extrapolations for initial estimates for the subsequent points to be calculated.

3 Step selection and stepsize control

The variable to be specified is initially selected as the pressure, but later other choices are for several reasons more convenient. First, in the vicinity of the critical point selection of either the temperature or the pressure as the specified variable may easily lead to the trivial solution, with subsequent breakdown as a result. Second, as pressure increases towards the maximum pressure on the two-phase boundary the sensitivities increase in magnitude and ultimately become infinite. Obviously, we are not able to 'pass' the point of maximum pressure in this manner. We have found it advantageous always to specify the variable, for which the magnitude of the sensitivity is largest. In this manner, all elements of the sensitivity vector will be limited in magnitude to about 1, and fixing the most rapidly varying variable makes it easier to obtain convergence. A disadvantage is that we have to 'compare' incomparable quantities like pressure and a K -factor, but in practice this does not seem to create problems. The automatic selection in most cases leads to selection of the $\ln K$ for the least volatile or the most volatile component in the mixture. Specifying the (non-zero) value of $\ln K$ for a component has the advantage that we eliminate the risk of arriving at the trivial solution.

The magnitude of the step is determined by the number of iterations used to converge the equations at the previous point. A very small number of iterations indicate that the initial estimate is very accurate and that it is

permissible to increase the stepsize, and many iterations indicate an initial estimate of poor quality requiring a more cautious approach. In case of indications of potential failure, such as too large steps being taken during the iterative solution, the current point is abandoned and a new attempt is made with a smaller stepsize. We have chosen to set a 'target iteration count' of 3 or 4. Fewer iterations cause the selection of an increase in the stepsize and more iterations to a decrease. In this manner the entire phase envelope can be traced, with no problems in passing the critical point or the pressure and temperature maxima. On passage of the critical point the value of the vapour fraction β is kept fixed, but the x -phase now becomes the lighter phase and the y -phase the heavier. The bubble line and the dew line are thus generated in the same sequence. The actual sequence of conditions for the individual calculations for the 7-component mixture is shown in Table 1.

Table 1: Calculated points on phase boundary.

Temperature (K)	Pressure (MPa)	Iterations	Spec. variable
133.53	0.51	1	P
153.51	1.29	3	C
166.21	2.08	2	C
178.49	3.12	2	C
189.40	4.25	2	C
198.19	5.29	2	C
201.68	5.71	3	C
204.59	6.07	4	C
209.59	6.71	4	C
221.18	7.80	4	C
242.82	7.93	3	C
255.85	6.17	3	C
257.41	5.72	3	P
258.72	5.23	2	P
259.84	4.56	2	P
260.23	3.72	2	P
259.03	2.74	3	P
255.94	1.90	3	P
251.02	1.22	2	P

4 Unusual phase envelopes

Frequently, the phase envelope construction results in intersecting phase boundaries. Figure 3 below is calculated for a 3-component mixture containing 80% methane, 15% ethane and 5% *n*-octane, and it is observed that the bubble line intersects itself. The intersection takes place in the low tem-

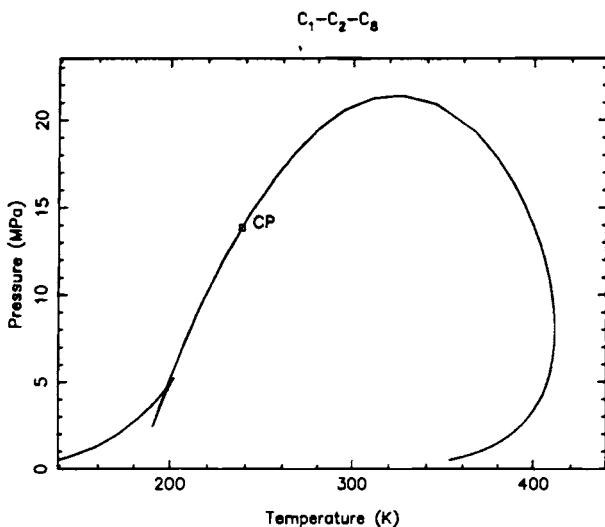


Figure 3: Phase envelope for methane-ethane-octane mixture.

perature region, and this part of the two-phase line is shown in detail in Figure 4, where the characteristic 'swallowtail' pattern is evident.

The phase envelope intersects itself at about 198 K, 4.86 MPa, and at this point we have coexistence between 3 phases. Following the phase envelope from temperatures below 185 K, the portion up to the intersection point represents vapour-liquid equilibrium. At 198 K, the vapour-liquid equilibrium line crosses the two-phase line and becomes unstable. As we follow the swallowtail part of the curve, the vapour phase gradually becomes closer and closer to the liquid in composition, and at the second intersection, as we follow the curve, the incipient phase is actually a liquid (-like) phase. The portion on the phase boundary from the three-phase point and up to the critical represents liquid-liquid equilibrium. In a region extending from the three-phase point we actually have 3 phases at equilibrium, but the boundaries of this region cannot be calculated with a procedure limited to 2 coexisting phases.

A different example of atypical behaviour is shown in Figure 5, where we

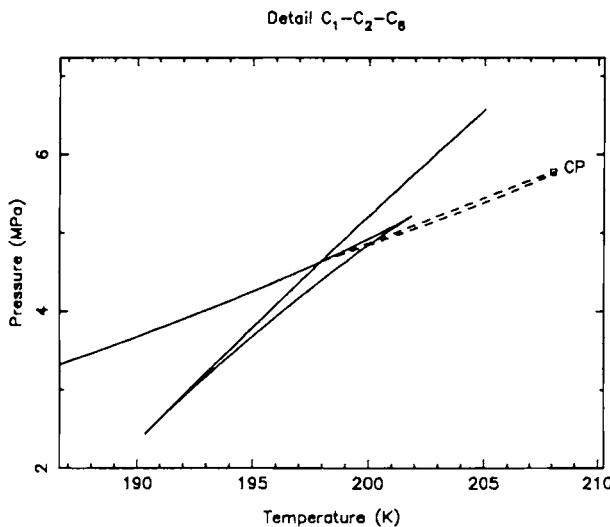


Figure 4: Detail of phase envelope for methane-ethane-octane mixture.

get separate dew line (starting from $\beta = 1$) and bubble line (starting from $\beta = 0$). In addition, this mixture has two critical points on the dew line, which at lower temperatures extends to infinite pressure. The ‘bubble line’ has a cusp at its endpoint and turns back, but the calculation is unable to proceed to lower pressures. A closer analysis of the mixture shows that the entire bubble line is unstable and that the mixture is capable of a liquid-liquid split at the calculated ‘bubble’-line. The correct phase diagram for the mixture is shown in Figure 6. A narrow three-phase region with a critical point near the top is located in the vicinity of the ‘false’ bubble line, at slightly higher temperatures. To the left of the 3-phase region two liquid phases are at equilibrium, and to the right we have ordinary vapour-liquid equilibrium. The false bubble line is thus found in the liquid-liquid region. Fugacities calculated for the overall liquid composition will be slightly higher than those obtained when the feed is allowed to split, and the incipient vapour formation thus appears to occur at slightly lower temperatures. A more complex example is found in Figure 7, where the phase envelope for a 5-component mixture (66% C₁, 3% C₂, 1% C₃, 5% CO₂ and 25% H₂S) is shown. Identical phase boundaries (the solid line) are obtained when starting from the bubble point and the dew point sides, and the mixture behaviour appears conventional. Stability calculations on the bubble point side, however, indi-

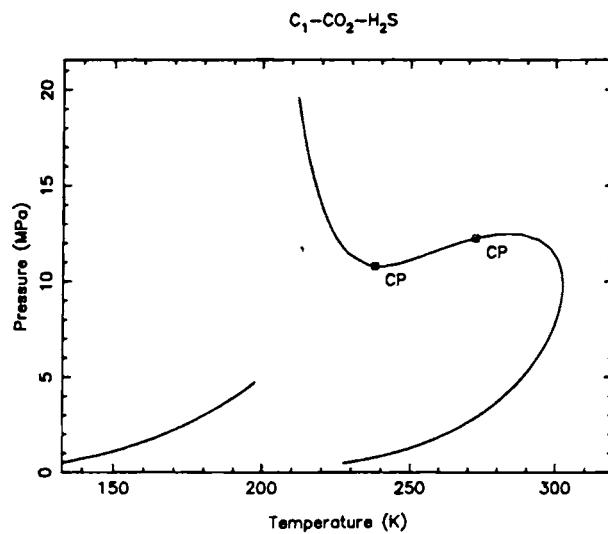


Figure 5: Phase envelope with low-pressure liquid liquid split.

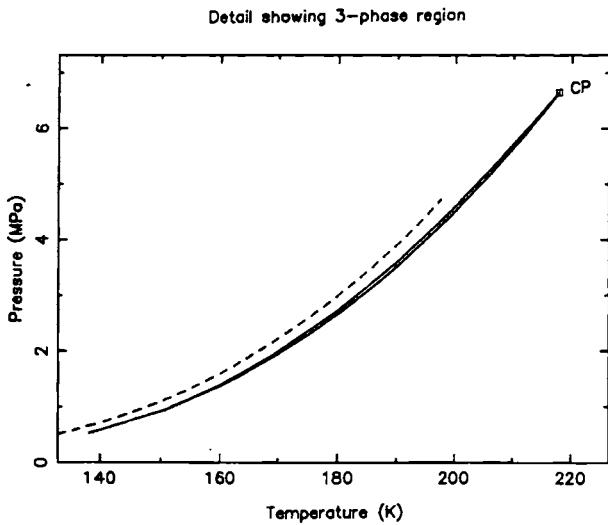


Figure 6: 3-Phase region for mixture of Figure 5, together with the false bubble line.

cates that a liquid-liquid split occurs and that a 3-phase region exists at low temperatures. The boundary of the 3-phase region is shown as the dashed line. Its upper part is almost coincident with the false bubble line, and a critical point is found on the lower part. A 3-phase point with 2 incipient phases at equilibrium with the overall mixture composition is located at the end of the 3-phase region, and the dot-dashed line extending from this point towards high pressures marks the liquid-liquid equilibrium phase boundary.

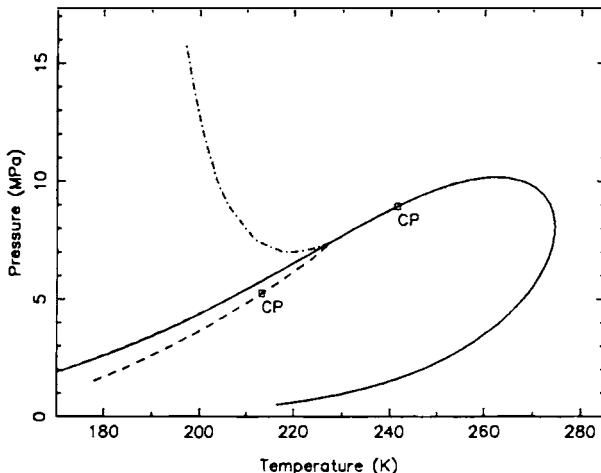


Figure 7: Phase diagram for 5-component mixture showing 3-phase region and liquid-liquid separation at high pressures.

The principles used for calculating phase boundaries for the two-phase region can easily be extended to enable calculation of the phase boundaries for three-phase regions by introducing as new variables an additional set of K -factors and a phase fraction for the phase split between the two phases. This calculation is, however, not as easily automated as that for the two-phase phase boundary, one complicating factor being that an initial estimate for the composition of the phases at liquid-liquid equilibrium is needed. In addition the calculation of liquid-liquid equilibrium is much less well-behaved than the calculation of vapour-liquid equilibrium. Even though the two-phase calculation presented here does not give quantitative information about the precise location of the three-phase region it is worthwhile to notice that many essential qualitative features of the phase diagram can be estimated purely from the 'erroneous' two-phase calculation.

5 Phase diagrams for binary mixtures

Experimental measurements of phase equilibria is frequently determined for binary mixtures, either at constant temperature or at constant pressure, and such data are subsequently used for regressing the parameters of thermodynamic model.

General conditions

Let us consider phase equilibrium between 2 phases, I and II. The compositions of the two phases are given by their mole fractions (x_1, x_2) and (y_1, y_2), where we formally consider the mole fractions independent.

Equilibrium between the two phases requires that the following equations are satisfied:

$$\ln f_i^I(T, P, x_1, x_2) - \ln f_i^{II}(T, P, y_1, y_2) = 0, \quad i = 1, 2 \quad (18)$$

$$x_1 + x_2 - 1 = 0, \quad y_1 + y_2 - 1 = 0 \quad (19)$$

that is 4 equations relating the 6 variables T, P, x_1, x_2, y_1 and y_2 . Usually, we fix either T or P and arrive at a family of solutions describing the relations between the remaining variables. These solutions are presented graphically as Pxy -diagrams (T specified) or Txy -diagrams (P specified), where, e.g. for the Pxy -diagram we plot P against both x ($=x_1$) and against y ($=y_1$). This plot therefore represents all features of the solution family.

Rather than using the mole fractions directly as variables we may also formulate the calculation in terms of the K -factors. The set of equations then becomes:

$$\ln \varphi_i^I(T, P, x_1, x_2) - \ln \varphi_i^{II}(T, P, y_1, y_2) - \ln K_i = 0, \quad i = 1, 2 \quad (20)$$

$$y_i - K_i x_i = 0, \quad i = 1, 2 \quad (21)$$

$$x_1 + x_2 - 1 = 0, \quad y_1 + y_2 - 1 = 0 \quad (22)$$

This is supplemented by a specification equation, where usually one of the $\ln K_i$ or temperature or pressure is specified.

Properties of the solutions

In the following we shall consider solutions derived at specified T , but completely similar results are obtained if P is specified. We assume that a specific solution, (P, x_1, x_2, y_1, y_2) satisfying (18,19) is available, and we shall investigate how this solution can change with a change in conditions.

Satisfaction of the equilibrium conditions require that

$$\Delta \ln f^I - \Delta \ln f^{II} = 0 \quad (23)$$

or

$$\left(\frac{\partial \ln f^I}{\partial P} - \frac{\partial \ln f^{II}}{\partial P} \right) \Delta P + \frac{\partial \ln f^I}{\partial x} \Delta x + \frac{\partial \ln f^{II}}{\partial y} \Delta y = 0 \quad (24)$$

together with

$$1^T \Delta x = 1^T \Delta y = 0 \quad (25)$$

In particular, we are interested in conditions, where we can arrive at a maximum or a minimum in pressure, i.e. conditions where the above equations can be satisfied with $\Delta P = 0$. Clearly, this requires that

$$\frac{\partial \ln f^I}{\partial x} \Delta x = \frac{\partial \ln f^{II}}{\partial y} \Delta y \quad (26)$$

By virtue of the Gibbs-Duhem equation we know that

$$x^T \frac{\partial \ln f^I}{\partial x} = y^T \frac{\partial \ln f^{II}}{\partial y} = 0^T \quad (27)$$

and $\Delta P = 0$ therefore requires that

$$y^T \frac{\partial \ln f^I}{\partial x} \Delta x = x^T \frac{\partial \ln f^{II}}{\partial y} \Delta y = 0 \quad (28)$$

which, using eqn. (27), we may also write

$$(y - x)^T \frac{\partial \ln f^I}{\partial x} \Delta x = (y - x)^T \frac{\partial \ln f^{II}}{\partial y} \Delta y = 0 \quad (29)$$

These relations are satisfied for nonzero Δx and Δy whenever $y = x$, i.e. for an azeotrope or at a critical point. When the phase compositions are different, we note that

$$y_1 - x_1 = -(y_2 - x_2)$$

and therefore,

$$y - x = k \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Similarly,

$$\Delta x = k_x \begin{pmatrix} 1 \\ -1 \end{pmatrix}, \quad \Delta y = k_y \begin{pmatrix} 1 \\ -1 \end{pmatrix},$$

which yields

$$k_x v^T \frac{\partial \ln f^I}{\partial x} v = k_y v^T \frac{\partial \ln f^{II}}{\partial y} v = 0, \quad v = \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad (30)$$

A nontrivial solution (k_x and k_y are not both zero) therefore requires that one of the quadratic forms that involve the 2×3 matrix of composition derivatives, equals zero. For e.g. phase I, the two eigenvectors of this matrix are

$$\mathbf{u}_1 = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}, \quad \mathbf{u}_2 = \begin{pmatrix} x_2 \\ -x_1 \end{pmatrix}$$

The first eigenvector corresponds to an eigenvalue of zero by virtue of the Gibbs-Duhem equation, and since \mathbf{v} is not proportional to \mathbf{u}_1 the quadratic form can only be zero provided the eigenvalue corresponding to \mathbf{u}_2 is also zero, i.e. that the composition is spinodal, which implies that the phase is unstable. This implies that phase I is at the limit of intrinsic stability and hence unstable. We also note that under these conditions k_y must equal zero.

An example of a diagram with maxima and minima is shown on Figure 8. The Px -line exhibits a maximum around $x=0.30$ and a minimum around $x=0.70$ and this part therefore corresponds to an unstable solution. Obviously the instability extends beyond this concentration range, as the adjoining compositions will be metastable. The corresponding Py line forms cusps at the two extrema in pressure, and in addition intersects itself. The point of intersection can be used to determine 3-phase equilibrium, since it represents

CH4-CO₂, T=180 K

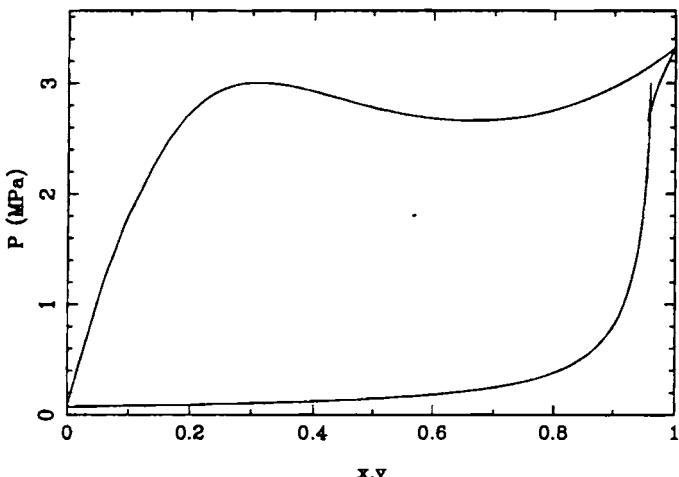


Figure 8: Pxy diagram for methane - carbon dioxide at 180 K.
Model: SRK, with $k_{12}=0.08$

0.70 and this part therefore corresponds to an unstable solution. Obviously the instability extends beyond this concentration range, as the adjoining compositions will be metastable. The corresponding Py line forms cusps at the two extrema in pressure, and in addition intersects itself. The point of intersection can be used to determine 3-phase equilibrium, since it represents

a point where the same vapour is at equilibrium with two different liquid phases.

