

The need for mole fraction derivatives

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This document will demonstrate:

- The need for unconstrained mole fraction derivatives in MS diffusion problems
- The relation between constrained mole fraction derivatives, unconstrained mole fraction derivatives and mole number derivatives
- The fact that unconstrained mole fraction derivatives (the derivatives of a property with respect to x_i , in which $x_{j \neq i}$ are kept constant, i.e. all x are treated as independent variables) allow reconstruction of constrained mole fraction derivatives as well as mole number derivatives
- The fact that mole number derivatives do not allow reconstruction of any mole fraction derivatives.

We therefore reason that:

- Since unconstrained mole fraction derivatives allow for reconstruction of all other flavours of composition derivatives, these are the most versatile values
- Since most thermodynamic and physical property calculation routines are set up in terms of mole fractions, unconstrained mole fraction derivatives are straightforward to obtain in most cases
- Perturbation in the principle directions of the above mentioned equations, i.e. in the directions of independent x , allow for easy verification of the values obtained for the derivatives, provided that the calculation routine does not choose to conclude that it cannot calculate a property if the sum of x is not unity
- In systems of equations where x are treated as independent variables, the proper derivatives of the equations towards x require the unconstrained mole fraction derivatives, without having to take into considerations constraints like having to be on the hyperplane of sum of x being unity (again provided that any calculation routine required for evaluation the equation does not choose to conclude that it cannot calculate its result when sum of x is not unity)

It is also important to notice that there is a desire for unconstrained mole fraction derivatives because these have traditionally been used in a number of simulation applications (for their availability and applicability). So not only would having support for these values in the thermodynamic CAPE OPEN version 1.1 standard allow these applications to readily exchange their values, it would also allow backward compatibility with the CAPE OPEN version 1.0 standard.

We therefore opt to adopt a definition of `.DmolFraction` as the unconstrained mole fraction derivative of properties using the following definition:

$$\left(\frac{\partial M}{\partial x_k} \right)_{x_{j \neq k}, T, P} = \frac{\partial M(x_1, \dots, x_N, T, P)}{\partial x_k} \quad (1)$$

MS DIFFUSION IN NONIDEAL FLUIDS – THE REQUIREMENT FOR MOLE FRACTION DERIVATIVES

The force acting on species i per unit volume of mixture tending to move the molecules of species i is $c_i RT \mathbf{d}_i$ where \mathbf{d}_i is related to the relative velocities, $(\mathbf{u}_i - \mathbf{u}_j)$, by

$$\mathbf{d}_i = \sum_{j=1}^n \frac{x_i x_j (\mathbf{u}_i - \mathbf{u}_j)}{D_{ij}} = \sum_{j=1}^n \frac{(x_i N_j - x_j N_i)}{c_i D_{ij}} \quad (2)$$

where D_{ij} is the Maxwell-Stefan diffusivity whose physical significance as an inverse drag coefficient is the same as in the ideal gas case. For non-ideal fluids \mathbf{d}_i , which can be considered to be a driving force, is defined by

$$\mathbf{d}_i \equiv \frac{x_i}{RT} \nabla_{T,P} \mu_i \quad (3)$$

The appearance of chemical potential gradients in these equations should not come as a surprise. Equilibrium is defined by equality of chemical potentials and departures from equilibrium are characterized by the presence of chemical potential gradients. Chemical potential gradients arise in the thermodynamics of irreversible processes as the fundamentally correct driving forces for diffusion. The subscripts T, P are to emphasize that the gradient in the equation is to be calculated under constant temperature, constant pressure conditions (pressure gradients and external forces also contribute to \mathbf{d}_i , but we shall ignore their influence). The driving force, \mathbf{d}_i , reduces to $(1/P) \nabla p_i$ for ideal gases, as it should. Also, the sum of the n driving forces vanishes

$$\sum_{i=1}^n \mathbf{d}_i = 0 \quad (4)$$

due to the Gibbs-Duhem restriction; this means that only $n-1$ driving forces are independent.

