

Memo

Apparent composition approach

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1 Introduction

Michelsen and Mollerup [2, Chap. 13, Sec. 7] describe the apparent composition approach in the context of chemical reactions. Maribo-Mogensen [1, App. C.3] uses this approach when modelling phase equilibrium for electrolyte system, using the salts as apparent composition.

The idea is to use a model with all species (\mathbf{n}) to model other species, the apparent species (\mathbf{e}). The relation between the apparent and real species are derived from the following,

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

and its differentials. We immediately see that the volume and temperature differentials are unaffected by the mole number representation.

Using salt (NaCl) to represent ions (Na^+, Cl^-) as an example, some additional differentials are required. The apparent mole vector will then be \mathbf{e} (salts) while the actual mole vector will be \mathbf{n} (ions). We then have,

$$F(T, V, \mathbf{n}) = F(T, V, \mathbf{e}), \quad (2)$$

$$F_i^{\text{APP}} = \left(\frac{\partial F}{\partial e_i} \right)_{T,V} = \sum_k \left(\frac{\partial F}{\partial n_k} \right)_{T,V} \left(\frac{\partial n_k}{\partial e_i} \right) = \sum_k v_{ik} \left(\frac{\partial F}{\partial n_k} \right)_{T,V}, \quad (3)$$

$$F_{ij}^{\text{APP}} = \sum_k v_{ik} \sum_m v_{jm} F_{ij}. \quad (4)$$

Here v_{ik} is the stoichiometric composition of ion j in salt i . For a system of NaCl, H₂O and CO₂, \mathbf{v} will look as follows,

$$\begin{array}{cccc} \text{H}_2\text{O} & \text{CO}_2 & \text{Na}^+ & \text{Cl}^- \\ \left[\begin{array}{cccc} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \end{array} \right] & \begin{array}{l} \text{H}_2\text{O} \\ \text{CO}_2 \\ \text{NaCl} \end{array} & & \end{array} \quad (5)$$

With this approach, no special handling of the charge balance in the phases are required when calculating phase equilibrium. Another advantage is equilibrium calculation of solid NaCl, as the solid fugacity only need to equate the fugacity of the fictitious dissolved salt component.

2 Thermodynamic differentials

If we consider the chemical potentials (enthalpy, entropy, Gibbs free energy, Helmholtz free energy or internal energy) as a function of the real or apparent composition, the value remains the same. IE. it is only the compositional differentials of the potentials that differ when introducing the apparent composition.

We therefore need to map only the fugacities, compressibility factor and their differentials.

2.1 Compressibility factor

For the compressibility factor, the following applies,

$$\frac{PV}{RT} = \sum_j e_j Z^{\text{APP}} = \sum_i n_i Z. \quad (6)$$

We therefore have

$$Z^{\text{APP}} = Z \frac{\sum_i n_i}{\sum_j e_j}. \quad (7)$$

The pressure and temperature differential must be scaled in the same manner for the apparent mode, while the compositional differentials are slightly more complicated.

2.2 Fugacity coefficients

$$\ln \left(x_{\text{NaCl}}^{\text{APP}} \varphi_{\text{NaCl}}^{\text{APP}} \right) = v_{\text{Na}^+} \ln (x_{\text{Na}^+} \varphi_{\text{Na}^+}) + v_{\text{Cl}^-} \ln (x_{\text{Cl}^-} \varphi_{\text{Cl}^-}) \quad (8)$$

Assuming we have one mole of water, and want to look at the infinite dilution value of $\ln \varphi_{\text{NaCl}}^{\text{App}}$. The mole number relation between NaCl and the ions Na^+ and Cl^- are one-to-one, giving,

$$\begin{aligned} \ln n_{\text{NaCl}} + \ln \varphi_{\text{NaCl}}^{\text{App}} - \ln(1 + n_{\text{NaCl}}) &= 2 \ln n_{\text{NaCl}} + \ln(\varphi_{\text{Na}^+} \varphi_{\text{Cl}^-}) - 2 \ln(1 + 2n_{\text{NaCl}}) \\ \ln \varphi_{\text{NaCl}}^{\text{App}} &= \ln n_{\text{NaCl}} + \ln(\varphi_{\text{Na}^+} \varphi_{\text{Cl}^-}) - 2 \ln(1 + 2n_{\text{NaCl}}) + \ln(1 + n_{\text{NaCl}}) \\ \lim_{n_{\text{NaCl}} \rightarrow 0} \ln \varphi_{\text{NaCl}}^{\text{App}} &= \lim_{n_{\text{NaCl}} \rightarrow 0} \ln(n_{\text{NaCl}} \varphi_{\text{Na}^+} \varphi_{\text{Cl}^-}) \rightarrow -\infty \end{aligned} \quad (9)$$