Three-phase equilibrium

A simple procedure for finding the 3-phase equilibrium conditions from the series of np two phase equilibrium results, given in the form

$$(x, y, P)^{(1)}, (x, y, P)^{(2)}, \dots (x, y, P)^{(np)}$$

where x and y represents the mole fraction of the first component, is given below:

The line connecting points k and $k + 1$ in the list is given by

$$P = P^{(k)} + \frac{y - y^{(k)}}{y^{(k+1)} - y^{(k)}} (P^{(k+1)} - P^{(k)})$$

Similarly, the line connection points m and $m + 1$ is given by

$$P = P^{(m)} + \frac{y - y^{(m)}}{y^{(m+1)} - y^{(m)}} (P^{(m+1)} - P^{(m)})$$

and the intersection between the two line segments is therefore found at the value of y where

$$\begin{aligned} & P^{(k)} + \frac{y - y^{(k)}}{y^{(k+1)} - y^{(k)}} (P^{(k+1)} - P^{(k)}) \\ &= P^{(m)} + \frac{y - y^{(m)}}{y^{(m+1)} - y^{(m)}} (P^{(m+1)} - P^{(m)}) \quad (31) \end{aligned}$$

1. Loop through the list of points, letting $k = 1, 2, \dots np - 1$.
2. For each k loop through the list, letting $m = k + 2, k + 3, \dots np - 1$. Calculate the intersection coordinate y between the segments starting at k and at m .
3. Investigate if the intersection point is located inside the two line segments. This requires that the two conditions

$$(y - y^{(k)})(y - y^{(k+1)}) < 0, \quad (y - y^{(m)})(y - y^{(m+1)}) < 0$$

are both satisfied.

4. If this is the case, calculate the corresponding compositions of the x -phase from

$$x^I = x^{(k)} + \frac{y - y^{(k)}}{y^{(k+1)} - y^{(k)}} (x^{(k+1)} - x^{(k)})$$

$$x^{II} = x^{(m)} + \frac{y - y^{(m)}}{y^{(m+1)} - y^{(m)}} (x^{(m+1)} - x^{(m)})$$

For the example shown in the figure we arrive at $P = 2.73 \text{ MPa}$, $y = 0.958$, $x^I = 0.199$ and $x^{II} = 0.781$.

Direct calculation of the three-phase line

The approach above is best suited for cases, where the region of liquid immiscibility is fairly small. With pronounced immiscibility it may prove difficult to trace through the entire unstable region, and, at the same time, a direct calculation of the three-phase line is much easier. Our direct search is based on the assumption of very limited immiscibility. Each of the liquid phases is therefore almost pure, and at low pressures the equilibrium pressure at three-phase equilibrium will be close to the sum of the individual pure component vapour pressures, i.e.,

$$P = P_1^{\text{sat}}(T) + P_2^{\text{sat}}(T)$$

We use this equation to determine either P (for T given) or T (for P given). Now, T as well as P are known, and we start our search for two liquid phases, \mathbf{x} and \mathbf{w} . We initialise the composition of the two phases to $x_1 = 0$, $w_1 = 1$. A simple successive substitution procedure for solving for phase equilibrium is as follows: Define K -factors by: $K_i = w_i/x_i$. The equilibrium conditions

$$x_i \hat{\varphi}_i(\mathbf{x}) = w_i \hat{\varphi}_i(\mathbf{w}) \quad (32)$$

thus yield:

$$K_i = \frac{w_i}{x_i} = \frac{\hat{\varphi}_i(\mathbf{x})}{\hat{\varphi}_i(\mathbf{w})}$$

The summation of mole fraction conditions:

$$x_1 + x_2 = 1; \quad w_1 + w_2 = 1$$

can be solved for the mole fractions in terms of the K -factors, resulting in:

$$x_1 = \frac{K_1 - 1}{K_1 - K_2}, \quad x_2 = \frac{1 - K_2}{K_1 - K_2}, \quad w_1 = K_1 x_1, \quad w_2 = K_2 x_2 \quad (33)$$

The successive substitution procedure proceeds as follows:

1. Calculate initial K -factors from the fugacity coefficient calculated from the pure phase composition estimates.
2. Calculate from the current K -factors new phase compositions from eqn. (33).
3. Calculate from the phase compositions calculated in step 2 new fugacity coefficients and new K -factors.

We perform a predetermined maximum number of successive substitution steps, e.g. 20, and terminate if the sequence converges, or leads to the trivial solution $\mathbf{x} = \mathbf{w}$. If neither case is encountered we proceed by solving the equilibrium equation, in the form

$$\begin{aligned} f_1 &= x_1 \hat{\varphi}_1(\mathbf{x}) - w_1 \hat{\varphi}_1(\mathbf{w}) = 0 \\ f_2 &= x_2 \hat{\varphi}_2(\mathbf{x}) - w_2 \hat{\varphi}_2(\mathbf{w}) = 0 \\ f_3 &= x_1 + x_2 - 1 = 0 \\ f_4 &= w_1 + w_2 - 1 = 0 \end{aligned} \quad (34)$$

using Newton's method.

For a mixture of hexane and water at $T = 350$ K the estimated equilibrium pressure was 0.178 MPa. The LLE calculation converged after 4 steps of successive substitution. For the methane-carbon dioxide mixture shown above, at 180 K, the calculated pressure was 3.42 MPa. Here the LLE calculation was not converged after 25 steps of successive substitution but required 2 Newton steps in addition.

Finding the vapour

Usually, assuming the pressure to be the sum of the two pure component pressures overestimates P at three-phase equilibrium. The next step is therefore to trace the LLE to lower pressures (or higher temperatures, if P is given) in order to arrive at conditions with three phases at equilibrium. We apply stability analysis to the calculated LLE, using as initial estimate for the vapour phase composition

$$Y_1 = \frac{x_1 \hat{\varphi}_1(\mathbf{x})}{x_1 \hat{\varphi}_1(\mathbf{x}) + x_2 \hat{\varphi}_2(\mathbf{x})}, \quad Y_2 = 1 - Y_1 \quad (35)$$

followed by 5 steps of successive substitution,

$$\ln Y_i^{(k+1)} = \ln x_i + \ln \hat{\varphi}_i(\mathbf{x}) - \ln \hat{\varphi}_i(\mathbf{y}^{(k)}), \quad i = 1, 2 \quad (36)$$

and finally convergence by Newton's method.

Table 2: Stability analysis of LLE for methane-carbon dioxide at 180 K.

P (MPa)	x_1	w_1	y_1	TPD
3.42	0.202	0.775	0.775	triv.
3.39	0.202	0.775	0.854	0.100
3.35	0.202	0.775	0.859	0.096
3.29	0.201	0.776	0.866	0.091
3.23	0.201	0.777	0.874	0.083
3.15	0.201	0.777	0.885	0.073
3.06	0.200	0.778	0.899	0.059
2.94	0.200	0.779	0.918	0.040
2.80	0.199	0.781	0.943	0.015
2.64	0.198	0.782	0.977	-0.019

When we arrive at a pressure (or a temperature) where the equilibrium is unstable, as indicated by $Y_1 + Y_2 > 1$ at the converged solution, we proceed directly to solve for three-phase equilibrium using Newton's method. The equation set is formulated as:

$$\begin{aligned}
 f_i &= x_i \hat{\varphi}_i(\mathbf{x}) - y_i \hat{\varphi}_i(\mathbf{y}) = 0, \quad i = 1, 2 \\
 f_{i+2} &= w_i \hat{\varphi}_i(\mathbf{w}) - y_i \hat{\varphi}_i(\mathbf{y}) = 0, \quad i = 1, 2 \\
 f_5 &= x_1 + x_2 - 1 = 0 \\
 f_6 &= w_1 + w_2 - 1 = 0 \\
 f_7 &= y_1 + y_2 - 1 = 0
 \end{aligned} \tag{37}$$

where the unknown are the 6 mole fractions and either pressure or temperature. The liquid phase mole fractions are taken from the last equilibrium calculation and the vapour phase initial estimate from the stability analysis.

The sequence of calculations for the methane - carbon dioxide mixture is shown in Table 2. The three-phase line was converged from the estimates given in the last row in 4 iterations.

Binary equilibrium lines

If three-phase equilibrium is found we utilise the equilibrium compositions at the starting point for calculating the two-phase equilibrium line. Three sets of phase lines originate from the three-phase line: Two sets corresponding to vapour-liquid equilibrium and one set corresponding to liquid-liquid equilibrium. We proceed by calculating, in turn these 3 sets.

The equilibrium equations are in general solved in the form:

$$\begin{aligned} f_i &= \ln K_i + \ln \hat{\varphi}_i(y) - \ln \hat{\varphi}_i(x) = 0, \quad i = 1, 2 \\ f_{i+2} &= y_i - K_i x_i = 0, \quad i = 1, 2 \\ f_5 &= x_1 + x_2 - 1 = 0 \\ f_6 &= y_1 + y_2 - 1 = 0 \\ f_7 &= X - X_{spec} = 0 \end{aligned} \tag{38}$$

where the last equation is a specification equation where we specify $\ln K_1$, $\ln K_2$ or either $\ln P$ or $\ln T$. Derivatives of the equation variables with respect to X_{spec} are used to determine the specification variable for the next step. When we start from the three-phase line it is necessary to ensure that the first step moves us in the direction of a stable 2-phase solution. This can be done as follows, where we assume that T is given and P is unknown:

Increase P by a small amount to $P^* = P + \Delta P$, from the pressure at the 3-phase line and solve for the equilibrium conditions (x^*, y^*) . Calculate at the new conditions the component fugacities, f^* and evaluate the tangent plane distance using the composition of the third phase as the trial phase, i.e.

$$tpd = w_1(\ln f_1(T, P^*, w) - \ln f_1^*) + w_2(\ln f_2(T, P^*, w) - \ln f_2^*) \tag{39}$$

A positive value of the tangent distance implies that the solution is stable in the direction of increasing pressure. If tpd is negative, the construction must be performed in the direction of decreasing pressures.

Once the initial direction is established, a sequence of equilibrium points can be calculated, until a termination condition occurs. The termination can occur for one of the following reasons:

1. We encounter a pure component limit, $x_1 = 0$ or $x_1 = 1$
2. We encounter a critical point, $x_1 = y_1$
3. We exceed a preselected upper limit in pressure or a lower limit in temperature.

When the construction is completed for all three initial composition pairs, we have completed the phase diagram. The correct phase diagram for methane - carbon dioxide is shown on Figure 9.

In the case where the initial search for a three-phase line fails, we just start the binary equilibrium calculation from the boiling point of the heaviest component in the mixture and continue until one of the termination conditions above occurs. Occasionally, an instability like that shown in Figure 1

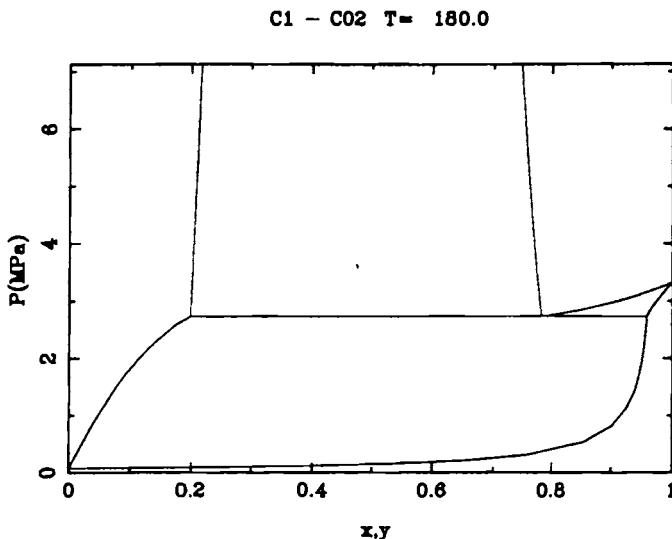


Figure 9: P_{xy} diagram for methane - carbon dioxide at 180 K.

will occur during this construction, and this will enable us to determine a 3-phase line. In other situations, we obtain a stable termination at a critical point, under conditions where both mixture components are subcritical. This requires that we perform a supplementary series of calculations, starting from the volatile pure component. The mixture ethane - carbon dioxide exemplifies this case, Figure 10.

Isolated regions

The procedures described above are not able to locate equilibrium lines that are not connected to the pure component saturation points. Such equilibrium lines are frequently found for specified P at pressures higher than the critical pressure of both pure components and also for specified P for mixtures where liquid-liquid equilibrium is found at temperatures below that where VLE occurs. We are able to search for such equilibria, as described below. Additional possibilities are equilibria at specified T , where the temperature exceeds the critical temperature for both the constituent binaries (called gas-gas equilibrium), or LLE at specified P , at pressures above where VLE occurs. These types of equilibria are fairly rare, and they are not dealt with here.

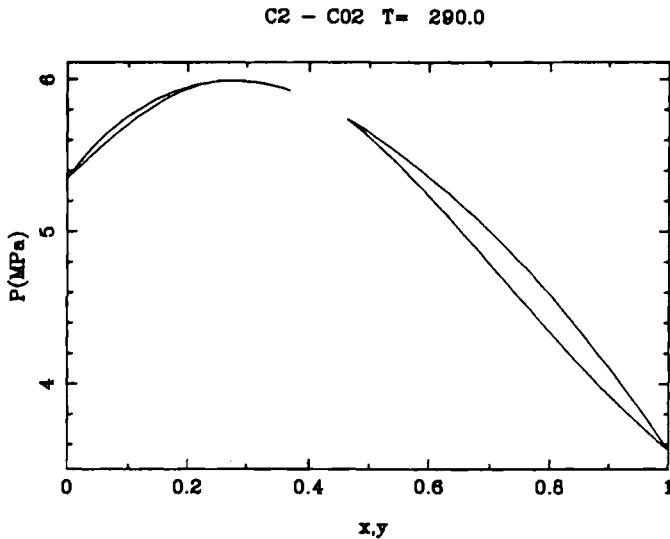


Figure 10: P_{xy} diagram for ethane - carbon dioxide at 295 K.
Model: SRK, with $k_{12} = 0.15$.

Supercritical pressure

We assume that the objective is to calculate a T_{xy} -diagram for a binary mixture, where the specified pressure exceeds the critical pressure of both components. We proceed as follows:

1. Calculate an initial temperature from the equation:

$$P = P_{c1} \exp(5.373(1 + \omega_1)(1 - T_{c1}/T)) + P_{c2} \exp(5.373(1 + \omega_2)(1 - T_{c2}/T))$$

2. We search for instability of the binary at this set of condition as follows:
The composition interval is divided into 100 equally sized subintervals, and for each of the 100 composition we calculate and tabulate the composition derivative of the fugacity coefficient,

$$d(x) = n_t \left(\frac{\partial \ln \hat{\varphi}_1}{\partial n_2} \right)_{T, P, n_1} \quad (40)$$

It is readily shown that $d > 1$ for an intrinsically unstable mixture and that $d = 1$ at the limit of intrinsic stability. We select from the

tabulated values the composition x_m at which d has the largest value. If this value exceeds 1, we proceed to step 5. Otherwise,

3. The derivative of d with respect to temperature at fixed x_m is calculated numerically, and a search is performed, by Newtons method to locate the temperature at which $d(x_m)$ equals 1. If a prescribed temperature range is exceeded the search is abandoned as unsuccessful. If we locate a temperature where d equals 1, we proceed to the next step.
4. The mixture has now proven unstable, and equilibrium conditions are calculated using 20 steps of successive substitution, where as initial estimates we take

$$x_1 = 0.5x_m, \quad y_1 = 0.5(1 + x_m)$$

5. The solution provides us with an initial point on the equilibrium curve. We now continue with calculating the entire curve, starting with the initial point, in the direction of increasing T . The curve will end in a critical point.
6. Finally, the curve is completed by moving in the direction of decreasing T from the initial point.

Example

The mixture methane - *n*-hexane is modelled with the SRK Equation of State, and the binary interaction parameter is set to zero. Determine the phase behaviour at 10 MPa. The results of the individual steps are:

1. $T = 222.5$
2. $d_{\max} = 1.29$ at $x_m = 0.94$
3. -
4. Successive substitution results in $x = 0.776$, $y = 0.990$
5. The phase diagram is shown on Figure 11.

Low temperature LLE

Another case of isolated equilibrium conditions at specified P is that where LLE occurs at lower temperatures than required for VLE. It is quite straightforward to investigate this possibility. We suggest to select a temperature that is 50 K lower than that at which the (failed) search for a three-phase line was

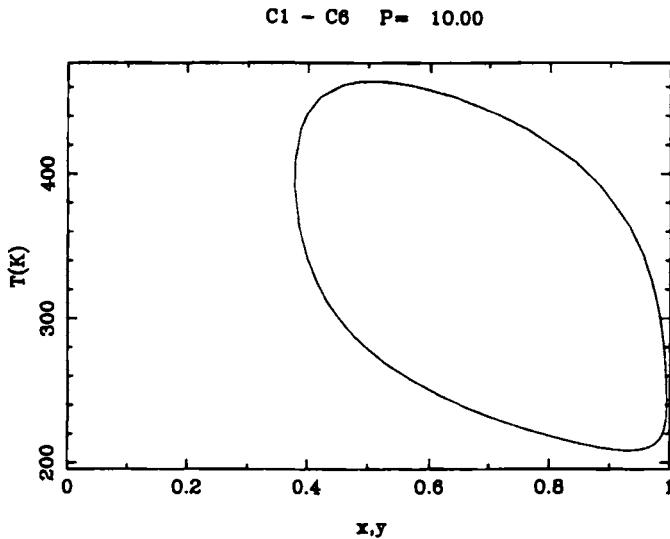


Figure 11: Txy diagram for methane - *n*-hexane at 10 MPa.
Model: SRK, with $k_{12} = 0$.

performed, and to apply a simple successive substitution procedure starting from the pure component corners, to locate immiscible liquids. If this calculation converges, the liquid-liquid equilibrium line can be continued to higher temperatures, and ultimately, it will terminate in a critical point. Figure 12 shows the Txy diagram for a mixture of methane and carbon dioxide at $P = 5$ MPa.

6 Phase diagrams for ternary mixtures

At constant temperature and pressure equilibrium in three-component mixtures is well illustrated by means of ternary diagrams. These have found widespread use in particular in connection with liquid-liquid equilibrium, and many different types of phase behaviour, including closed loops not connecting to the sides of the diagram, have been observed. We shall here discuss procedures for automated calculation of such diagrams, at least for cases where such closed loops do not occur.

