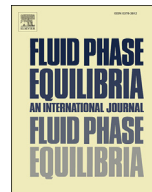




Contents lists available at ScienceDirect

## Fluid Phase Equilibria

journal homepage: [www.elsevier.com/locate/fluid](http://www.elsevier.com/locate/fluid)

## Differential equations for the calculation of fluid phase equilibria

Ulrich K. Deiters

Institute of Physical Chemistry, University of Cologne, Luxemburger Str. 116, D-50939 Köln, Germany

## ARTICLE INFO

## Article history:

Received 9 March 2016

Received in revised form

13 April 2016

Accepted 14 April 2016

Available online xxx

## Keywords:

Fluid phase equilibria

Gibbs–Konovalov equations

Algorithm

Multicomponent mixtures

## ABSTRACT

The thermodynamic conditions for isothermal or isobaric two-phase boundaries of fluid mixtures are expressed as sets of first-order ordinary differential equations. In contrast to the Gibbs–Konovalov equations, the new equations use molar densities instead of mole fractions. The resulting formalism is applicable to multicomponent mixtures, well-suited for machine calculations, and allows a very rapid calculation of phase diagrams.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

In 1881, 125 years ago, D. Konovalov proved that, in phase diagrams of binary mixtures, azeotropes lie at extrema of the phase boundary curves [1,2].<sup>1</sup> Gibbs extended Konovalov's proof to multicomponent mixtures and derived sets of differential equations for two-phase equilibria, which later became known as "coexistence equations" or Gibbs–Konovalov equations [3]. The equations for isothermal phase boundaries of a binary mixture are given here as an example [4,5]:

$$\frac{dp}{dx_1'} = -\frac{x_1'' - x_1'}{x_2' [x_1'' (V_1' - V_1'') + x_2'' (V_2' - V_2'')] } \left( \frac{\partial \mu_1'}{\partial x_1} \right) \quad (1)$$

$$\frac{dp}{dx_1''} = -\frac{x_1' - x_1''}{x_2'' [x_1' (V_1' - V_1'') + x_2' (V_2' - V_2'')] } \left( \frac{\partial \mu_1''}{\partial x_1} \right) \quad (2)$$

Here  $p$  denotes the pressure,  $x_i^\alpha$  the mole fraction,  $V_i^\alpha$  the partial molar volume, and  $\mu_i^\alpha$  the chemical potential of component  $i$  in the phase  $\alpha = ', ''$ . Analogous equations exist for isobaric phase equilibria or for phase boundaries at fixed composition (isopleths).

The textbook of Haase (1956) [6] contains a stringent formulation of Gibbs–Konovalov equations for multicomponent mixtures

<sup>1</sup> E-mail address: [ulrich.deiters@uni-koeln.de](mailto:ulrich.deiters@uni-koeln.de).

<sup>1</sup> These publications appeared in a German journal, hence his name was transliterated there as "Konowalow".

<http://dx.doi.org/10.1016/j.fluid.2016.04.014>

0378-3812/© 2016 Elsevier B.V. All rights reserved.

with the use of determinants.

Nowadays, however, these equations seem to be missing from most textbooks of thermodynamics, at least in the field of fluid thermodynamics. They do appear, although seldom, in journal articles; examples are the works of Goodman et al. [7], who discuss features of metallurgical phase diagrams, of Deiters [8] on double retrograde behavior, or of Serafimov et al. [9] on azeotropy in multicomponent mixtures. In these publications, however, the Gibbs–Konovalov equations are merely used for proving thermodynamic theorems, but not for the calculation of phase diagrams.

Why is this so? There are several reasons:

- The Gibbs–Konovalov equations have complicated structures and can be solved—except for a few special cases—numerically only. At the end of the 19th Century, before the advent of electronic computing devices, solving these equations was impractical. Therefore thermodynamicists of the early 20th Century preferred using Raoult's law and its extensions (activity/fugacity coefficient models) for the calculation of vapor–liquid phase equilibria. When electronic computers became available around 1960, the Gibbs–Konovalov equations were remembered at best as parts of mathematical proofs, but not as practical computational methods.
- The Gibbs–Konovalov equations constitute systems of nonlinear first-order ordinary differential equations—and for the integration of such equations, an initial state must be known. For vapor–liquid equilibria of mixtures, the vapor–liquid equilibria of the pure components are natural starting points.

Liquid–liquid equilibria, however, do not occur in pure fluids, and therefore they cannot be treated as initial-value problems.

Alternatively, it might be possible to formulate the conditions of phase equilibrium as a set of *partial* differential equations. But because of the required mathematical effort and the topological complexity of phase envelopes, this approach has, to our knowledge, never been pursued.

- Moreover, the partial molar volumes and the chemical potentials in Eqs. (1) and (2) are functions of composition, pressure, and temperature; they need to be recalculated at every step of the integration of the differential equation, and this usually necessitates the calculation of the density—which means solving a nonlinear equation within the integration algorithm. This would not only slow down the computation, but might also affect its numerical stability.

Because of these points, calculations of fluid phase equilibria have usually been performed with methods based on algebraic equations since more than 100 years.

Traditionally, such methods use the Gibbs or Helmholtz energy as central thermodynamic potential, and mole fractions and pressure or molar volume, respectively, as thermodynamic coordinates. It could be shown recently, however, that the use of the Helmholtz energy density  $\Psi \equiv A/V$  as central thermodynamic potential and densities  $\rho_i \equiv n_i/V$  ( $n_i$ : amount of substance of component  $i$ ) offers several advantages [10].