Chemical potential gradients are not the easiest of quantities to deal with. For non-ideal liquids we may express the driving force \mathbf{d}_i in terms of the mole fraction gradients as follows:

$$\begin{aligned}
\mathbf{d}_i &= \frac{x_i}{RT} \nabla_{T,p} \mu_i \\
&= \frac{x_i}{RT} \sum_{j=1}^{n-1} \left. \frac{\partial \mu_i}{\partial x_j} \right|_{T,P,\Sigma} \nabla x_j \\
&= \frac{x_i}{RT} \sum_{j=1}^{n-1} RT \left. \frac{\partial \ln \gamma_i x_i}{\partial x_j} \right|_{T,P,\Sigma} \nabla x_j \\
&= x_i \sum_{j=1}^{n-1} \left(\left. \frac{\partial \ln x_i}{\partial x_j} + \frac{\partial \ln \gamma_i}{\partial x_j} \right|_{T,P,\Sigma} \right) \nabla x_j \\
&= \sum_{j=1}^{n-1} \left(\delta_{ij} + x_i \left. \frac{\partial \ln \gamma_i}{\partial x_j} \right|_{T,P,\Sigma} \right) \nabla x_j \\
&= \sum_{j=1}^{n-1} \Gamma_{ij} \nabla x_j
\end{aligned} \tag{5}$$

where γ_i is the activity coefficient of species i in the mixture and where

$$\Gamma_{ij} = \delta_{ij} + x_i \left. \frac{\partial \ln \gamma_i}{\partial x_j} \right|_{T,P,\Sigma} \tag{6}$$

The symbol Σ is used to indicate that the differentiation of $\ln \gamma_i$ with respect to mole fraction x_j is to be carried out while keeping constant the mole fractions of all other species except the n -th. The mole fraction of species n must be eliminated using the fact that the x_i sum to unity. More specifically:

$$\left. \frac{\partial \ln \gamma_i}{\partial x_j} \right|_{T,P,\Sigma} = \left. \frac{\partial \ln \gamma_i}{\partial x_j} \right|_{T,P,x_k, k \neq j=1 \dots n-1} \tag{7}$$

This matches the definition of constrained mole fraction derivatives (equation 16)

For dense gas mixtures exhibiting deviations from ideal gas behavior the above formulation can be used with the activity coefficient, γ_i , replaced by the fugacity coefficient, ϕ_i :

$$\Gamma_{ij} \equiv \delta_{ij} + x_i \left. \frac{\partial \ln \phi_i}{\partial x_j} \right|_{T,P,\Sigma} \tag{8}$$

An equation of state needs to be used for calculation of the molar density, c_i and the derivatives of the fugacity coefficients (see, for example, Walas, S. Phase Equilibria in Chemical Engineering, Butterworth, 1985)

Mole number and unconstrained mole fraction differentials

If we treat all mole fractions as independent variables, we obtain for the differentials

$$dn_i = d(n x_i) = n dx_i + x_i dn \quad (9)$$

$$dn_i - x_i \sum_j dn_j = n dx_i \quad (10)$$

or

$$dx_i = \frac{1}{n} \sum_j (\delta_{ij} - x_i) dn_j \quad (11)$$

A comparison with the total differential, $dx_i = \sum_j \left(\frac{\partial x_i}{\partial n_j} \right) dn_j$, yields

$$\left(\frac{\partial x_i}{\partial n_j} \right)_{n_{k \neq j}} = \frac{1}{n} (\delta_{ij} - x_i) \quad (12)$$

This follows also immediately from the definition $x_i = \frac{n_i}{\sum_j n_j}$ by differentiation.

We also can write the differentials in matrix notation.

$$d\bar{x} = \frac{1}{n} \left[\frac{\partial \bar{x}}{\partial \bar{n}} \right] d\bar{n} \quad (13)$$

It can be shown that the determinant of Jacobean is given by

$$\det \left[\frac{\partial \bar{x}}{\partial \bar{n}} \right] = 1 - \sum_i x_i \quad (14)$$

Hence, the matrix $\left[\frac{\partial \bar{x}}{\partial \bar{n}} \right]$ is singular on the manifold $1 = \sum_i x_i$

Definition of unconstrained mole fraction derivatives $\left(\frac{\partial M}{\partial x_k} \right)_{x_{j \neq k}}$

$$\left(\frac{\partial M}{\partial x_k} \right)_{x_{j \neq k}} = \frac{\partial M(x_1, \dots, x_N)}{\partial x_k} \quad (15)$$

We assume that all mole fractions are independent. Hence, we keep N-1 mole fractions constant when differentiating. These derivatives are a mathematical construction and do not have a physical meaning. Moreover, the derivatives depend on the implementation of M in a property package, and so might not be unique for all property packages.

Definition of constrained mole fraction derivatives $\left(\frac{\partial M}{\partial x_k}\right)_{T,p,x_{j \neq i,k}}$

$$\left(\frac{\partial M}{\partial x_k}\right)_{x_{j \neq i,k}} = \frac{\partial M(x_1, \dots, x_{i-1}, 1 - \sum_{j \neq i} x_j, x_{i+1}, \dots, x_N)}{\partial x_k} \quad (16)$$

One of the mole fractions is substituted by the summation equation. Therefore, N-2 mole fractions are kept constant when differentiating.