Equilibrium conditions

Equilibrium may involve two phases, which we shall denote x and y , or three phases, where the additional phase is called w . For the two-phase case we

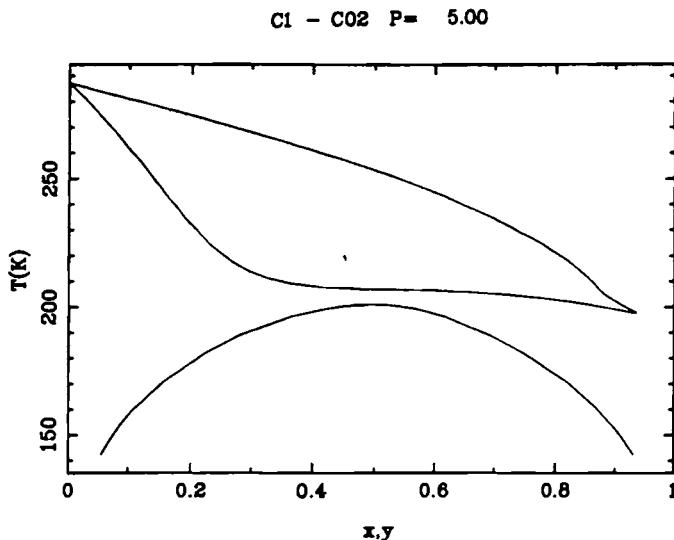


Figure 12: Txy diagram for methane - carbon dioxide at 5 MPa.
Model: SRK, with $k_{12} = 0.12$.

formulate the following 5 equations

$$\begin{aligned} x_i \hat{\varphi}_i(T, P, \mathbf{x}) - y_i \hat{\varphi}_i(t, P, \mathbf{y}) &= 0, \quad i = 1, 2, 3 \\ x_1 + x_2 + x_3 - 1 &= 0 \\ y_1 + y_2 + y_3 - 1 &= 0 \end{aligned} \tag{41}$$

which leaves us with one specification equation and a family of solutions, and for three-phase equilibrium we get the nine equations

$$\begin{aligned} x_i \hat{\varphi}_i(T, P, \mathbf{x}) - y_i \hat{\varphi}_i(t, P, \mathbf{y}) &= 0, \quad i = 1, 2, 3 \\ w_i \hat{\varphi}_i(T, P, \mathbf{w}) - y_i \hat{\varphi}_i(t, P, \mathbf{y}) &= 0, \quad i = 1, 2, 3 \\ x_1 + x_2 + x_3 - 1 &= 0 \\ y_1 + y_2 + y_3 - 1 &= 0 \\ w_1 + w_2 + w_3 - 1 &= 0 \end{aligned} \tag{42}$$

with no additional degrees of freedom.

The procedure used for constructing the phase diagram is fairly simple. We start with the three binary pairs that can be formed from the three components. For each of these pairs we determine the phase splits that may

occur at the given T and P . This is done by setting up a composition table with 101 entries, constructed as

$$\begin{aligned}s(i) &= 0.05i + 6 \times 10^{-5}i^3, \quad i = -50, -49, \dots, 49, 50 \\ r(i) &= \exp s(i), \quad x_1(i) = \frac{1}{1+r(i)}, \quad x_2(i) = \frac{r(i)}{1+r(i)}\end{aligned}\quad (43)$$

We calculate for each point the value of the Gibbs energy and the slope of the tangent to the Gibbs energy curve at the point. In the next step points are marked as stable or unstable, depending on whether their tangent plane distance, when checked against the remaining points, stays positive or becomes negative, and in a final step the equilibrium conditions are refined using Newton's method. The outcome for the binary pair may be one of the following:

1. No phase equilibrium
2. One equilibrium solution, either VLE or LLE.
3. Separate regions with VLE and LLE, i.e. two sets of equilibrium solutions.

All such equilibrium solutions are used as starting points for determining additional solutions to the set of equations, eqn. (41). Initially, we specify as the remaining equations a small value for the mole fraction of the component absent from the binary pair in the phase where this component has the smallest infinite solution fugacity coefficient (and thus, the largest solubility). Subsequent points are determined sequentially by specifying the mole fraction for the component that varies most rapidly.

The sequential construction may terminate for the following reasons:

1. It ends at another phase boundary, matching a binary pair that has already been determined.
2. It ends at a critical point.
3. The calculated tieline becomes unstable. To determine whether this is the case, every calculated tieline is tested for stability by tangent plane minimization, converging 4 different sets of initial estimates, namely
 - Three sets of liquid initial estimates where the constituent pure components are used.

- A vapour-like estimate created by assuming an ideal trial phase with fugacity coefficients of unity, i.e.

$$Y_i = x_i \hat{\varphi}_i(T, P, \mathbf{x}), \quad i = 1, 2, 3$$

where \mathbf{x} is one of the tieline compositions.

If instability is revealed, the composition minimizing the tangent plane distance is used, together with the two tieline compositions, as initial estimates for solving the three-phase equilibria. If convergence is not obtained, it may be necessary to go back and calculate new tielines between the current unstable and the last stable line until we are able to determine the three-phase solution.

The three-phase region creates two additional starting points for tieline constructions, namely the two other sides of the triangle. This also points to an additional possibility for terminating the construction, namely that

4. We arrive at a three-phase region which has already been located earlier.

Getting the entire diagram thus essentially requires that we keep track of all 'open' continuation possibilities and properly mark these as completed when they have been used as starting points or found as endpoints for the sequential construction.

Ternary example

The ternary diagrams can become quite complex, in particular in case one or more of the constituent binaries exhibit both VLE and LLE. Figure 13 shows the mixture methane (1) - carbon dioxide (2) - hydrogen sulphide (3) at 170 K, 1.95 MPa. The SRK Equation of state is used, with the following binary interaction parameters: $k_{12} = k_{23} = 0.12$, $k_{13} = 0.08$.

We observe here 5 separate two-phase regions, two separate three-phase regions and three separate single phase regions (the third being in the methane-rich corner). Decreasing the pressure slightly leads to the vanishing of the small single phase 'island' and of the two three-phase regions. Elevating the pressure moves the narrow three-phase region on top closer to the side in the diagram representing the methane - carbon dioxide binary, where it ultimately vanishes, as separate regions with VLE and LLE for the methane-carbon dioxide binary forms.

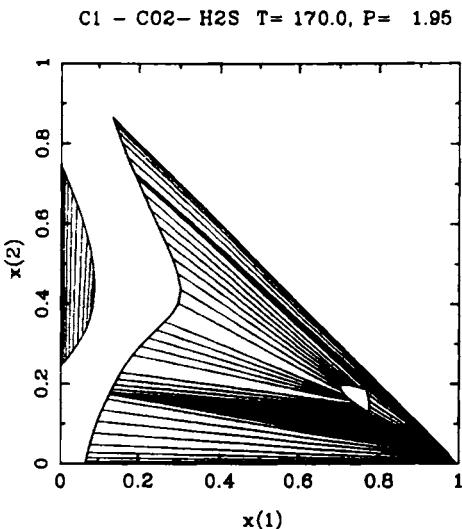


Figure 13: Ternary diagram for methane - carbon dioxide - hydrogen sulphide 170 K, 1.95 MPa.

References

The standard approach for calculation of saturation points is the partial Newton's method where composition derivatives are not explicitly accounted for (Prausnitz et al., 1980). Michelsen (1985) provided relations that utilise the insensitivity to the composition of the incipient phase to improve the reliability under near-critical conditions and derived relations for the temperature and pressure maxima on the phase boundary.

Sequential construction of coexistence curves has found widespread use. Early examples are Asselineau et al. (1979) and Michelsen (1980) for calculation of the phase envelope for mixtures described by an equation of state, and Fredenslund et al. (1980) who used a fast construction of the binodal curve for ternary liquid-liquid equilibrium for the purpose of determining parameters in excess Gibbs energy models. Phase envelopes at constant temperature with the overall composition varying linearly between two compositions were constructed by Nghiem and Li (1984) similar to that used by Michelsen. A more exotic application is that of Michelsen (1986) for determining tricritical points in ternary mixtures by following a three-phase region of fixed shape through shrinking size. A more recent simplified method for constructing

phase envelopes has been developed by Michelsen (1995), and an example describing the extension to multiphase phase boundaries is given in Pedersen et al. (1996).

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Chapter 13

Chemical Reaction Equilibrium

Introduction

The calculation of chemical equilibrium at specified temperature and pressure is in many ways similar to the calculation of phase equilibrium. In both cases the equilibrium state corresponds to a global minimum of the Gibbs energy subject to a set of material balance constraints.

For the phase equilibrium calculation these constraints represent component material balances, and they are usually eliminated explicitly by calculating the molar component amounts in one of the equilibrium phases from that in the other. A similar procedure can be used to convert the chemical equilibrium calculation to an unconstrained optimization problem, through the use of the ‘reaction extents’ formulation which ensures automatic satisfaction of all material balance constraints. Alternatively, a formulation can be set up by means of classical methods for constrained optimization where the constraints are handled by means of Lagrange multipliers. The computational aspects, including advantages and disadvantages of both approaches, are discussed here.

In addition, the utilization of chemical reaction equilibrium to model non-ideality in so-called ‘chemical models’ is described, and a framework for the numerical treatment of such models is given. This section makes extensive use of the theory for constrained optimization. Readers unfamiliar with this subject can find a short introduction in the Appendix on numerical methods, page 365.

1 Chemical reaction equilibrium

In phase equilibrium calculations for a given feed at specified temperature and pressure a material balance must be satisfied for each component in the

mixture, the total amount in the combined product phases being identical to that in the feed. When chemical reactions occur, additional degrees of freedom are available, resulting in a set of material balance constraints, which is smaller than the number of components in the mixture.

The mixture composition at chemical equilibrium at constant T and P satisfies the condition of minimum Gibbs energy,

$$\min G = \min \sum_{i=1}^C n_i \mu_i \quad (1)$$

subject to a set of $M < C$ material balance constraints. In addition we must require that

$$n_i \geq 0, \quad i = 1, 2, \dots, C \quad (2)$$

The material balance constraints can be formulated in different ways, and the most important formulations are outlined below. To illustrate the concepts, we shall consider a specific example, the combustion of a mixture of 1 mole propane (C_3H_8) and 5 moles oxygen (O_2), at 2200 K, 4.0 MPa. Under these conditions the reaction mixture is assumed to contain the following species (components) at equilibrium:

CO_2 (1), CO (2), H_2O (3), O_2 (4), H_2 (5), O (6), H (7) and OH (8).

2 Independent chemical reactions and reaction extents

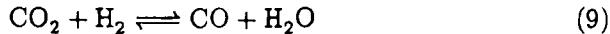
One approach eliminates the material balance constraints by formulating a complete set of *independent* chemical reactions between the mixture components. In our example, the following reactions could be chosen:



Each reaction is characterised by a *stoichiometric vector*, ν , where the i 'th element of the vector represents the stoichiometric coefficient of component i in the reaction, with a negative sign for components on the left hand side and positive on the right hand side. Thus,

$$\nu_1 = (-2, 2, 0, 1, 0, 0, 0, 0)^T \quad (8)$$

The chosen set of chemical reactions must have *linearly independent* stoichiometric vectors, i.e., none of the reactions may be linear combinations of other reactions. If e.g. the reaction



was chosen a candidate for a potential 6th reaction, its stoichiometric vector

$$\nu_6 = (-1, 1, 1, 0, -1, 0, 0, 0)^T \quad (10)$$

shows that the choice is illegal, since $\nu_6 = \frac{1}{2}(\nu_1 - \nu_2)$.

The R (here, $R = 5$) stoichiometric vectors are combined into an $C \times R$ matrix \mathbf{E} , given by

$$\mathbf{E} = (\nu_1, \nu_2, \dots, \nu_R) \quad (11)$$

A test for linear independence of the stoichiometric vectors is that the matrix \mathbf{E} must be of rank R . Given an initial composition vector \mathbf{n}_0 consistent with the overall feed composition, the vector of moles \mathbf{n} can be written in the general form

$$\mathbf{n} = \mathbf{n}_0 + \sum_{k=1}^R \nu_k \zeta_k \quad (12)$$

or

$$\mathbf{n} = \mathbf{n}_0 + \mathbf{E} \zeta \quad (13)$$

where ζ_k is called the *extent* of the k 'th reaction.

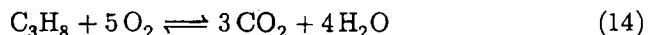
The composition vector \mathbf{n}_0 can be chosen as the feed composition, if all components present in the feed are also found in the equilibrium mixture. For the present example, the equilibrium concentration of propane is likely to be extremely small (below 10^{-30}) and propane is therefore not included in the vector of possible product components. Some consistent choices of \mathbf{n}_0 are

$$\mathbf{n}_0 = (3, 0, 4, 0, 0, 0, 0, 0)^T$$

(3 moles CO₂, 4 moles H₂O) or

$$\mathbf{n}_0 = (0, 3, 0, 3.5, 4, 0, 0, 0)^T$$

(3 moles CO, 3.5 moles O₂, 4 moles H₂). An alternative possibility is of course to introduce C₃H₈ as an additional component in the reaction mixture, together with a reaction involving propane, e.g.



in which case the feed composition is chosen as the \mathbf{n}_0 -vector.

The substitution of the mole vector by eqn. (13) enables us to formulate the equilibrium calculation in terms of the R independent variables ζ_k , i.e.,

$$\min G = \min G(\mathbf{n}(\zeta_k))$$

At equilibrium the derivatives of G with respect to the reaction extents must equal zero

$$\frac{\partial G}{\partial \zeta_k} = \sum_{i=1}^C \frac{\partial G}{\partial n_i} \frac{\partial n_i}{\partial \zeta_k} = \sum_{i=1}^C \mu_i E_{i,k} = 0, \quad k = 1, 2, \dots, R \quad (15)$$

Any suitable procedure can be used for minimizing G , and the approach based on reaction extents can be used without essential differences for ideal as well as for non-ideal mixtures.

One potential problem is associated with components that are present at equilibrium in very small amounts. The composition calculation from eqn. (13) can be sensitive to round-off and can well result in negative concentrations for trace components. This can normally be avoided by proper choice of the set of independent reactions where a set of 'base components' consisting of the components present in large amounts at equilibrium is used to form the remaining components. Consider for example a 3-component mixture (H_2 , O_2 , H_2O), equimolar in hydrogen and oxygen, at low temperature. At equilibrium, essentially all hydrogen is converted to water. The composition balance, with hydrogen and oxygen as base components, is

$$\begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} + \begin{pmatrix} -2 \\ -1 \\ 2 \end{pmatrix} \eta$$

and the solution corresponds to an extent of reaction of about 0.5, with the amount of hydrogen determined as the (very small) difference of two numbers close to 1. As a consequence the logarithm of the mole fraction of hydrogen (required for the chemical potential) cannot be determined accurately. If alternatively we use oxygen and water as the base components, we arrive at

$$\begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0.5 \\ 1 \end{pmatrix} + \begin{pmatrix} -2 \\ -1 \\ 2 \end{pmatrix} \eta$$

The extent of reaction will be negative and very close to zero, and the amount of hydrogen present at equilibrium can be determined with high relative accuracy even though the amount is close to zero. Unfortunately, it may not

be easy to decide in advance which components to select as the base components, and it may therefore become necessary to redefine the reaction set or the initial composition vector during the iterative solution of the problem.

Multiphase equilibrium can be handled by defining the formation of new phases as 'reactions'. Each additional phase thus introduces a number of new, independent reactions corresponding to the number of mixture components.

The reaction extent approach is best suited for problems where the number of independent reactions is small, or where the mixture is highly non-ideal. In many other situations, the alternative approaches described below are preferable.

3 Formula matrix and element balances

We may note that the components in our reaction mixture only contain 3 different chemical elements, C, H and O. The alternative formulation of the constraints is based on the requirement of conservation of chemical elements. A key concept in this approach is the *formula matrix* for the reaction components. In this matrix, A_{ji} is the formula content of element j in component i . For our example,

$$\mathbf{A} = \begin{pmatrix} 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 2 & 0 & 1 & 1 \\ 2 & 1 & 1 & 2 & 0 & 1 & 0 & 1 \end{pmatrix}$$

The *element conservation* constraints can be written

$$\mathbf{A} \mathbf{n} = \mathbf{b} \quad (16)$$

where b_k is the total amount of element k in the reaction mixture. In our example, $b_1 = 3$, $b_2 = 8$ and $b_3 = 10$. The matrix \mathbf{A} has $M = C - R$ rows, where R is the number of independent reactions. It is readily shown that \mathbf{A} , \mathbf{b} , \mathbf{n}_0 and \mathbf{E} are related as follows: Substitution of eqn. (13) into eqn. (16) yields

$$\mathbf{A} \mathbf{n} = \mathbf{A} \mathbf{n}_0 + \mathbf{A} \mathbf{E} \zeta \quad (17)$$

This equation must be satisfied for all values of ζ , and therefore

$$\mathbf{A} \mathbf{E} = \mathbf{0} , \quad \mathbf{A} \mathbf{n}_0 = \mathbf{b} \quad (18)$$

The M rows of \mathbf{A} must be linearly independent. If this is not the case, it is necessary to redefine the chosen 'elements'. Consider e.g. the vapour phase dimerization of acetic acid, $\text{HAc} = \text{C}_2\text{H}_4\text{O}_2$:



Conventional use of the formula matrix in terms of chemical elements would give

$$\mathbf{A} = \begin{pmatrix} 2 & 4 \\ 4 & 8 \\ 2 & 4 \end{pmatrix}$$

which is only of rank 1. We therefore define our "element" as HAc, yielding $\mathbf{A} = (1 \ 2)$. In fact, we are generally free to choose our elements as *any reaction invariant measure* of the overall composition, and in many cases atomic elements are not the most advantageous choice.

4 Solution by constrained optimization

The constraints defined by eqn. (16) can be incorporated into the Gibbs energy minimization by means of *Lagrange multipliers*, λ . We find it preferable to work with the reduced Gibbs energy and form the augmented objective function,

$$\mathcal{L}(\mathbf{n}, \boldsymbol{\lambda}) = \sum_i^C \frac{n_i \mu_i}{RT} - \sum_{j=1}^M \lambda_j \left(\sum_i^C A_{ji} n_i - b_j \right) \quad (20)$$

by adding to the original objective function the constraint terms, multiplied by the Lagrange multipliers.