Therefore it seems worthwhile to revisit the Gibbs–Konovalov equations and to rewrite them in terms of density coordinates.

## 2. Theory

### 2.1. The Gibbs–Konovalov equations

For the readers' convenience, we briefly report the isothermal Gibbs–Konovalov equations for  $N$ -component mixtures ( $N \geq 2$ ).

Starting point is the observation that the total differential of the chemical potential  $\mu_j(p, T, \mathbf{x})$  of a component  $j$  as a function of the pressure  $p$ , the temperature  $T$ , and the vector of mole fractions  $\mathbf{x}$  can be written as

$$d\mu_j = -S_j dT + V_j dp + \sum_{i=1}^{N-1} \left( \frac{\partial \mu_j}{\partial x_i} \right) dx_i. \tag{3}$$

$S_j$  and  $V_j$  are the partial molar entropy and partial molar volume, respectively, of component  $j$ ,

$$S_j \equiv \left( \frac{\partial S}{\partial n_j} \right)_{p, T, n_{i \neq j}} \tag{4}$$

$$V_j \equiv \left( \frac{\partial V}{\partial n_j} \right)_{p, T, n_{i \neq j}},$$

where  $n_j$  denotes the amount of substance of component  $j$ .

Along the coexistence curve of two phases, denoted here as ' and ', the changes of the chemical potentials must be equal,

$$d\mu_j^{\prime} = d\mu_j^{\prime\prime}, \quad j = 1, \dots, N. \tag{5}$$

Substituting Eq. (3) and sorting the terms leads to

$$\sum_{i=1}^{N-1} \left( \frac{\partial \mu_j^{\prime}}{\partial x_i} \right) dx_i^{\prime} - \sum_{i=1}^{N-1} \left( \frac{\partial \mu_j^{\prime\prime}}{\partial x_i} \right) dx_i^{\prime\prime} = (S_j^{\prime} - S_j^{\prime\prime}) dT - (V_j^{\prime} - V_j^{\prime\prime}) dp, \quad j = 1, \dots, N. \tag{6}$$

For an isothermal phase diagram,  $dT = 0$ , and therefore Eq. (3), after division by  $dp$ , represents a set of linear equations in the derivatives  $dx_i^{\prime}/dp$  and  $dx_i^{\prime\prime}/dp$ . Lengthy, but straightforward algebra and application of the Gibbs–Duhem equation (see Appendix A) lead to

$$\sum_{i=1}^{N-1} \left[ \sum_{j=1}^{N-1} \left( x_j^{\prime\prime} - \frac{x_N^{\prime\prime} x_j^{\prime}}{x_N^{\prime}} \right) \left( \frac{\partial \mu_j^{\prime}}{\partial x_i} \right) \right] \frac{dx_i^{\prime}}{dp} = - \sum_{j=1}^N x_j^{\prime\prime} (V_j^{\prime} - V_j^{\prime\prime}) \tag{7}$$

and a second equation in which the phases are switched.

For a binary mixture—but only here—the sums on the left hand side have merely one term. Furthermore,

$$x_1^{\prime\prime} - \frac{x_2^{\prime\prime} x_1^{\prime}}{x_2^{\prime}} = \frac{x_1^{\prime} - x_1^{\prime\prime}}{x_2^{\prime}}, \tag{8}$$

and thus the first of the Gibbs–Konovalov equations, Eq. (1), is recovered. Eq. (2) is obtained in a similar fashion.

The Gibbs–Konovalov equations for an *isobaric* equilibrium curve would be obtained by setting  $dp = 0$  instead of  $dT$  in Eq. (6).

In the general multicomponent case, Eq. (7) provides one equation for  $dx^{\prime}/dp$  only. But this is sufficient: According to Gibbs' phase rule, for an isothermal  $N$ -component two-phase system,  $N-2$  mole fractions can be set to fixed values. For a ternary mixture, for example, one might set  $x_2^{\prime}$  to a constant value by specifying  $dx_2^{\prime}/dp = 0$ , use Eq. (7) to determine  $dx_1^{\prime}/dp$ , and then Eq. (6) to determine the  $dx_1^{\prime\prime}/dp$  and  $dx_2^{\prime\prime}/dp$ . Thus all relevant derivatives would be known, and the equilibrium curve could be determined by integrating the resulting system of differential equations.

This approach, however, would require the calculation of *all* partial molar volumes at every step. As these are volume derivatives at constant pressure, but equations of state for fluids are usually functions of density, the numerical effort for the computation of the partial molar volumes would be rather significant.

### 2.2. Density-based formulation

The central thermodynamic potential in the density-based formulation of thermodynamics [10] is the Helmholtz energy density  $\Psi$ ,

$$\Psi \equiv \frac{A}{V}, \tag{9}$$

where  $A$  denotes the Helmholtz energy and  $V$  the total volume.  $\Psi$  has the temperature  $T$  and the densities  $\rho_i$  as its natural variables. The latter are defined by

$$\rho_i \equiv \frac{n_i}{V}. \tag{10}$$

As the  $n_i$  can be regarded as the independent variables and  $V$  as a constant, this approach is sometimes called "isochoric thermodynamics". The  $\rho_i$  are related to the mole fractions and the molar volume by

$$\rho_i = \frac{x_i}{V_m}, \quad \rho = \sum_{i=1}^N \rho_i = \frac{1}{V_m}, \quad x_i = \frac{\rho_i}{\rho}, \tag{11}$$

Download English Version:

<https://daneshyari.com/en/article/4768242>

Download Persian Version:

<https://daneshyari.com/article/4768242>

[Daneshyari.com](https://daneshyari.com)