Relation between constrained and unconstrained derivatives

The total differentials for constrained and unconstrained derivatives are given by:

$$dM(x_1, \dots, x_N) = \sum_k \left(\frac{\partial M}{\partial x_k}\right)_{x_{j \neq k}} dx_k \quad (17)$$

$$dM(x_1, \dots, x_{i-1}, x_{i+1}, \dots, x_N) = \sum_{k \neq i} \left(\frac{\partial M}{\partial x_k}\right)_{T,p,x_{j \neq k,i}} dx_k \quad \text{with } x_i = 1 - \sum_{j \neq i} x_j \quad (18)$$

For constrained derivatives we know that N-2 mole fractions are kept constant ($dx_l = 0$ for $l \neq k, i$). The differentials for the varying components are related by $dx_k = -dx_i$. Hence, comparing equation (3) and (4) yields

$$\left(\frac{\partial M}{\partial x_k}\right)_{T,p,x_{j \neq k,i}} = \left(\frac{\partial M}{\partial x_k}\right)_{T,p,x_{j \neq k}} - \left(\frac{\partial M}{\partial x_i}\right)_{T,p,x_{j \neq i}} \quad (19)$$

Relation between mole number derivatives and mole fraction derivatives

The mole number derivatives are defined by

$$\left(\frac{\partial M}{\partial n_i}\right)_{n_{k \neq i}} = \sum_i \left(\frac{\partial M}{\partial x_i}\right)_{x_{k \neq i}} \left(\frac{\partial x_i}{\partial n_j}\right)_{n_{k \neq j}} \quad (20)$$

Using equation (1) yields

$$\left(\frac{\partial M}{\partial n_j}\right)_{n_{k \neq i}} = \sum_i \left(\frac{\partial M}{\partial x_i}\right)_{x_{k \neq i}} \frac{1}{n} (\delta_{ij} - x_i) \quad (21)$$

or

$$\begin{aligned} \left(\frac{\partial M}{\partial n_j} \right)_{n_{k \neq i}} &= \frac{1}{n} \left(\left(\frac{\partial M}{\partial x_j} \right)_{x_{k \neq j}} - \sum_i x_i \left(\frac{\partial M}{\partial x_i} \right)_{x_{k \neq i}} \right) \\ &= \frac{1}{n} \left(\sum_{i \neq j} x_i \left(\frac{\partial M}{\partial x_j} \right)_{x_{k \neq j}} - \left(\frac{\partial M}{\partial x_i} \right)_{x_{k \neq i}} \right) \end{aligned} \quad (22)$$

In terms of constrained derivatives we obtain

$$\left(\frac{\partial M}{\partial n_j} \right)_{n_{k \neq i}} = -\frac{1}{n} \sum_{i \neq j} x_i \left(\frac{\partial M}{\partial x_i} \right)_{x_{k \neq i, j}} \quad (23)$$

Equation (6) can also be written in matrix form

$$\left(\frac{\partial M}{\partial \bar{n}} \right)^T = \left(\frac{\partial M}{\partial \bar{x}} \right)^T \left[\frac{\partial \bar{x}}{\partial \bar{n}} \right] \quad (24)$$

Following the consideration in the first paragraph it should be clear that the Jacobean is singular on the hyperspace. Hence, it is not possible to express mole fraction derivatives with mole number derivatives.

Relation between partial molar derivatives and mole fraction derivatives

The partial derivatives are defined by

$$\left(\frac{\partial n M}{\partial n_i} \right)_{n_{j \neq i}} = M \underbrace{\left(\frac{\partial n}{\partial n_i} \right)_{n_{j \neq i}}}_{=1} + n \left(\frac{\partial M}{\partial n_i} \right)_{n_{j \neq i}} \quad (25)$$

Making use of equation (7) yields

$$\left(\frac{\partial n M}{\partial n_i} \right)_{n_{j \neq i}} = M - \sum_{j \neq i} x_j \left(\frac{\partial M}{\partial x_j} \right)_{x_{k \neq i, j}} \quad (26)$$

In matrix notation (using unconstrained derivatives) we obtain

$$\left(\frac{\partial n M}{\partial \bar{n}} \right)^T = M (I)^T + n \left(\frac{\partial M}{\partial \bar{x}} \right)^T \left[\frac{\partial \bar{x}}{\partial \bar{n}} \right] \quad (27)$$

where I is a unity vector. Again, it is not possible to express mole fraction derivatives with mole number derivatives since the Jacobean is singular.