At the minimum it is required that the derivatives of the Lagrange function are equal to zero

$$\frac{\partial \mathcal{L}}{\partial n_i} = \frac{\mu_i}{RT} - \sum_{j=1}^M A_{ji} \lambda_j = 0 \quad (21)$$

$$\frac{\partial \mathcal{L}}{\partial \lambda_j} = - \sum_{i=1}^C A_{ji} n_i + b_j = 0 \quad (22)$$

which yields a total of $C + M$ equations to determine the $C + M$ variables. The condition of eqn. (21) corresponds to that required in eqn. (15) which is readily shown by means of the relation between the matrices \mathbf{E} and \mathbf{A} given in eqn. (18). The conditions of eqn. (22) just express that the material balances must be satisfied.

The solution to eqns. (21)-(22) has some interesting properties. The mixture

(reduced) Gibbs energy at the solution is given by

$$\begin{aligned}\frac{G_{\min}}{RT} &= \sum_{i=1}^C \frac{n_i \mu_i}{RT} = \sum_{i=1}^C n_i \sum_{j=1}^M \lambda_j A_{ji} \\ &= \sum_{j=1}^M \lambda_j \sum_{i=1}^C A_{ji} n_i = \sum_{j=1}^M b_j \lambda_j\end{aligned}\quad (23)$$

In addition, if we multiply all elements of the b -vector by the same constant, k , it is clear that the Lagrange multipliers in the solution of eqns. (21)-(22) are unchanged. Therefore,

$$G_{\min}(kb) = k G_{\min}(b) \quad (24)$$

The equilibrium Gibbs energy is thus a homogeneous function of degree one in the elemental composition. As a consequence,

$$\frac{1}{RT} \frac{\partial G_{\min}}{\partial b_j} = \lambda_j \quad (25)$$

These results can be compared with the conventional Gibbs energy expressions

$$\frac{G}{RT} = \sum_{i=1}^C \frac{n_i \mu_i}{RT}, \quad \frac{1}{RT} \frac{\partial G}{\partial n_i} = \frac{\mu_i}{RT} \quad (26)$$

The formal similarity in these expressions show that we can consider b as a 'pseudo' composition vector with the λ_j being the reduced potential corresponding to pseudocomponent j . This analogy is highly useful in connection with chemical models.

The numerical solution of eqns. (21)-(22) is simplified when the reaction mixture forms an *ideal solution*. In this case, we can write

$$\frac{\mu_i}{RT} = \frac{\mu_i^*}{RT} + \ln x_i + \ln \hat{\phi}_i + \ln \frac{P}{P_0} = \frac{\mu_i^{pure}}{RT} + \ln x_i$$

where μ_i^{pure} is the chemical potential of pure component i at the system temperature and pressure. The set of equations (21) then yields

$$\ln x_i = \sum_{j=1}^M A_{ji} \lambda_j - \frac{\mu_i^{pure}}{RT} \quad (27)$$

Substituting $n_i = n_t x_i$ into eqns. (22), where n_t is the total number of moles, we obtain the $M + 1$ equations

$$n_t \sum_{i=1}^C A_{ji} x_i - b_j = 0, \quad j = 1, 2, \dots, M \quad (28)$$

$$\sum_{i=1}^C x_i - 1 = 0 \quad (29)$$

with x_i given by eqn. (27). The number of unknowns is now reduced to $M+1$: The M Lagrange multipliers and the total number of moles present, n_t .

The approach is readily generalised to multiphase systems. Let the chemical potential of pure component i in phase k at the system temperature and pressure be $\mu_{i,k}^{\text{pure}}$. Then,

$$\ln x_{i,k} = \sum_{j=1}^M A_{ji} \lambda_j - \frac{\mu_{i,k}^{\text{pure}}}{RT} \quad (30)$$

and we arrive at the following set of $M+F$ equations

$$\sum_{k=1}^F n_{t,k} \sum_{i=1}^C A_{ji} x_{i,k} - b_j = 0, \quad j = 1, 2, \dots, M \quad (31)$$

$$\sum_{i=1}^C x_{i,k} - 1 = 0, \quad k = 1, 2, \dots, F \quad (32)$$

For moderately non-ideal mixtures, a successive substitution procedure is attractive. We just replace $\mu_{i,k}^{\text{pure}}$ by $\mu_i^*(T) + RT \ln(\hat{\varphi}_{i,k} P/P_0)$, where $\mu_i^*(T)$ is the ideal gas chemical potential at temperature T and pressure P_0 , and $\hat{\varphi}_{i,k}$ is the fugacity coefficient of component i in phase k . A composition estimate provides initial values of the fugacity coefficients, and the set of equations above are solved, yielding new phase compositions. These are in turn used to update the fugacity coefficients in an outer loop, and the process is repeated until convergence. Conceptually, we can consider the use of the above equations as an approach where the equilibrium relations are satisfied automatically (through the explicit relation, eqn. (30)) whereas the material balances (eqns. (31) and (32)) are solved iteratively.

Initial estimates for the single phase as well as for the multiphase equilibrium calculation can be generated by means of *linear programming*. We construct an approximate solution based on the assumption that the chemical potentials are composition independent. Evidently, this approximation is poor except for components with a mole fraction near 1, but it enables us to use a simple safe solution procedure. For the single phase equilibrium calculation the Gibbs energy minimization becomes

$$\min \sum_{i=1}^C \frac{n_i \mu_i^{\text{pure}}}{RT} \quad (33)$$

subject to

$$\sum_{i=1}^C A_{ji} n_i - b_j = 0, \quad n_i \geq 0, \quad j = 1, 2, \dots, M \quad (34)$$

which is the standard form of a *linear programming problem*. The solution is (except in degenerate cases) a set of M non-zero values of the component mole numbers that enable a unique determination of the corresponding Lagrange multipliers from

$$\frac{\mu_i^{pure}}{RT} = \sum_{j=1}^M A_{ji} \lambda_j, \quad n_i = 0 \quad (35)$$

The initial estimate from linear programming will yield a reasonable approximation for the Lagrange multipliers and the total number of moles, which enables us to proceed with eqns. (31) and (32). Components present in small amounts at equilibrium are of course not well estimated using linear programming, but since eqns. (31)-(32) essentially iterate on the material balances this is of minor consequence for the method.

Problems can arise in cases where the solution to the LP-subproblem corresponds to a number of equilibrium components which is smaller than M . A simple example is given by the mixture (H_2O , H_2 , O_2). If the overall mixture composition corresponds to a b -vector with a ratio of H to O of exactly 2:1, the LP-solution at low temperature will be formation of water only, and we are unable to determine individual Lagrange multipliers for H and O.

The Rand method

An alternative approach, the *Rand method* utilises a composition vector n that at all iterations satisfies the material balance constraints, eqn. (34). The classical Rand method was developed for ideal solutions, but we shall here present a more general variant due to Greiner (1991) which accounts explicitly for non-ideal behaviour.

The reduced chemical potential is written as follows

$$\frac{\mu_i}{RT} = \frac{\mu_i^*}{RT} + \ln \frac{n_i}{n_t} + \ln \hat{\varphi}_i + \ln \frac{P}{P_0} \quad (36)$$

where $n_t = \sum_i n_i$. The working equations (21), are linearised around the current composition estimate

$$\frac{\mu_i}{RT} + \sum_l \frac{\partial}{\partial n_l} \left(\frac{\mu_i}{RT} \right) \Delta n_l + \frac{\partial}{\partial n_t} \left(\frac{\mu_i}{RT} \right) \Delta n_t - \sum_j \lambda_j A_{ji} = 0 \quad (37)$$

or, from eqn. (36),

$$\frac{\mu_i}{RT} + \sum_l M_{il} \Delta n_k - \frac{1}{n_t} \Delta n_t - \sum_j \lambda_j A_{ji} = 0 \quad (38)$$

where $M_{il} = \frac{1}{n_i} \delta_{il} + \frac{\partial \ln \varphi_i}{\partial n_i} = \frac{1}{n_i} \delta_{il} + \Phi_{il}$.

This equation is solved for the correction vector,

$$\Delta n = M^{-1} (A^T \lambda - \mu) + n s \quad (39)$$

where $s = \Delta n_t / n_t$ and we have utilised that $M n = 1$.

The correction vector must satisfy the $M + 1$ relations

$$\begin{aligned} A \Delta n &= 0 \\ 1^T \Delta n - \Delta n_t &= 0 \end{aligned} \quad (40)$$

Substitution of eqns. (39) into eqns. (40) finally yields the set of working equations

$$\begin{pmatrix} A M^{-1} A^T & b \\ b^T & 0 \end{pmatrix} \begin{pmatrix} \lambda \\ s \end{pmatrix} = \frac{1}{RT} \begin{pmatrix} A M^{-1} \mu \\ n^T \mu \end{pmatrix} \quad (41)$$

These are solved for the Lagrange multipliers and for s , and the correction to the composition vector is subsequently calculated from eqn. (39). In the case of an ideal solution the matrix M becomes diagonal, $M_{ii} = 1/n_i$, and we recover the classical Rand method.

The approach is readily extended to the case of multiple phases. We arrive at

$$\begin{pmatrix} A (\sum_{k=1}^F M_k^{-1}) A^T & B \\ B^T & 0 \end{pmatrix} \begin{pmatrix} \lambda \\ s \end{pmatrix} = \frac{1}{RT} \begin{pmatrix} A \sum_{k=1}^F (M_k^{-1} \mu_k) \\ d \end{pmatrix} \quad (42)$$

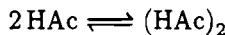
where $B = A (n_1, n_2, n_3, \dots)$ and $d_k = \sum_i n_{ik} \mu_{ik}$

The extended Rand method is quadratically convergent, and it has the additional advantage that the automatic satisfaction of the material balance constraints enable us to check each step for a reduction in the mixture Gibbs energy. One disadvantage is that corrections by eqn. (39) may lead to negative mole numbers. This obviously requires corrective action and precautions to ensure that the material balances remain satisfied. Furthermore, convergence may be slow when mixture components are present in very small amounts. Finally, the initial estimate from the linear programming approach cannot be used directly, since a number of the mixture components as calculated from this initialization are present in zero amount which prevents the calculation of a value for the chemical potential.

5 Chemical models

Chemical models for physical properties are models in which chemical equilibrium considerations form an essential part. A simple and practically important example is the vapour phase dimerization of organic acids.

Consider e.g. a vapour phase consisting of pure acetic acid at 373 K and 0.2 atm. We would expect that the molar volume for this vapour could be calculated accurately by means of the ideal gas law and that the fugacity coefficient of acetic acid in the vapour phase is close to 1. In practice, however, the molar volume deviates about 30% from the ideal gas value. The reason for this is that a reaction equilibrium between acetic acid monomer and dimer exist in the vapour phase



Let the equilibrium constant (on a mole fraction basis) be K , i.e.,

$$\frac{y_{(\text{HAc})_2}}{y_{\text{HAc}}^2} = K$$

Then the 'true' composition of the vapour phase is given by the equations

$$y_{(\text{HAc})_2} = K y_{\text{HAc}}^2 ,$$

$$y_{(\text{HAc})_2} + y_{\text{HAc}} = 1$$

yielding a 'true' mole fraction of HAc which is smaller than the 'apparent' mole fraction of 1. One mole of HAc corresponds to a 'true' number of moles given by $n_t (y_{\text{HAc}} + 2y_{(\text{HAc})_2}) = 1$ from which we obtain $n_t = 1/(1 + y_{(\text{HAc})_2})$. The 'true' number of vapour phase moles, and hence the 'molar volume' of the vapour phase is therefore less than that calculated from the ideal gas law. Similarly, the 'apparent fugacity coefficient' for HAc is given by

$$z_{\text{app}} \hat{\varphi}_{\text{app}} = y_{\text{true}} \hat{\varphi}_{\text{true}} ,$$

or, with $z_{\text{app}} = 1$ and $\hat{\varphi}_{\text{true}} = 1$, $\hat{\varphi}_{\text{app}} = y_{\text{HAc}} (< 1)$.

In practical applications it is desirable to work in terms of the apparent composition using the corresponding molar volume and fugacity coefficient. Our 'chemical model' provide us with these properties, even though the 'true' mixture obeys the ideal gas law.

Next, we shall consider a more complex example in order to demonstrate how the methodology for calculation of chemical equilibrium can be utilised. We consider (at specified T, P) a binary mixture of HAc and an inert gas, I, at a pressure, P , where the ideal gas law applies. Let the composition

be (n_1, n_2) . Our purpose is, again, to determine the apparent fugacity coefficients for the two mixture components. The 'true' composition of this mixture is given by the mole fractions (y_1, y_2, y_3) of HAc, I and $(\text{HAc})_2$, respectively. The formula matrix for the mixture is written, using the 'apparent' components HAc and I as our "elements", i.e.,

$$\mathbf{A} = \begin{pmatrix} 1 & 0 & 2 \\ 0 & 1 & 0 \end{pmatrix}$$

The equations determining the Lagrange multipliers λ_1 , λ_2 and the total 'true' number of moles n_t are

$$n_t(y_1 + 2y_3) = n_1$$

$$n_t y_2 = n_2$$

$$y_1 + y_2 + y_3 = 1$$

with the true mole fractions given by

$$\ln y_1 = \lambda_1 - \ln \frac{P}{P_0} - \frac{\mu_{\text{HAc}}^*}{RT}$$

$$\ln y_2 = \lambda_2 - \ln \frac{P}{P_0} - \frac{\mu_I^*}{RT}$$

$$\ln y_3 = 2\lambda_1 - \ln \frac{P}{P_0} - \frac{\mu_{(\text{HAc})_2}^*}{RT}$$

Knowledge of the chemical potential of the individual constituents is not required for solving the equilibrium calculation. The information required can be obtained from the equilibrium constant for the dimerization reaction, as follows: Introduce the new variables

$$\alpha_1 = \lambda_1 - \ln \frac{P}{P_0} - \frac{\mu_{\text{HAc}}^*}{RT}, \quad \alpha_2 = \lambda_2 - \ln \frac{P}{P_0} - \frac{\mu_I^*}{RT}$$

Then, $\ln y_1 = \alpha_1$, $\ln y_2 = \alpha_2$, $\ln y_3 = 2\alpha_1 - C + \ln P/P_0$, with $C = (\mu_{(\text{HAc})_2}^* - 2\mu_{\text{HAc}}^*)/(RT)$. From these equations, $y_3/y_1^2 = P \exp(-C) = K$, i.e., the equilibrium constant K provides all the necessary information. Alternatively, we might arbitrarily assign a value of zero to the standard state chemical potential of the elements (the monomer and the inert) and assign a value of the chemical potential for the dimer which would be consistent with the equilibrium constant.

From the solution we obtain the apparent chemical potentials of HAc and inert, and from these again the component fugacity coefficients

$$\frac{\mu_{\text{HAc}}}{RT} = \lambda_1 = \alpha_1 + \ln \frac{P}{P_0} + \frac{\mu_{\text{HAc}}^*}{RT} = \ln z_1 + \ln \varphi_1 + \ln \frac{P}{P_0} + \frac{\mu_{\text{HAc}}^*}{RT}$$

$$\frac{\mu_I}{RT} = \lambda_2 = \alpha_2 + \ln \frac{P}{P_0} + \frac{\mu_I^*}{RT} = \ln z_2 + \ln \varphi_2 + \ln \frac{P}{P_0} + \frac{\mu_I^*}{RT}$$

or $\ln \varphi_1 = \alpha_1 - \ln z_1$, $\ln \varphi_2 = \alpha_2 - \ln z_2$. Differentiation of the equilibrium equations with respect to n_1 , n_2 , T and P readily yields the composition, temperature and pressure derivatives of the fugacity coefficients.

The approach outlined above is easily extended to a mixture containing any number of dimerizing acids and to acids forming cross dimers.

6 Combined physical and chemical models

In particular for liquid phase models an approach based entirely on chemical equilibrium may prove inadequate. Incorporation of physical deviations from ideal behaviour, e.g. by means of an excess Gibbs energy expression, might on the other hand make the derivation of physical properties computationally expensive. A pragmatic approach could be to assume that the excess contribution to the mixture Gibbs energy,

$$G = G^{id} + G^E$$

depends only on the 'apparent' composition of the mixture, whereas the G^{id} accounts for the chemical reaction terms. This assumption implies that the chemical equilibrium calculation is not complicated by the presence of the excess Gibbs energy contribution and can be performed as an ideal solution calculation.

7 Chemical models and equations of state

We consider once again a mixture containing C components in molar amounts (e_1, e_2, \dots, e_C) . These components are called the external or 'real' components of the mixture. It is assumed that these components can react chemically and that a total of t species can be present in the reaction mixture. At equilibrium the molar amounts of these 'true' or internal species are (n_1, n_2, \dots, n_t) . The set of 'true' species could, in addition to the 'real' components, comprise dimers, polymers and association products.

The total external composition, total volume and temperature fully define the 'true' composition of the mixture, and, given standard state chemical

potentials for all species and a model for the residual Helmholtz energy of the mixture, permit calculation of the equilibrium composition and the total Helmholtz energy at equilibrium. The equilibrium composition is determined by the condition that the Helmholtz energy is at a minimum, subject to the material balance constraints given by the overall composition. The equilibrium Helmholtz energy is thus uniquely related to external composition, volume and temperature, i.e.,

$$A^{eq} = A(\mathbf{e}, T, V) \quad (43)$$

The chemical potentials of the external components are given by

$$\hat{\mu}_j = \left(\frac{\partial A^{eq}}{\partial e_j} \right)_{T,V} \quad (44)$$

and the pressure can be found from

$$P = - \left(\frac{\partial A^{eq}}{\partial V} \right)_{T,\mathbf{e}} \quad (45)$$

Differentiation of a relation for A^{eq} therefore enables us to perform all phase equilibrium calculations in terms of the external composition of the mixture. The ‘true’ composition is only of relevance for the determination of A^{eq} .

8 Mixture Helmholtz energy

The total mixture reduced Helmholtz energy in terms of the true species is given by

$$\frac{A_{mix}}{RT} = \sum_{i=1}^t n_i \left(\frac{\mu_i^*}{RT} + \ln \frac{n_i RT}{P_0 V} - 1 \right) + \frac{A^r(\mathbf{n}, T, V)}{RT} \quad (46)$$

where μ_i^* is the standard state chemical potential (perfect gas, pressure P_0) of species i .

The equilibrium Helmholtz energy is given by

$$A^{eq} = \min A_{mix}(\mathbf{n}) \quad (47)$$

subject to a set of material (element) balance constraints of the form

$$\sum_{i=1}^t A_{ji} n_i - e_j = 0 \quad (48)$$

where \mathbf{A} represents the ‘formula matrix’ for the ‘true’ species in terms of the external components.

When t is much larger than C and the residual contribution to the mixture Helmholtz energy depends on the true mixture composition solution of the minimization defined by eqns. (47)-(48) can be quite expensive. However, the calculation of the derivatives of the equilibrium Helmholtz energy with respect to volume (in order to determine the pressure) and with respect to the external composition (to get apparent chemical potentials) is simple. The derivatives with respect to the e_i are just the corresponding Lagrange multipliers, and the derivative of A^{eq} with respect to V becomes

$$\begin{aligned}\frac{\partial A^{eq}}{\partial V} &= \left(\frac{\partial A_{mix}}{\partial V} \right)_n + \sum_i \left(\frac{\partial A_{mix}}{\partial n_i} \right)_V \left(\frac{\partial n_i}{\partial V} \right)_{eq} \\ &= \left(\frac{\partial A_{mix}}{\partial V} \right)_n + \sum_i \mu_i \left(\frac{\partial n_i}{\partial V} \right)_{eq}\end{aligned}\quad (49)$$

However,

$$\sum_i \mu_i \left(\frac{\partial n_i}{\partial V} \right)_{eq} = \sum_j \sum_i \lambda_j A_{ji} \left(\frac{\partial n_i}{\partial V} \right)_{eq} = 0$$

where we utilise the material balance constraint, $\sum_i A_{ji} n_i - e_j = 0$. Thus, we arrive at the simple result

$$\frac{\partial A^{eq}}{\partial V} = \left(\frac{\partial A_{mix}}{\partial V} \right)_n$$

The temperature derivative of the Helmholtz energy can be determined in a similar manner. If a Newton-based approach is used for solving the minimization problem, eqns. (47)-(48), second derivatives can be evaluated at little extra cost.

Frequently, simplifying assumptions are used whereby the computational effort in solving for the ‘true’ reaction equilibrium is substantially reduced. We shall here as an example consider the situation where the composition dependence of A^r enables a partial decoupling of the ‘physical’ and the ‘chemical’ contribution to the Helmholtz energy. In particular, we shall assume that A^r can be written

$$\frac{A^r}{RT} = N Q_1(\mathbf{e}, T, V) + Q_2(\mathbf{e}, T, V) \quad (50)$$

where $N = \sum_{i=1}^t n_i$.

The factors Q_1 and Q_2 are thus assumed to depend only on the external composition of the mixture. Evidently, Q_1 and Q_2 must be homogeneous functions of (\mathbf{e}, V) of degree 0 and 1, respectively. Substituting the above

expression for A^r into eqn. (46) yields

$$\frac{A_{mix}}{RT} = \sum_{i=1}^t n_i \left(\frac{\mu_i^*}{RT} + \ln \frac{n_i RT}{P_0 V} - 1 + Q_1 \right) + Q_2 \quad (51)$$

which is a *convex function* of \mathbf{n} , as the matrix of second composition derivatives is diagonal with positive elements. The corresponding Lagrange function is

$$\mathcal{L}(\mathbf{n}, \boldsymbol{\lambda}) = \frac{A_{mix}}{RT} - \sum_{j=1}^C \lambda_j \left(\sum_{i=1}^t A_{ji} n_i - e_j \right) \quad (52)$$

The duality transformation Fletcher (1981) converts the problem of minimizing A_{mix} with respect to \mathbf{n} to that of maximizing \mathcal{L} with respect to $\boldsymbol{\lambda}$, subject to the constraints

$$\frac{\partial \mathcal{L}}{\partial n_i} = 0, \quad i = 1, 2, \dots, t \quad (53)$$

Differentiation of eqn. (52) yields

$$\frac{\partial \mathcal{L}}{\partial n_i} = \frac{\mu_i^*}{RT} + \ln n_i - \ln \frac{P_0 V}{RT} + Q_1 - \sum_{j=1}^C A_{ji} \lambda_j \quad (54)$$

and the condition, eqn. (53) thus results in

$$\ln n_i = \sum_{j=1}^C A_{ji} \lambda_j - \frac{\mu_i^*}{RT} + \ln \frac{P_0 V}{RT} - Q_1 \quad (55)$$

Substituting $\mathbf{n}(\boldsymbol{\lambda})$ into eqn. (52) finally yields

$$\mathcal{L}(\boldsymbol{\lambda}, \mathbf{n}(\boldsymbol{\lambda})) = \sum_{j=1}^C e_j \lambda_j - N(\boldsymbol{\lambda}) + Q_2 \quad (56)$$

and the reduced equilibrium Helmholtz energy is therefore given by

$$\frac{A^{eq}}{RT} = \max \mathcal{L}(\boldsymbol{\lambda}) = \max \left(\sum_{j=1}^C e_j \lambda_j - N(\boldsymbol{\lambda}) + Q_2 \right) \quad (57)$$

The maximum of \mathcal{L} is found where

$$g_j = \frac{\partial \mathcal{L}}{\partial \lambda_j} = e_j - \frac{\partial N}{\partial \lambda_j} = e_j - \sum_{i=1}^t A_{ji} n_i(\boldsymbol{\lambda}) = 0 \quad (58)$$

and the corresponding Hessian matrix is

$$\frac{\partial g_j}{\partial \lambda_k} = - \sum_{i=1}^t A_{ji} A_{ki} n_i(\lambda) = -H_{jk} \quad (59)$$

Since $t > C$ and since all the n_i are positive, the matrix \mathbf{H} is positive definite. The maximum is therefore unique and can be located safely and effectively by means of Newton's method, combined with a line search. We recognise the condition imposed by eqn. (58) as the material balance constraint.

We are now able to determine the external component chemical potentials

$$\begin{aligned} \frac{\hat{\mu}^j}{RT} &= \left(\frac{\partial \mathcal{L}}{\partial e_j} \right)_V = \left(\frac{\partial \mathcal{L}}{\partial e_j} \right)_{\lambda, V} + \left(\frac{\partial \mathcal{L}}{\partial \lambda} \right)_e \left(\frac{\partial \lambda}{\partial e_j} \right)_V \\ &= \left(\frac{\partial \mathcal{L}}{\partial e_j} \right)_{\lambda, V} \end{aligned} \quad (60)$$

as the second term is identically zero (eqn. (58)) at the maximum. Thus, we arrive at

$$\frac{\hat{\mu}}{RT} = \lambda + N \mathbf{q}_1 + \mathbf{q}_2 \quad (61)$$

where \mathbf{q}_1 and \mathbf{q}_2 are the vectors of composition derivatives (wrt. \mathbf{e}) of Q_1 and Q_2 . Similarly, differentiation of \mathcal{L} with respect to V yields

$$-\frac{P}{RT} = -\frac{N}{V} + N Q_{1,V} + Q_{2,V} \quad (62)$$

Second derivatives are found by repeated differentiation of eqns. (61) and (62). In vector-matrix notation we arrive at the following relations

$$\frac{1}{RT} \frac{\partial \hat{\mu}}{\partial \mathbf{e}} = (\mathbf{I} + \mathbf{q}_1 \mathbf{e}^T) \mathbf{H}^{-1} (\mathbf{I} + \mathbf{e} \mathbf{q}_1^T) - N \mathbf{q}_1 \mathbf{q}_1^T + N \mathbf{Q}_1 + \mathbf{Q}_2 \quad (63)$$

$$\begin{aligned} \frac{1}{RT} \frac{\partial \hat{\mu}}{\partial V} &= \left(Q_{1,V} - \frac{1}{V} \right) \left(-N \mathbf{q}_1 + (\mathbf{I} + \mathbf{q}_1 \mathbf{e}^T) \mathbf{H}^{-1} \mathbf{e} \right) \\ &\quad + N \mathbf{q}_{1,V} + \mathbf{q}_{2,V} \end{aligned} \quad (64)$$

and

$$\begin{aligned} -\frac{1}{RT} \frac{\partial P}{\partial V} &= \left(Q_{1,V} - \frac{1}{V} \right)^2 (\mathbf{e}^T \mathbf{H}^{-1} \mathbf{e} - N) \\ &\quad + N \left(Q_{1,VV} + \frac{1}{V^2} \right) + Q_{2,VV} \end{aligned} \quad (65)$$

Since \mathbf{H}^{-1} is available from the solution for λ , derivatives of the chemical potentials are very easily calculated. Temperature derivatives can be evaluated by similar relations.

The derivations above correspond to the model used by Heidemann and Prausnitz (1976), where NQ_1 and Q_2 correspond to the repulsive and the attractive terms, respectively, in a Redlich-Kwong expression for the residual Helmholtz energy. Somewhat simpler results are obtained with the models used by Anderko (1989) and by Economou and Donohue (1991), where the residual Helmholtz energy is assumed to be conversion independent, corresponding to $Q_1 = 0$. Computationally, this latter simplification involves few, if any, advantages.

In phase equilibrium calculations, pressure rather than volume is usually specified, and the derivations have to be supplemented with an adjustment of V to produce the specified pressure. This could be accomplished by minimizing the objective function $A + VP^{spec}$. Explicit elimination of V is, however, difficult, and keeping V as an independent variable after the duality transformation unfortunately converts the maximization in λ to a saddle point search in (λ, V) .

9 SAFT-type models

Current association models like SAFT (Chapman et al, 1989) and its variants treat chemical contributions in a slightly different manner. Hydrogen bonding molecules like water and alcohols have multiple binding sites, and if we consider association between molecule A and molecule B as involving one site from each molecule we open up for formation of arbitrary complexes of the type A_mB_n . This leads partly to the problem that we have to ascribe properties to all such reaction products, and partly that we end with an infinity of species and therefore, except in special cases, with an unsolvable model.

These problems are circumvented if we consider the reactions as occurring between sites only, independent of the state of the molecules carrying these sites. In this manner we only have to consider dimerisation reaction between a countable number of 'species', i.e., the different types of sites, and consequently the number of reaction products remains countable. The contribution from the chemical equilibrium thus becomes equivalent to that observed in a mixture of dimerising and cross-dimerising species.

Let us therefore consider a mixture of C species at temperature T , total volume V and present in amounts (e_1, e_2, \dots, e_C) . We assume that these species can dimerise and cross-dimerise, and first, for simplicity, we also assume that the reaction mixture forms an ideal gas. Our objective is to cal-

culate the true composition of this mixture, in terms of the moles of the monomers, n_i and the dimers, n_{ij} , where $j \geq i$.

Formulation

The change in the Helmholtz energy due to the reaction equilibrium can be written as the difference between the Helmholtz energy of the equilibrated mixture and that of the unreacted mixture, i.e.

$$\begin{aligned} \frac{\Delta A^{asc}}{RT} = & \sum_{i=1}^C n_i \left(\frac{\mu_i^*}{RT} + \ln \frac{n_i RT}{P_0 V} - 1 \right) \\ & + \sum_{i=1}^C \sum_{j=i}^C n_{ij} \left(\frac{\mu_{ij}^*}{RT} + \ln \frac{n_{ij} RT}{P_0 V} - 1 \right) \\ & - \sum_{i=1}^C e_i \left(\frac{\mu_i^*}{RT} + \ln \frac{e_i RT}{P_0 V} - 1 \right) \end{aligned} \quad (66)$$

where the first term is the contribution from monomers, the second from dimers and the third from the unreacted mixture.

The equilibrium composition minimises ΔA , subject to the material balance constraints,

$$n_i + \sum_{j=1}^i n_{ji} + \sum_{j=i}^C n_{ij} - e_i = 0 \quad (67)$$

The minimum is again determined as the stationary point of the Lagrange function,

$$\mathcal{L}(n, \lambda) = \frac{\Delta A^{asc}}{RT} - \sum_i \lambda_i \left(n_i + \sum_{j=1}^i n_{ji} + \sum_{j=i}^C n_{ij} - e_i \right) \quad (68)$$

that is,

$$\frac{\partial \mathcal{L}}{\partial n_i} = 0, \quad i = 1, 2, \dots, C \quad (69)$$

$$\frac{\partial \mathcal{L}}{\partial n_{ij}} = 0, \quad i = 1, 2, \dots, C, \quad j = i, i+1, \dots, C \quad (70)$$

$$\frac{\partial \mathcal{L}}{\partial \lambda_i} = 0, \quad i = 1, 2, \dots, C \quad (71)$$

We obtain

$$\frac{\partial \mathcal{L}}{\partial n_i} = \frac{\mu_i^*}{RT} + \ln \frac{n_i RT}{P_0 V} - \lambda_i = 0 \quad (72)$$

and similarly,

$$\frac{\partial \mathcal{L}}{\partial n_{ij}} = \frac{\mu_{ij}^*}{RT} + \ln \frac{n_{ij}RT}{P_0V} - \lambda_i - \lambda_j = 0 \quad (73)$$

and

$$\frac{\partial \mathcal{L}}{\partial \lambda_i} = - \left(n_i + \sum_{j=1}^i n_{ji} + \sum_{j=i}^C n_{ij} - e_i \right) = 0 \quad (74)$$

Transformed formulation

As in the previous case we can take advantage of convexity and solve instead the *dual problem*

$$\max \mathcal{L}(n, \lambda)$$

subject to the constraints

$$\frac{\partial \mathcal{L}}{\partial n} = 0$$

i.e., for our case,

$$\frac{\partial \mathcal{L}}{\partial n_i} = 0 \Rightarrow \lambda_i = \frac{\mu_i^*}{RT} + \ln \frac{n_i RT}{P_0 V} \quad (75)$$

$$\frac{\partial \mathcal{L}}{\partial n_{ij}} = 0 \Rightarrow \lambda_i + \lambda_j = \frac{\mu_{ij}^*}{RT} + \ln \frac{n_{ij} RT}{P_0 V} \quad (76)$$

These expressions imply, that we can calculate the composition from the Lagrange multipliers, i.e.,

$$n_i = \frac{P_0 V}{RT} \exp \left(\lambda_i - \frac{\mu_i^*}{RT} \right)$$

and

$$n_{ij} = \frac{P_0 V}{RT} \exp \left(\lambda_i + \lambda_j - \frac{\mu_{ij}^*}{RT} \right)$$

Substitution into \mathcal{L} yields

$$\begin{aligned} \mathcal{L} &= \sum_{i=1}^C n_i (\lambda_i - 1) + \sum_{i=1}^C \sum_{j=i}^C n_{ij} (\lambda_i + \lambda_j - 1) \\ &\quad - \sum_{i=1}^C e_i \left(\frac{\mu_i^*}{RT} + \ln \frac{e_i RT}{P_0 V} - 1 \right) \\ &\quad - \sum_{i=1}^C \lambda_i \left(n_i + \sum_{j=1}^i n_{ji} + \sum_{j=i}^C n_{ij} - e_i \right) \\ &= - \sum_{i=1}^C n_i - \sum_{i=1}^C \sum_{j=i}^C n_{ij} + \sum_{i=1}^C e_i \left(\lambda_i - \frac{\mu_i^*}{RT} - \ln \frac{e_i RT}{P_0 V} + 1 \right) \end{aligned} \quad (77)$$

At the maximum,

$$\frac{\partial \mathcal{L}}{\partial \lambda_j} = e_j - n_j - \sum_{k=1}^j n_{kj} - \sum_{k=j}^C n_{jk} = 0 \quad (78)$$

i.e., we recover the material balance constraints.

New variables

We shall next replace the Lagrange multipliers with a set of new variables \mathbf{X} given by:

$$\lambda_i - \ln \frac{RT}{P_0 V} - \frac{\mu_i^*}{RT} = \ln(X_i e_i) \quad (79)$$

from which

$$n_i = e_i X_i, \quad n_{ij} = \frac{e_i e_j X_i X_j K_{ij}}{V} \quad (80)$$

where

$$K_{ij} = \frac{RT}{P_0} \exp\left(\frac{\mu_i^* + \mu_j^* - \mu_{ij}^*}{RT}\right)$$

We observe that X_i is the fraction of species i present in momomeric form.

For the Lagrange function,

$$\begin{aligned} \mathcal{L}(\mathbf{X}) &= \sum_{i=1}^C e_i (\ln X_i - X_i + 1) - \frac{1}{V} \sum_{i=1}^C \sum_{k=i}^C e_i e_k X_i X_k K_{ik} \\ &= \sum_{i=1}^C e_i (\ln X_i - X_i + 1) - \frac{1}{2V} \sum_{i=1}^C \sum_{k=1}^C e_i e_k X_i X_k K_{ik}^* \end{aligned} \quad (81)$$

$$\text{with } K_{ik}^* = K_{ki}^* = \begin{cases} K_{ik} & i \neq k \\ 2K_{ik} & i = k \end{cases}$$

The optimality conditions, eqn. (80), become:

$$e_j - e_j X_j - \frac{1}{V} \sum_{k=1}^C e_j e_k X_j X_k K_{jk}^* = 0 \quad (82)$$

or

$$X_j = \frac{1}{1 + \frac{1}{V} \sum_{k=1}^C e_k X_k K_{jk}^*} \quad (83)$$

Substitution of this result back in eqn. (81) yields

$$\begin{aligned}\mathcal{L}^{opt} &= \sum_{i=1}^C e_i (\ln X_i - X_i + 1) - \frac{1}{2} \sum_{i=1}^C X_i (1/X_i - 1) \\ &= \sum_{i=1}^C e_i \left(\ln X_i - \frac{1}{2} X_i + \frac{1}{2} \right)\end{aligned}\quad (84)$$

We may now relax our assumption that the equilibrium mixture forms an ideal gas. The resulting expression for the reaction contribution can still be used with the less stringent assumption that the equilibrium constants K_{ik}^* depend only on T , V and the monomeric composition e .

The SAFT formulation

In the SAFT formulation, the reacting species are the hydrogen bonding sites, named A, B, C, etc, tied to the mixture species. The association contribution is here given by

$$\frac{\Delta A^{asc}}{RT} = \sum_{i=1}^C n_i \sum_{A_i} \left(\ln X_{A_i} - \frac{1}{2} X_{A_i} + \frac{1}{2} \right) \quad (85)$$

Here, X_{A_i} is the fraction of A-type sites in species i that are not bonded to other sites. The sites fractions are determined from

$$X_{A_i} = \frac{1}{1 + \frac{1}{V} \sum_{j=1}^C n_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (86)$$

where the association constants $\Delta^{A_i B_j}$ correspond to our equilibrium constants and are assumed to depend on temperature, density and composition but not on the extent of bonding. The underlying Lagrange function is

$$\begin{aligned}\mathcal{L}(\mathbf{X}) &= \sum_{i=1}^C n_i \sum_{A_i} (\ln X_{A_i} - X_{A_i} + 1) \\ &\quad - \frac{1}{V} \sum_{i=1}^C \sum_{j=1}^C n_i n_k \sum_{A_i} \sum_{B_j} X_{A_i} X_{B_j} \Delta^{A_i B_j}\end{aligned}\quad (87)$$

and differentiation of the Lagrange function with respect to the appropriate variables provides us with the association contribution to the mixture properties. In particular,

$$\frac{P^{asc}}{RT} = -\frac{\partial A^{asc}}{\partial V} = -\frac{\partial L^{max}}{\partial V} \quad (88)$$

where, as before,

$$\frac{\partial L^{max}}{\partial V} = \left(\frac{\partial L}{\partial V} \right)_X + \left(\frac{\partial L^{max}}{\partial X} \right)_V \frac{\partial X}{\partial V} = \left(\frac{\partial L}{\partial V} \right)_X \quad (89)$$

since the second term vanishes due to the optimality conditions. We therefore arrive at

$$\frac{P^{asc}}{RT} = \sum_{i=1}^C \sum_{j=1}^C n_i n_j \sum_{A_i} \sum_{B_j} X_{A_i} X_{B_j} \frac{\partial \Delta^{A_i B_j} / V}{\partial V} \quad (90)$$

Further simplification may be possible. For certain equation variants the logarithmic derivatives of the association constants are taken to be independent of the summation indices. In CPA, for example, the equilibrium constants are calculated from

$$\Delta^{A_i B_j} = \frac{b_i + b_j}{2} g(nb/V) \beta^{A_i B_j} \left(\exp \left(\frac{\epsilon^{A_i B_j}}{T} \right) - 1 \right)$$

and therefore the derivative is the same for all terms,

$$\frac{\partial \ln \Delta^{A_i B_j}}{\partial V} = \frac{\partial \ln \Delta}{\partial V} \quad \left(= \frac{\partial \ln g}{\partial V} \right)$$

resulting in

$$\begin{aligned} \frac{P^{asc}}{RT} &= \left(\frac{\partial \ln \Delta}{\partial V} - \frac{1}{V} \right) \sum_{i=1}^C \sum_{j=1}^C n_i n_j \sum_{A_i} \sum_{B_j} X_{A_i} X_{B_j} \\ &= \frac{1}{2} \left(\frac{\partial \ln \Delta}{\partial V} - \frac{1}{V} \right) \sum_i n_i \sum_{A_i} X_{A_i} \end{aligned} \quad (91)$$

The contribution to the chemical potential is similarly given by

$$\frac{\mu_i^{asc}}{RT} = \left(\frac{\partial L^{max}}{\partial n_i} \right)_{T,V} = \left(\frac{\partial L}{\partial n_i} \right)_{X,T,V} \quad (92)$$

with the result

$$\frac{\mu_i^{asc}}{RT} = \sum_{A_i} \ln X_{A_i} - \frac{1}{2V} \sum_{l=1}^C \sum_{j=1}^C n_l n_j \sum_{A_l} \sum_{B_j} X_{A_l} X_{B_j} \frac{\partial \Delta^{A_l B_j}}{\partial n_i} \quad (93)$$

which, provided the composition derivatives satisfy the same conditions as the volume derivatives, i.e.

$$\frac{\partial \ln \Delta^{A_l B_j}}{\partial n_i} = \frac{\partial \ln \Delta}{\partial n_i}$$

finally yields

$$\frac{\mu_i^{asc}}{RT} = \sum_{A_i} \ln X_{A_i} - \frac{1}{2V} \frac{\partial \ln \Delta}{\partial n_i} \sum_{j=1}^C n_j \sum_{B_j} (1 - X_{B_j}) \quad (94)$$

Solving the association equations

In the usual case where temperature, pressure and composition is known, solving the Equation of State for association equations is demanding since the site fractions are given implicitly, in terms of the composition and the (unknown) mixture volume. Two approaches are possible, i.e.

1. to solve simultaneously for the volume and the site fractions, or
2. to solve sequentially, by adjusting the volume in an outer loop with the objective of matching the specified pressure, and calculating the site fractions for a given volume in an inner loop.

The first approach would clearly be the more efficient, but safety reasons currently makes the second the preferred choice, since the inner loop solution for the site fractions can be formulated as an unconstrained maximization. The very simple form of the objective function enables inexpensive calculation of first and second derivatives and therefore efficient solution of the association equations by a second order optimiser.

We shall next look in more detail at how the site fractions are determined. To avoid the cumbersome notation with double summations we index according to the different type of sites present in the mixture. Assume that a mixture contains S site types with site fractions

$$X_i, \quad i = 1, 2, \dots, S$$

Our objective the, given mixture composition, temperature and volume, to solve for the site fractions. The objective function can be written

$$\mathcal{L}(\mathbf{X}) = \sum_{i=1}^S N_i (\ln X_i - X_i + 1) - \frac{1}{2} \sum_{i=1}^S \sum_{j=1}^S N_i N_j X_i X_j C_{ij} \quad (95)$$

where N_i is the number of moles of the compound hosting site i , and C_{ij} is the effective binding constant between sites of type i and j .

The desired solution is found by solving for a gradient of zero,

$$g_i = \frac{\partial \mathcal{L}}{\partial X_i} = N_i (1/X_i - 1) - N_i \sum_{j=1}^S C_{ij} N_j X_j = 0 \quad (96)$$

leading to the well-known result

$$X_i = \frac{1}{1 + \sum_{j=1}^S C_{ij} N_j X_j} \quad (97)$$

The Hessian matrix is given by

$$H_{ij} = \frac{\partial g_i}{\partial X_j} = -\frac{N_i}{X_i^2} \delta_{ij} - N_i N_j C_{ij} \quad (98)$$

We note that except for the diagonal elements the Hessian is constant and can be precalculated.

Successive substitution

The form of eqn. (96) immediately suggests solution by *successive substitution*, using

$$X_i^{(k+1)} = \frac{1}{1 + \sum_{j=1}^S C_{ij} N_j X_j^{(k)}} \quad (99)$$

The procedure is extensively analysed by Michelsen (2006). It is efficient for the easily solved case of weak association (small equilibrium constants) but exhibits strong oscillatory behaviour when the equilibrium constants are large. Damped successive substitution was shown to be useful for a number of cases, even when the equilibrium constants are large.

Second order approach

The preferred choice is the quadratically convergent second order approach, coupled with a steplength adjustment in case the objective function does not exhibit an increase in the current step. The Hessian, as given by eqn. (98) might be indefinite, but a small modification, suggested by Michelsen (2006) provides for a negative definite Hessian. The diagonal contribution is modified as follows:

From eqn. (96) we get

$$\frac{N_i}{X_i} = g_i + N_i + N_i \sum_j C_{ij} N_j X_j$$

and therefore

$$\frac{N_i}{X_i^2} = \frac{g_i + N_i + N_i \sum_j C_{ij} N_j X_j}{X_i} \approx \frac{N_i + N_i \sum_j C_{ij} N_j X_j}{X_i}$$

where we have dropped a contribution that is identically zero at the solution. The modification was shown to make the Hessian negative definite, and the Newton step found from

$$\mathbf{H} \Delta \mathbf{X} + \mathbf{g} = \mathbf{0}$$

there defines an ascent direction. In the rare case the current step does not result in an increase of the objective function, Michelsen found the simple remedy of bisecting the step until an increase takes place, efficient.

Volume iteration

When the outer loop is close to converge, excellent initial estimates for the site fractions in the inner loop are available from the converged values of the previous solution. These estimates may be further improved by calculation of the derivatives of the site fractions with respect to V . From the stationarity condition,

$$\mathbf{g}(\mathbf{X}, V) = \mathbf{0} \quad (100)$$

we obtain by differentiation,

$$\left(\frac{\partial \mathbf{g}}{\partial \mathbf{X}} \right)_V \frac{\partial \mathbf{X}}{\partial V} + \left(\frac{\partial \mathbf{g}}{\partial V} \right)_\mathbf{X} = \mathbf{0} \quad (101)$$

or

$$\mathbf{H} \frac{\partial \mathbf{X}}{\partial V} + \left(\frac{\partial \mathbf{g}}{\partial V} \right)_\mathbf{X} = \mathbf{0} \quad (102)$$

where the elements of the gradient derivatives are found from (eqn. (96))

$$\frac{\partial g_i}{\partial V} = -N_i \sum_{j=1}^S \frac{\partial C_{ij}}{\partial V} N_j X_j \quad (103)$$

The Hessian in factorised form is available from the solution for the site fractions, and the derivatives of \mathbf{X} with respect to the molar volume is thus available at virtually no additional cost.

If the volume iterate in step $k+1$ changes from $V^{(k)}$ to $V^{(k+1)}$, initial estimates for the site fractions are calculated from

$$\mathbf{X}^{(k+1)} = \mathbf{X}^{(k)} + \frac{\partial \mathbf{X}}{\partial V} (V^{(k+1)} - V^{(k)})$$

As a result a single iteration in the inner loop is usually adequate.

Other derived properties

For use in the volume solver, the derivatives of pressure with respect to volume are of interest. For the association contribution to the pressure eqn. (90) can be written

$$P^{asc} = p(\mathbf{X}, V, \mathbf{n}, T) \quad (104)$$

which yields for the derivatives

$$\left(\frac{\partial P^{asc}}{\partial V} \right)_{T, \mathbf{n}} = \left(\frac{\partial p}{\partial V} \right)_{T, \mathbf{n}, \mathbf{X}} + \left(\frac{\partial p}{\partial \mathbf{X}} \right)_{T, V, \mathbf{n}} \left(\frac{\partial \mathbf{X}}{\partial V} \right)_{T, \mathbf{n}} \quad (105)$$

Finally, at the converged solution we need to calculate the association contribution to the component chemical potentials (fugacity coefficients) and the derivatives of these properties with respect to temperature, pressure and total composition. These derivatives are obtained by differentiation of eqn. (93) in a similar manner, and they require that we calculate temperature, as well as composition derivatives of \mathbf{X} .

We can again use eqn. (102), replacing the volume derivative with the appropriate differentiation variable, and we note that no new Hessian is required.

References

An excellent description of the basic principles of chemical reaction equilibrium is found in the textbook by Smith and Missen (1982), where the classical procedures for calculation of chemical equilibrium in ideal solutions are described in detail. The extension of the Rand method to non-ideal mixtures is described in Gautam and Seider (1979), and Castier et al. (1989) extended the approach used by Michelsen for the *PT*-flash for reaction equilibrium. Michelsen (1994) described how the multiphase ideal solution phase equilibrium calculation could be extended to include chemical reactions, and Phoenix and Heidemann (1998) used this approach supplemented with successive substitution for the calculation of non-ideal multiphase chemical equilibrium.

The classical application of chemical models is for the description of non-ideal behaviour of organic acid vapours at low pressure (Prausnitz et al., 1980). Models incorporating chemical association in the liquid phase has also been the subject of many investigations, e.g. Anderko (1989); Heidemann and Prausnitz (1976) and Economou and Donohue (1991). More recently, association models like SAFT (Chapman et al., 1990) and CPA (Kontogeorgis et al., 1996) are widely used.

The formal treatment of chemical models in terms of the Lagrange multipliers as the chemical potentials with the material balance constraint corresponding to the composition vector is given by Perez-Cisneros et al. (1997).

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Chapter 14

Other State Function Based Specifications

Introduction

In addition to the equilibrium calculation at specified temperature and pressure a number of other flash specifications of practical importance can formally be treated as a state function minimization. This implies the existence of a unique, correct solution, and stability analysis can be used in the same manner as for the *PT*-flash to verify the correctness of the phase distribution and to add new phases in case of instability. Traditional examples are specification of pressure and enthalpy (the ‘isenthalpic flash’) and pressure and entropy (the ‘isentropic flash’), but in addition specification of temperature and volume (storage vessels, pipeline shutdown) and specification of volume and internal energy (unsteady state operations) are of importance.

1 State functions

In Table 1 are listed the state functions to be minimised for a number of important specifications. The phase equilibrium calculation for these specifications is, however, not as straightforward as for the *PT*-flash, where the calculation can be performed as an *unconstrained* minimization by treating the mole numbers in one phase as dependent variables. For e.g. the two-phase isenthalpic flash, the minimization formulation is

$$\min (-S)(T, P, v, l) \quad (1)$$

subject to

$$P = P^{spec}, \quad 1 + v = z, \quad H(T, P, v, l) - H^{spec} = 0 \quad (2)$$

Table 1: State function to be minimised for a given specification.

Specification	State function
P, T	G
P, H	$-S$
P, S	H
T, V	A
U, V	$-S$
S, V	U

The linear material balance constraint can be eliminated as for the PT -flash, $\mathbf{l} = \mathbf{z} - \mathbf{v}$, resulting in

$$\min (-S)(T, P^{spec}, \mathbf{v}, \mathbf{z} - \mathbf{v}) \quad (3)$$

subject to

$$H(T, P^{spec}, \mathbf{v}, \mathbf{z} - \mathbf{v}) - H^{spec} = 0 \quad (4)$$

The constraint of specified enthalpy is, however, non-linear in the independent variables, and we cannot eliminate the constraint explicitly. The complicating factor associated with constrained minimization is that the individual steps in the iterative sequence cannot be tested for a reduction in the objective function. Therefore, we do not have the same guarantee of convergence as for the unconstrained minimization.

2 Modified objective functions

It is possible to transform the objective function to a form that formally eliminates the constraints. Consider for example the two-phase isenthalpic flash where the material balance constraints have been eliminated by expressing the liquid flows in terms of the vapour flows. We form the function Q , defined by

$$Q(T, P^{spec}, \mathbf{v}, \mathbf{z} - \mathbf{v}) = \frac{1}{T} (G - H^{spec}) \quad (5)$$

where the independent variables are T and \mathbf{v} . The gradient vector is

$$\begin{aligned} \frac{\partial Q}{\partial v_i} &= \frac{1}{T} \frac{\partial G}{\partial v_i} = \frac{1}{T} (\mu_i^v - \mu_i^l) \\ \frac{\partial Q}{\partial (1/T)} &= \frac{\partial(G/T)}{\partial(1/T)} - H^{spec} = H - H^{spec} \end{aligned} \quad (6)$$

and we observe that at the desired solution the gradient of Q , i.e. the derivatives with respect to all independent variables, equals 0. The solution is thus a *stationary point* for Q , but unfortunately not a minimum, since

$$\frac{\partial^2 Q}{\partial(1/T)^2} = -T^2 C_p < 0 \quad (7)$$

and the Hessian matrix is therefore not positive definite.

Similar Q -functions, all with the Gibbs energy as the 'core function', can be formed for the other specifications, as summarised in Table 2. It is

Table 2: Q -functions for state function based specifications.

Specification	Q -function
P, H	$\frac{1}{T} (G - H^{spec})$
P, S	$G + TS^{spec}$
T, V	$G - PV^{spec}$
U, V	$\frac{1}{T} (G - U^{spec} - PV^{spec})$
S, V	$G + TS^{spec} - PV^{spec}$

worthwhile mentioning that it may be possible to define modified Q -functions for which the desired solution is the unconstrained minimum. One example is the isenthalpic flash with

$$Q^{mod} = \frac{1}{T} (G - H^{spec}) + \alpha (H - H^{spec})^2 \quad (8)$$

where α is a constant, chosen sufficiently large. Procedures based on this choice, together with a similar formulation for the isentropic flash, have been investigated by Michelsen (1987).

It should also be mentioned that the TV -flash can be solved as an unconstrained minimization of the Helmholtz energy, if we abandon the traditional calculation of thermodynamic properties at specified temperature, pressure and composition in favour of a calculation at specified temperature, volume and composition (which is, in fact, the 'natural' choice of independent variables for an equation of state model). This formulation is advantageous in itself for critical point calculations and in connection with chemical models or models with density-dependent mixing rules. It is also interesting to note

that the *PT*-flash can be carried out using unconstrained minimization with 'volume-based' thermodynamics. The objective function

$$Q = A + VP^{spec} \quad (9)$$

where v , V_v and V_l are chosen as the independent variables, satisfies the equilibrium conditions

$$\begin{aligned}\frac{\partial Q}{\partial v_i} &= \mu_i^v - \mu_i^l \\ \frac{\partial Q}{\partial V_v} &= -P_v + P^{spec} \\ \frac{\partial Q}{\partial V_l} &= -P_l + P^{spec}\end{aligned} \quad (10)$$

and in addition, the second derivatives have the correct sign,

$$\frac{\partial^2 Q}{\partial V_v^2} = -\frac{\partial P_v}{\partial V_v} > 0, \quad \frac{\partial^2 Q}{\partial V_l^2} = -\frac{\partial P_l}{\partial V_l} > 0 \quad (11)$$

The 'volume-based' *PT*-flash has at present only found modest use, Nagarajan et al. (1991) being one example.

Q -functions for the remaining specifications with the Helmholtz energy as the 'core function', i.e. based on temperature and volume as the independent variables, are listed in the table below. Only for the specifications (T, V) and (T, P) does the solution correspond to a minimum of Q .

Table 3: Q -functions using temperature and volume as the independent variables.

Specification	Q -function
P, T	$A + VP^{spec}$
P, H	$\frac{1}{T} (A + VP^{spec} - H^{spec})$
P, S	$A + TS^{spec} + VP^{spec}$
T, V	A
U, V	$\frac{1}{T} (A - U^{spec})$
S, V	$A + TS^{spec}$

3 Maximizing Q

The desired stationary point of the above Q -functions are all *saddle points* of the Q -surface, having positive curvature in the composition directions and negative curvature in the T - and/or P -direction. This opens up the possibility to nest a PT -flash calculation (i.e. an *unconstrained* optimization in the composition variables) with a *maximization* with respect to the remaining variables. Using the isentropic flash as an example, the problem can be formulated as

$$\max (G_{min} + TS^{spec}) \quad (12)$$

with respect to T , where G_{min} is the solution to $\min G(T, P, \mathbf{v}, \mathbf{z} - \mathbf{v})$ at the current temperature. In a similar manner all the other specifications can be solved by maximizing Q , combined with an inner loop minimization of the Gibbs energy at the current temperature and pressure, i.e. an isothermal flash.

If only a single phase is known to form at the specified condition, the inner loop is unnecessary, and the outer loop calculation is therefore essentially equivalent to a single phase equilibrium calculation. The flash performed in the inner loop is readily differentiated with respect to temperature and pressure to provide the gradient and the Hessian required for the determination of the maximum. For the isentropic flash, with $Q = G_{min}(T) + TS^{spec}$, we obtain

$$\frac{\partial Q}{\partial T} = \frac{\partial G_{min}}{\partial T} + S^{spec} = -S_{min} + S^{spec} \quad (13)$$

where S_{min} is available from the current phase distribution. The second derivative is found from

$$\frac{\partial^2 Q}{\partial T^2} = -\frac{\partial S_{min}}{\partial T} = -\frac{C_{p,min}}{T} \quad (14)$$

but its evaluation requires the derivatives of the flash solution since

$$\begin{aligned} C_{p,min} &= \left(\frac{\partial H}{\partial T} \right)_{P,z} \\ &= \left(\frac{\partial H_l}{\partial T} \right)_{P,l} + \left(\frac{\partial H_v}{\partial T} \right)_{P,v} + \sum_{i=1}^C \left(\frac{\partial H_l}{\partial l_i} \frac{\partial l_i}{\partial T} + \frac{\partial H_v}{\partial v_i} \frac{\partial v_i}{\partial T} \right) \\ &= C_{p,l} + C_{p,v} + \sum_{i=1}^C \left(\frac{\partial H_v}{\partial v_i} - \frac{\partial H_l}{\partial l_i} \right) \frac{\partial v_i}{\partial T} \end{aligned} \quad (15)$$

where $C_{p,l}$ and $C_{p,v}$ are the total heat capacities for the equilibrium phases. It is the last contribution that requires information about the change in the equilibrium composition with temperature.

The main advantage of the nested loop approach is that it enables us to handle a variety of specifications in a fairly simple manner, provided an efficient and reliable *PT*-flash is available. The outer loop iteration involves only a single or two independent variables, and reliability is assured by the use of a maximization approach. Finally, the extension to multiphase calculations, possibly also involving multiple solid phases, only requires the corresponding multiphase abilities of the *PT*-flash.

4 A Newton approach

An obvious drawback of the nested loop approach is its lack of efficiency as compared with a simultaneous convergence of all independent variables. When good initial estimates are available, a Newton-based approach may therefore be preferable. For the two-phase equilibrium calculation we can derive a general formulation that is capable of handling all the above specifications with the same Jacobian matrix. As independent variables are used the vapour phase flows, v , $\ln T$ and $\ln P$ (provided one or both are not specified). The Newton iteration uses the general formulation

$$\begin{pmatrix} M & g_T & g_P \\ g_T^T & E_{TT} \cdot E_{TP} \\ g_P^T & E_{PT} & E_{PP} \end{pmatrix} \begin{pmatrix} \Delta v \\ \Delta \ln T \\ \Delta \ln P \end{pmatrix} + \begin{pmatrix} g \\ r_T \\ r_P \end{pmatrix} = 0 \quad (16)$$

where only the elements r_T and r_P depend on the specification. The deviation vector is given by

$$g_i = \ln y_i + \ln \hat{\varphi}_i(y, T, P) - \ln x_i + \ln \hat{\varphi}_i(x, T, P), \quad i = 1, 2, \dots, C \quad (17)$$

with the two variable elements r_T and r_P given in Table 4 and the elements of the symmetric Jacobian matrix are

$$M_{ij} = \frac{\partial g_i}{\partial v_j}, \quad i = 1, 2, \dots, C, \quad j = 1, 2, \dots, C$$

$$g_{T,i} = T \left(\frac{\partial \ln \hat{\varphi}_i(y, T, P)}{\partial T} - \frac{\partial \ln \hat{\varphi}_i(x, T, P)}{\partial T} \right), \quad i = 1, 2, \dots, C$$

$$g_{P,i} = P \left(\frac{\partial \ln \hat{\varphi}_i(\mathbf{y}, T, P)}{\partial P} - \frac{\partial \ln \hat{\varphi}_i(\mathbf{x}, T, P)}{\partial P} \right), \quad i = 1, 2, \dots, C$$

$$E_{TT} = -\frac{C_p}{R}, \quad E_{TP} = \frac{P}{R} \frac{\partial V}{\partial T}, \quad E_{PP} = \frac{P^2}{RT} \frac{\partial V}{\partial P} \quad (18)$$

where C_p and V are the heat capacity and the volume of the combined phases.

5 Solution strategy

When no initial estimates are available, the Wilson K -factors can be used to generate approximate values of phase properties. Assuming the vapour phase to be ideal, we obtain

$$\ln \hat{\varphi}_i^l = \ln K_i^{Wilson} = \ln \frac{P_{ci}}{P} + 5.373 (1 + \omega_i) \left(1 - \frac{T_{ci}}{T} \right) \quad (19)$$

combined with an expression for the ideal gas heat capacity as a function of temperature this enables us to calculate all relevant thermodynamic properties.

Our recommended approach for solving the flash equations can be summarised as follows:

1. Converge the equations, using the Wilson K -factor based relations. With composition independent fugacity coefficients, a very inexpensive and well-behaved ‘thermodynamic model’ and in essence only 3 independent variables (T , P and β) this calculation is straightforward and

Table 4: The elements r_T and r_P for a given specification.

Specification	r_T	r_P
(T, P)	-	-
(P, H)	$\frac{1}{RT} (H^{spec} - H)$	-
(P, S)	$\frac{1}{R} (S^{spec} - S)$	-
(T, V)	-	$\frac{P}{RT} (V - V^{spec})$
(V, U)	$\frac{1}{RT} (U^{spec} + PV^{spec} - H)$	$\frac{P}{RT} (V - V^{spec})$
(V, S)	$\frac{1}{R} (S^{spec} - S)$	$\frac{P}{RT} (V - V^{spec})$

cost effective. The resulting estimate of temperature, pressure phase fraction and phase composition cannot be expected to be very accurate but will often prove 'reasonable'.

2. Continue with a few (5 – 10) steps of a partial Newton's method based on the equations derived above, but neglecting the composition derivatives of the fugacity coefficients. The partial Newton's method is likely to *underestimate* the magnitude of the corrections, and this may be advantageous at an early stage; in particular when the initial estimates are inaccurate. When composition derivatives are neglected, the structure of M enables us to reduce the effective size of the set of equations to 3. For moderately non-ideal mixtures this successive substitution like approach may well converge set of equations.
3. Attempt to converge the set of equations using the full Newton's method (including explicitly the composition dependence of the fugacity coefficients in the Jacobian).
4. In case of a failure in step 2 or step 3, e.g. lack of convergence, excessive corrections in temperature or pressure or removal of a phase, switch to the (safe) nested loop approach.
5. Check the final result for stability, and introduce new phases if required.

In our experience step 4 is rarely necessary, but the availability of a slower but reliable procedure enables us to take full advantage of the efficient but more risky Newton-based approach.

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Appendix A

Numerical Methods

Introduction

In this appendix we give a very brief overview of the numerical methods used for solving non-linear algebraic equations and for solving unconstrained and constrained minimization problems. It is assumed that the reader is familiar with basic concepts from linear algebra. A mathematically rigorous treatment is beyond our scope but references are provided for more extensive coverage.

1 Non-linear algebraic equations

The general set of N algebraic equations with N unknown, \mathbf{x} , can be written in the form

$$\mathbf{f}(\mathbf{x}) = \mathbf{0} \quad (1)$$

We shall apply a general iterative method of the form

$$\mathbf{A}^{(k)} \Delta^{(k)} + \mathbf{f}^{(k)} = \mathbf{0}, \quad \mathbf{x}^{(k+1)} = \mathbf{x}^{(k)} + \Delta^{(k)} \quad (2)$$

where k is the iteration count and \mathbf{A} is a matrix characterizing the chosen solution method. It is assumed that an initial estimate \mathbf{x}^0 , which is ‘sufficiently close’ to the desired solution \mathbf{x}^* , is available, and it is furthermore assumed that the iterative sequence is convergent with the proper choice of the matrix \mathbf{A} . Our concern is how the error $\mathbf{e}^{(k)} = \mathbf{x}^{(k)} - \mathbf{x}^*$ is reduced with increasing k . As the measure of progress we shall use the Euclidian norm of the error vector,

$$\|\mathbf{e}\| = \sqrt{\mathbf{e}^T \mathbf{e}} = \sqrt{\sum_i e_i^2} \quad (3)$$

Solution of the set of linear equations for Δ is usually carried out as a two-step procedure. In the first step, the matrix of coefficients, A , is decomposed into the product of a lower triangular matrix L and an upper triangular matrix U , and in the second step the resulting equations

$$Ly = f, \quad U\Delta = y \quad (4)$$

are solved to yield the intermediate, y and subsequently Δ . The first step, the triangular decomposition, is the more expensive, requiring about $N^3/3$ multiplications, whereas the back substitution steps only require about N^2 multiplications.

2 The Newton-Raphson method

The Newton-Raphson method is obtained using $A = J$, where J is the *Jacobian matrix*,

$$J_{ij} = \frac{\partial f_i}{\partial x_j} \quad (5)$$

A Taylor series expansion of $f^{(k)}$ from $x = x^*$ yields

$$f^{(k)} = f^* + J^* (x^{(k)} - x^*) + O(\|x^{(k)} - x^*\|) = J^* e^{(k)} + O(\|e^{(k)}\|^2) \quad (6)$$

and

$$\begin{aligned} \Delta^{(k+1)} &= e^{(k+1)} - e^{(k)} = -(J^{(k)})^{-1} J^* e^{(k)} + O(\|e^{(k)}\|^2) \\ &= -e^{(k)} + O(\|e^{(k)}\|^2) \end{aligned} \quad (7)$$

provided J is non-singular everywhere in a region around x^* . The error associated with the iteration hence satisfies

$$\|e^{(k+1)}\| \approx \|e^{(k)}\|^2 \quad (8)$$

and the Newton-Raphson iteration is said to be second order convergent or *quadratically convergent*.

Second order convergence of an iterative sequence can be tested by plotting the logarithm of $\|e^{(k+1)}\|$ vs. the logarithm of $\|e^{(k)}\|$. For sufficiently large k the cross plot should yield a straight line of slope 2. An essential advantage of the Newton-Raphson method is that machine accuracy is obtainable with very little additional effort. Reduction of the error from 10^{-4} to 10^{-16} typically requires two additional iterations. Furthermore, the sensitivity of the solution x^* to changes in the parameters of the problem can be determined exactly very inexpensively.

Let the solution $\mathbf{x}^*(\alpha)$ of the set of equations

$$\mathbf{f}(\mathbf{x}, \alpha) = \mathbf{0} \quad (9)$$

be known at $\alpha = \alpha^*$. Then, the derivative $\partial\mathbf{x}/\partial\alpha$ is given by

$$\mathbf{J} \frac{\partial \mathbf{x}}{\partial \alpha} + \frac{\partial \mathbf{f}}{\partial \alpha} = \mathbf{0} \quad (10)$$

where \mathbf{J} and \mathbf{f} are evaluated at (\mathbf{x}^*, α^*) . The set of linear equations defining $\partial\mathbf{x}/\partial\alpha$ has a matrix of coefficients which is identical to that used for calculating the increment vector. Evaluation of the sensitivity wrt. to a parameter thus only involves substituting a new RHS for the set of linear equations, i.e. the inexpensive back substitution step. The availability of the sensitivities are of particular importance where the solution of a set of equations must be traced in dependence of the parameters of the problem, or where the purpose of the calculation is to adjust model parameters in order to obtain the best fit between model predictions and experimental data.

The main drawbacks of the Newton-Raphson method are:

- i) The method requires that the Jacobian is calculated. Analytic evaluation can be cumbersome and error-prone, and numerical evaluation is expensive.
- ii) Solution of a set of linear equations is necessary at each iteration. For large N , this might be expensive.
- iii) Convergence is only assured, when 'good' initial estimates are available. In general it is very difficult to ascertain that initial estimates are of adequate quality.

For phase equilibrium calculations the third drawback is in our opinion the most important. The Jacobian matrix for such calculations has a well-defined structure where the essential derivatives required for its construction are the composition derivatives of the component fugacity coefficients. For all practically important models these derivatives can be coded efficiently by a systematic approach. The cost associated with solving the set of linear equations is only of importance in multiphase calculations, where the size of the equations set equals the number of components times the number of phases - 1. Initial estimates are, however, typically of low quality, and alternative convergence methods for phase equilibrium calculations tend to reduce the magnitude of the correction steps, thereby enhancing the stability of the iterative process. It is therefore often advantageous to use alternative methods for the initial iterations.

3 Other choices of \mathbf{A}

We shall next consider the situation where we choose an iteration matrix \mathbf{A} which differs from the Jacobian matrix \mathbf{J} . One reason for doing this could be that the exact Jacobian is difficult or cumbersome to evaluate, and an alternative motivation could be that a specific choice of \mathbf{A} facilitates the solution for the correction vector such that solution of a set of N linear equations is avoided. Combining eqns. (2) and (7), we obtain

$$\mathbf{e}^{(k+1)} = (\mathbf{I} - (\mathbf{A}^{(k)})^{-1} \mathbf{J}^{(k)}) \mathbf{e}^{(k)} + O(\|\mathbf{e}^{(k)}\|^2) \quad (11)$$

Unless \mathbf{A} converges to \mathbf{J} when k becomes large the second term on the RHS can be neglected, and we may write for large k , assuming that convergence occurs

$$\mathbf{e}^{(k+1)} \approx \mathbf{S} \mathbf{e}^{(k)}, \quad \mathbf{S} = \mathbf{I} - (\mathbf{A}^*)^{-1} \mathbf{J}^* \quad (12)$$

where $\mathbf{A}^* = \mathbf{A}^{(k \rightarrow \infty)}$. The convergence will therefore be *linear*, i.e. with an error that ultimately decreases by a constant factor. The rate of convergence will depend on the properties of \mathbf{S} , and obviously, the error decreases most rapidly the 'smaller' \mathbf{S} is.

To obtain a quantitative measure it is necessary to investigate the *eigenvalues* of the matrix \mathbf{S} . We expand the error vector on the *eigenvectors* \mathbf{u}_i of \mathbf{S} ,

$$\mathbf{e}^{(k)} = \sum_i \alpha_i \mathbf{u}_i \quad (13)$$

where \mathbf{u}_i is the eigenvector corresponding to the i 'th eigenvalue,

$$\mathbf{S} \mathbf{u}_i = \lambda_i \mathbf{u}_i \quad (14)$$

Assume that the eigenvalues are indexed after descending magnitude, i.e.,

$$|\lambda_1| > |\lambda_2| > \dots \dots > |\lambda_N| \quad (15)$$

We then obtain

$$\mathbf{e}^{(k+1)} = \sum_i \alpha_i \lambda_i \mathbf{u}_i \quad (16)$$

and

$$\mathbf{e}^{(k+m)} = \sum_i \alpha_i \lambda_i^m \mathbf{u}_i = \lambda_1^m \sum_i \alpha_i \left(\frac{\lambda_i}{\lambda_1} \right)^m \mathbf{u}_i \approx \lambda_1^m \alpha_1 \mathbf{u}_1 \quad (17)$$

for m sufficiently large. The error vector becomes aligned with the eigenvector of \mathbf{S} corresponding to the eigenvalue of largest magnitude, and the magnitude of the error vector is multiplied by λ_1 in each subsequent iterations. A necessary condition for convergence is therefore that the largest eigenvalue of

S must be smaller than 1 in magnitude. If for a convergent process the norm of the error vector (or the norm of the correction vector) is plotted against the iteration count k , we obtain for large k a straight line with of slope $|\lambda_1|$.

If the magnitude of this eigenvalue is close to zero convergence is rapid, while values close to 1 in magnitude lead to slow convergence. For example, the number of iterations required to reduce the error by a factor of 10 is 22 for $\lambda_1 = 0.9$ and 229 for $\lambda_1 = 0.99$. When the eigenvalue of largest magnitude (often called the *dominant eigenvalue*) is negative, convergence is oscillatory. The iteration scheme is therefore of most value in situations where A is a good approximation to the Jacobian J , and one application of the method could be to select a A as the exact Jacobian evaluated at an early iteration and subsequently kept constant for the following iterations. This will be particularly useful if the initial estimate is known to be of high quality or if the set of equations is nearly linear.

It is worthwhile to keep in mind that quadratic convergence is obtainable with an approximate Jacobian provided $A^{(k)}$ differs from $J^{(k)}$ by an amount proportional to the magnitude of $e^{(k)}$. This can often be utilised for simplifying the Jacobian, e.g. by neglecting terms that are known to vanish at x^* .

4 Successive substitution

Eqn. (1) can be rewritten in the form

$$x = g(x) \quad (18)$$

where $g(x) = x - f(x)$. Using $A = I$ leads to the iteration

$$x^{(k+1)} = g(x^{(k)}) \quad (19)$$

that is, the well-known successive substitution method. From eqn. (12) we obtain $J = I - G$, $S = G$, where $G_{ij} = \partial g_i / \partial x_j$, with the requirement for convergence that the eigenvalue of G of largest modulus must satisfy $|\lambda_i| < 1$. Consequently, successive substitution is of greatest utility in situations where the set of equations can be formulated such that g depends only weakly on x .

An advantage frequently observed with successive substitution in thermodynamic calculations is that the method is less sensitive to the quality of the initial estimates than the Newton-Raphson method. A typical example is the solution for the *PT*-flash, where x represents the vector of K -factors and g represents the corresponding fugacity coefficient ratios. Successive substitution is based on the assumption that the fugacity coefficients are composition

independent, and when this is a good approximation rapid convergence is obtained. Most non-ideal mixtures exhibit positive deviations from ideality, and in practice all important eigenvalues of \mathbf{S} are positive (and smaller than 1). The sequence of iterations therefore converge monotonically to the solution. If the Newton-Raphson method is initiated with a poor estimate, there is a risk that the correction vector 'overshoots' the solution by a wide margin. In addition, successive substitution in equilibrium calculations appear to make best progress in the initial steps and it is therefore sound to use this approach initially with a later switch to the second-order method, if convergence is not obtained readily.

Various acceleration procedures can be used to increase the rate of convergence for successive substitution. A simple example will be used for illustration here. Assuming that the dominant eigenvalue, λ_1 , is much larger than the remaining eigenvalues of \mathbf{S} , we rapidly reach a stage where

$$\Delta^{(k)} \approx \alpha_1 \mathbf{u}_1, \quad \Delta^{(k+1)} \approx \alpha_1 \lambda_1 \mathbf{u}_1 \quad (20)$$

and all subsequent increments are parallel to \mathbf{u}_1 . Now, λ_1 can be determined from the equation

$$\lambda_1 \Delta^{(k)} - \Delta^{(k+1)} = 0 \quad (21)$$

Furthermore, we may write

$$\mathbf{x}^* = \mathbf{x}^{(k)} + \Delta^{(k)} + \Delta^{(k+1)} + \Delta^{(k+2)} + \dots$$

$$= \mathbf{x}^{(k)} + \alpha_1 \mathbf{u}_1 (1 + \lambda_1 + \lambda_1^2 + \dots) = \mathbf{x}^{(k)} + \frac{1}{1 - \lambda_1} \Delta^{(k)} \quad (22)$$

In practice eqn. (20) will not hold exactly, and it is impossible to satisfy eqn. (21). Instead, we select λ_1 to minimise

$$h(\lambda_1) = \left\| \lambda_1 \Delta^{(k)} - \Delta^{(k+1)} \right\|^2 \quad (23)$$

yielding

$$\lambda_1 = \frac{(\Delta^{(k)})^T \Delta^{(k+1)}}{(\Delta^{(k)})^T \Delta^{(k)}}$$

Similarly, we cannot expect \mathbf{f} to be $\mathbf{0}$ at the extrapolated value for \mathbf{x}^* , but in most cases the extrapolated value provides a much better starting point for continued iteration than is the case with $\mathbf{x}^{(k+2)}$.

The approach described above is the *Dominant Eigenvalue Method* of Orbach and Crowe (1971). The limitation that λ_1 must be substantially larger

than the remaining eigenvalue is remedied in the extension of the method, the *General Dominant Eigenvalue Method* (Crowe and Nishio, 1975). Here, a limited number of eigenvalues, typically $M = 2 - 4$, are assumed to be of importance with the consequence that the error vectors after a few iterations are confined to the subspace spanned by the corresponding eigenvectors. Rather than estimating the numerical values of the individual eigenvalues, coefficients of the characteristic polynomial are evaluated using a criterion similar to that used above. GDEM requires a sequence of $M + 1$ correction vectors in order to calculate an estimate of the solution vector. The method is very inexpensive in terms of the associated algebraic operations, and it is particularly efficient for problems where a reasonable value of M , the number of 'important' eigenvalues, can be assessed in advance.

5 Quasi-Newton methods

The main motivation for Quasi-Newton methods is to avoid explicit evaluation of the Jacobian matrix. The iteration matrix \mathbf{A} is an approximation to the Jacobian which is re-evaluated recursively as iterations proceed.

In *Broyden's method* $\mathbf{A}^{(k+1)}$ is calculated from

$$\mathbf{A}^{(k+1)} = \left(\mathbf{A} + \frac{(\mathbf{y} - \mathbf{A} \Delta) \Delta^T}{\Delta^T \Delta} \right)^{(k)} \quad (24)$$

where $\mathbf{y}^{(k)} = \mathbf{f}^{(k+1)} - \mathbf{f}^{(k)}$. The motivation for this choice is that

i) $\mathbf{A}^{(k+1)}$ must satisfy the *Quasi-Newton condition*

$$\mathbf{A}^{(k+1)} (\mathbf{x}^{(k+1)} - \mathbf{x}^{(k)}) = \mathbf{f}^{(k+1)} - \mathbf{f}^{(k)} \quad (25)$$

which is satisfied for the true Jacobian provided the change in \mathbf{x} is sufficiently small.

ii) Since the step form $\mathbf{x}^{(k)}$ to $\mathbf{x}^{(k+1)}$ can only yield new information about the variation of \mathbf{f} in the step direction $\mathbf{A}^{(k+1)}$ is selected such that

$$\mathbf{A}^{(k+1)} \Delta = \mathbf{A}^{(k)} \Delta \quad (26)$$

for any vector Δ which is orthogonal to $\Delta^{(k)}$. These two conditions uniquely define the update formula, eqn. (24).

Broyden's method has super-linear convergence, i.e. $\|\mathbf{e}^{(k+1)}\| / \|\mathbf{e}^{(k)}\| \rightarrow 0$ for $k \rightarrow \infty$.

The requirement for solving a set of linear algebraic equation at each step can be avoided in Broyden's method if we choose instead to update an approximation to the inverse Jacobian. Taking $\mathbf{B} = \mathbf{A}^{-1}$, we obtain the iteration

$$\Delta^{(k)} = -\mathbf{B}^{(k)} \mathbf{f}^{(k)}, \quad \mathbf{x}^{(k+1)} = \mathbf{x}^{(k)} + \Delta^{(k)} \quad (27)$$

where the update formula for \mathbf{B} is

$$\mathbf{B}^{(k+1)} = \left(\mathbf{B} + \frac{(\Delta - \mathbf{B} \mathbf{y}) \Delta^T \mathbf{B}}{\Delta^T \mathbf{B} \mathbf{y}} \right)^{(k)} \quad (28)$$

The essential advantage of Quasi-Newton methods relative to the Newton-Raphson method is as mentioned that explicit evaluation of the Jacobian matrix is avoided. In addition, the number of algebraic operations required for the calculation of the correction is reduced from $O(N^3)$ to $O(N^2)$ when the inverse update is used. This may be of importance when N is large. The price paid is that the rate of convergence is reduced from second order to superlinear. Furthermore, convergence of \mathbf{x} does not in general imply that \mathbf{A} also converges to the Jacobian matrix J , and hence sensitivities are not readily available. Finally, as the Quasi-Newton methods use all earlier information in constructing \mathbf{A} there is a danger that retained information from 'unlucky' early steps may have an adverse effect on convergence. The initial \mathbf{A} -matrix is usually selected as the Jacobian at the starting point, or as an approximation to the Jacobian at the starting point. Broyden's method therefore is particularly convenient to apply in problems where successive substitution is convergent, since $\mathbf{A} = \mathbf{I}$ (or $\mathbf{B} = \mathbf{I}$) can be used as the initial estimate without the requirement for explicit evaluation of the Jacobian and, in the second case, explicit inversion of the matrix.

6 Unconstrained minimization

Frequently, the set of algebraic equations to be solved can be formulated as an optimization problem, i.e., the solution corresponds to an extremum of an objective function, $Q(\mathbf{x})$. In the following we shall assume that a minimum is desired (a maximum can be found by changing the sign of Q).

The necessary condition for \mathbf{x}^* representing a minimum of Q is that the gradient vector equals 0

$$\mathbf{g}(\mathbf{x}^*) = \left(\frac{\partial Q}{\partial \mathbf{x}} \right)_{\mathbf{x}^*} = 0 \quad (29)$$

Any point that satisfies eqn. (29) is called a *stationary point* of Q . A sufficient condition for a stationary point \mathbf{x}^* being a minimum is that the *Hessian*

matrix $\mathbf{H}(\mathbf{x}^*)$, where

$$H_{ij} = \frac{\partial g_i}{\partial x_j} \quad (30)$$

must be positive definite. The Hessian matrix, which from its definition is symmetric, hence corresponds to the Jacobian for the corresponding set of algebraic equations, eqn. (29).

The essential difference between solving a general set of algebraic equations and determining a local minimum is that for minimization problems procedures can be constructed which guarantee *global convergence*, i.e. convergence from arbitrary initial estimates. Global convergence should not be confused with convergence to a *global minimum*, which in general is an intractable task. To enforce global convergence we apply iterations of the type

$$\mathbf{A}^{(k)} \Delta^{(k)} + \mathbf{g}^{(k)} = \mathbf{0}, \quad \mathbf{x}^{(k+1)} = \mathbf{x}^{(k)} + \alpha \Delta^{(k)} \quad (31)$$

where the step length $\alpha (> 0)$ is chosen such that $Q(\mathbf{x}^{(k+1)}) < Q(\mathbf{x}^{(k)})$. A method with this property is called a *descent method*, and its implementation requires that $\mathbf{A}^{(k)}$ is selected in a manner that makes Δ a *descent direction*. Except for the case where $\mathbf{x}^{(k)}$ is a saddle point the solution for Δ of eqn. (31) is a descent direction provided \mathbf{A} is a positive definite matrix, and one of the simplest minimization methods, the method of steepest descent, takes $\mathbf{A} = \mathbf{I}$ at all steps. Unfortunately, convergence is only linear and frequently very slow.

In *Newton's method*, which is quadratically convergent, we take $\mathbf{A}^{(k)} = \mathbf{H}^{(k)}$. Complications arise when \mathbf{H} is not positive definite at all steps, and modifications of the method are required. In these modifications one usually uses $\mathbf{A} = \mathbf{H} + \mathbf{D}$, where \mathbf{D} is a diagonal matrix with non-negative elements selected such that \mathbf{A} becomes positive definite.

In the *method of Murray* (Fletcher, 1981) the modification of \mathbf{A} (if required) is performed during the factorization of \mathbf{A} , whereas *restricted step methods* preselect a maximum size of the correction vector and increases the magnitude of \mathbf{D} if this step size is exceeded or if the expected reduction in the objective function for the given step is not obtained. When the minimum is approached, these modifications revert to the full step ($\alpha = 1$) Newton method, and second order convergence is preserved.

When a phase equilibrium calculation can be formulated as a minimization problem, it is highly recommended to solve the problem using minimization methods. The same thermodynamic properties are required as for the equation solving approach, and the fact that a minimum is desired provides us with the ability to recover from inadequate initial estimates at no extra

cost. One additional advantage is that solving for the correction vector is only half as expensive when the matrix of coefficients is symmetric.

Quasi-Newton methods for minimization evaluate \mathbf{A} recursively as an approximation to the Hessian matrix. It is advantageous to choose an update formula with the property of *hereditary positive definiteness*, i.e. a formula with the property that a positive definite $\mathbf{A}^{(k)}$ yields a positive definite $\mathbf{A}^{(k+1)}$. A variety of update procedures have been suggested, and the so-called *BFGS-formula* currently appears to be superior. For the inverse Hessian, this update formula is

$$\mathbf{B}^{(k+1)} = \left(\mathbf{B} + \left(1 - \frac{\mathbf{y}^T \mathbf{B} \mathbf{y}}{\mathbf{y}^T \Delta} \right) \frac{\Delta \Delta^T}{\mathbf{y}^T \Delta} - \frac{\Delta \mathbf{y}^T \mathbf{B} + \mathbf{B} \mathbf{y} \Delta^T}{\mathbf{y}^T \Delta} \right)^{(k)} \quad (32)$$

The update formula for the BFGS-method is of rank 2, whereas the Broyden update for algebraic equations is only of rank one. We may therefore expect that the approximation to the Hessian will be better than the corresponding approximation to the Jacobian.

The solution of a general set of algebraic equations can be reformulated as a minimization problem with the objective function $Q(\mathbf{x}) = \mathbf{f}^T \mathbf{f} = \|\mathbf{f}\|^2$. The gradient vector and the Hessian for this objective function becomes

$$\frac{\partial Q}{\partial \mathbf{x}} = 2\mathbf{J}^T \mathbf{f}, \quad \mathbf{H} = 2\mathbf{J}^T \mathbf{J} + 2 \sum_i f_i \mathbf{G}_i \quad (33)$$

where

$$(\mathbf{G}_i)_{jk} = \frac{\partial^2 f_i}{\partial x_j \partial x_k}$$

The last term on the RHS is proportional to the norm of \mathbf{f} and can therefore be neglected, and Newton's method in the form

$$(\mathbf{J}^T \mathbf{J})^{(k)} \Delta^{(k)} + (\mathbf{J}^{(k)})^T \mathbf{f}^{(k)} = 0, \quad \mathbf{x}^{(k+1)} = \mathbf{x}^{(k)} + \alpha \Delta^{(k)} \quad (34)$$

will be quadratically convergent. Unfortunately, there is no guarantee that $\mathbf{f} = 0$ at a minimum of Q , and furthermore the Jacobian is required for the calculation of the gradient vector. Finally the effort in forming the product $\mathbf{J}^T \mathbf{J}$ exceeds the savings associated with symmetry and may in addition create round-off problems. The use of a minimization method for solving algebraic equations may offer advantages in some cases, but its success is likely to depend on a suitable scaling of the equations and the variables.

7 Constrained minimization

We shall frequently encounter minimization problems of the form: Minimise $Q(\mathbf{x})$, subject to the k equality constraints

$$c_j(\mathbf{x}) = 0, \quad j = 1, 2, \dots, k \quad (35)$$

and the m inequality constraints

$$c_j(\mathbf{x}) \geq 0, \quad j = k+1, k+2, \dots, k+m \quad (36)$$

A typical equality constraint could be that the sum of mole fractions in a phase must equal one, or that the sum of moles for each component in the different phases must equal that in the feed. Inequality constraints could specify that total moles in each phase must be positive or zero. We shall here mostly be concerned with *linear constraints*, i.e. constraints of the form $c(\mathbf{x}) = \sum_j a_j x_j - b$.

For the solution of constrained minimization problems it is advantageous to introduce an additional set of variables, the so-called *Lagrange multipliers* λ , with one element for each constraint. In addition we introduce the *Lagrange function*, defined by

$$\mathcal{L}(\mathbf{x}, \lambda) = Q(\mathbf{x}) - \sum_i \lambda_i c_i \quad (37)$$

When only equality constraints are present, it can be shown that the minimiser \mathbf{x}^* is a stationary point of the Lagrange function, i.e., the solution must satisfy

$$\begin{aligned} \frac{\partial \mathcal{L}}{\partial x_i} &= 0, \quad i = 1, 2, \dots, N \\ \frac{\partial \mathcal{L}}{\partial \lambda_j} &= 0, \quad j = 1, 2, \dots, k \end{aligned} \quad (38)$$

When inequality constraints are present, the corresponding conditions are

$$\begin{aligned} \frac{\partial \mathcal{L}}{\partial x_i} &= 0, \quad i = 1, 2, \dots, N \\ \frac{\partial \mathcal{L}}{\partial \lambda_j} &= 0, \quad j = 1, 2, \dots, k \\ c_j(\mathbf{x}) &\geq 0, \quad j = k+1, k+2, \dots, k+m \\ \lambda_j &\geq 0, \quad j = k+1, k+2, \dots, k+m \\ \lambda_j c_j(\mathbf{x}) &= 0, \quad j = k+1, k+2, \dots, k+m \end{aligned} \quad (39)$$

that is, for inequality constraints, either the equality sign in the constraint must hold and the corresponding Lagrange multiplier must be non-negative, or the Lagrange multiplier must be zero and c positive. Inequality constraints which satisfy the first condition are called *active* and those that satisfy the second, *inactive*. The Lagrange multipliers are a measure of the sensitivity of the objective function to changes in the corresponding constraints. For a linear constraint, $c_1 = \sum_i a_{i1}x_i - b_1$, the Lagrange multiplier λ_1 equals $\partial Q_{\min}/\partial b_1$.

The solution procedures for constrained minimization are more complex than those for unconstrained minimization. When only linear equality constraints are present, it is often advantageous to utilise the constraints to solve for k of the independent variables in terms of the $N - k$ remaining, resulting in an unconstrained minimization problem with $N - k$ independent variables.

8 Eigenvalues and Eigenvectors

The *eigenvalues* λ_1 and the corresponding normalised *eigenvectors* \mathbf{u}_1 of a real matrix \mathbf{B} are the solutions to the set of equations

$$\mathbf{B}\mathbf{u} = \lambda\mathbf{u}, \quad \mathbf{u}^T\mathbf{u} = 1 \quad (40)$$

In general the $N \times N$ matrix \mathbf{B} will have N different eigenvalues with corresponding eigenvectors, and these may be real or complex. For symmetric matrices all eigenvalues are real and the eigenvectors are orthogonal, $\mathbf{u}_i^T\mathbf{u}_j = 0$ for $i \neq j$, and if the symmetric matrix is positive definite, all the eigenvalues are positive. Very efficient general purpose methods for determining the complete set of eigenvalues and eigenvectors are available as subprogram libraries, e.g. the *QR*-algorithm (Wilkinson, 1965). We shall, however, only be interested in special methods for determining selected eigenvalues, typically the eigenvalue of smallest or of largest magnitude, and the corresponding eigenvectors.

A simple method for determining the numerically largest eigenvalue of \mathbf{B} is the *power method* (Wilkinson, 1965, Chapter IX). We select an initial estimate of the eigenvector, $\mathbf{x}^{(0)}$ and calculate subsequent estimates from

$$\mathbf{x}^{(k+1)} = \mathbf{B}\mathbf{x}^{(k)} \quad (41)$$

For large k we obtain

$$\mathbf{u} = \frac{\mathbf{x}^{(k+1)}}{\|\mathbf{x}^{(k+1)}\|}, \quad \lambda = \frac{(\mathbf{x}^{(k+1)})^T\mathbf{x}^{(k)}}{(\mathbf{x}^{(k)})^T\mathbf{x}^{(k)}} \quad (42)$$

which can be seen as follows: $\mathbf{x}^{(0)}$ can be expanded on the eigenvectors \mathbf{u}_i of \mathbf{B} ,

$$\mathbf{x}^{(0)} = \sum_i \alpha_i \mathbf{u}_i \quad (43)$$

Then $\mathbf{x}^{(1)} = \mathbf{B} \mathbf{x}^{(0)} = \sum_i \alpha_i \mathbf{B} \mathbf{u}_i = \sum_i \alpha_i \lambda_i \mathbf{u}_i$, and similarly,

$$\mathbf{x}^{(k)} = \sum_i \alpha_i \lambda_i^k \mathbf{u}_i \quad (44)$$

If we arrange the eigenvalues after magnitude in descending order, the first term will eventually dominate (assuming that α_1 is non-zero), i.e.

$$\mathbf{x}^{(k)} \approx \alpha_1 \lambda_1^k \mathbf{u}_1 \quad (45)$$

from which eqn. (37) follows. The power method is linearly convergent with a rate determined by the ratio $|\lambda_2|/|\lambda_1|$. When this ratio is small, i.e. when there is good separation between the two eigenvalues, convergence is rapid. To avoid overflow or underflow, it is recommendable to normalise the \mathbf{x} -vectors between iterations, i.e.,

$$\mathbf{y} = \mathbf{B} \mathbf{x}^{(k)}, \quad \mathbf{x}^{(k+1)} = \mathbf{y}/\|\mathbf{y}\| \quad (46)$$

The iteration vectors are now normalised and the eigenvalue is simply determined from

$$\lambda_1 \approx \mathbf{y}^T \mathbf{x}^{(k)} \quad \text{for } k \text{ large} \quad (47)$$

If desired, Broyden's method or the GDEM-method can be used to increase the rate of convergence.

The power method can also be used to obtain the numerically smallest eigenvalue λ_N if we replace \mathbf{B} by its inverse. This process, which is called *inverse iteration* is described by the following equations

$$\mathbf{B} \mathbf{y} = \mathbf{x}^{(k)}, \quad \mathbf{x}^{(k+1)} = \mathbf{y}/\|\mathbf{y}\| \quad (48)$$

The cost of inverse iteration exceeds that of the power method since the initial decomposition of \mathbf{B} is required. The subsequent iterations are, however, no more expensive than those of the power method.

References

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