Since the fugacity depend on the composition, and the infinite dilution fugacity approaches an infinity value, this approach can be challenging to handle numerically.

2.2.1 Differentials

Additionally there is an effect of the difference in overall mole numbers, as $\sum_i n_i \neq \sum_i e_i$. See Maribo-Mogensen [1, App. C.3].

The equilibrium condition becomes,

$$\ln \left(\frac{x^{\text{App}} \varphi^{\text{App}} P}{P^0} \right) = \sum_j v_{ij} \ln \left(\frac{x_j \varphi_j P}{P^0} \right) \quad (10)$$

To describe the apparent fugacity coefficient, the relation become,

$$\ln \varphi_i^{\text{App}} = \sum_j v_{ij} \ln x_j \varphi_j - \ln x_i^{\text{App}} - \left(1 - \sum_j v_{ij} \right) \ln \frac{P}{P^0} \quad (11)$$

Differentiating with respect to temperature,

$$\frac{\partial \ln \varphi_i^{\text{App}}}{\partial T} = \sum_j v_{ij} \ln \frac{\partial \varphi_j}{\partial T}. \quad (12)$$

Differentiating with respect to pressure,

$$\frac{\partial \ln \varphi_i^{\text{App}}}{\partial P} = \sum_j v_{ij} \ln \frac{\partial \varphi_j}{\partial P} - \frac{1}{P} + \frac{\sum_j v_{ij}}{P}. \quad (13)$$

Differentiating with respect to mole numbers, using $\sum_i e_i = e_T$, $n_T = \sum_j \sum_i v_{ij} e_i = n_T$, and

$$\begin{aligned} x_j &= \frac{\sum_l v_{jl} e_l}{n_T} \\ \frac{\partial \ln x_j}{\partial e_k} &= \sum_l \left(\frac{\partial n_l}{\partial e_k} \right) \left(\frac{\partial \ln x_j}{\partial n_l} \right) = \sum_l v_{kl} \left(\frac{\partial \ln n_j}{\partial n_l} - \frac{\partial \ln n_T}{\partial n_l} \right) \\ &= \sum_l v_{kl} \left(\frac{\delta_{jl}}{n_l} - \frac{1}{n_T} \right) = \frac{v_{kj}}{n_j} - \frac{\sum_l v_{kl}}{n_T}, \end{aligned} \quad (14)$$

$$\quad (15)$$

$$\begin{aligned}
 \frac{\partial \ln \varphi_i^{\text{App}}}{\partial e_k} &= -\frac{\delta_{ik}}{e_k} + \frac{1}{e_T} + \sum_j v_{ij} \frac{\partial \ln \varphi_j}{\partial e_k} + \sum_j v_{ij} \frac{\partial \ln x_j}{\partial e_k} \\
 &= -\frac{\delta_{ik}}{e_k} + \frac{1}{e_T} + \sum_j v_{ij} \sum_l v_{kl} \frac{\partial \ln \varphi_j}{\partial n_l} + \sum_j v_{ij} \left(\frac{v_{kj}}{n_j} - \frac{\sum_l v_{kl}}{n_T} \right)
 \end{aligned} \quad (16)$$

2.3 Ideal properties

In order to calculate equilibrium between a salt (solid), and the apparent composition in the fluid phases, the ideal Gibbs free energy is required.

For the enthalpy we have,

$$h^{\text{Id}}(\mathbf{e}, T) = \sum_j e_j h_j^{\text{Id}}(T), \quad (17)$$

and for the entropy,

$$s^{\text{Id}}(\mathbf{e}, T, P) = \sum_j e_j \left(s_j^{\text{Id},*}(T) - R \ln \frac{e_j}{e_T} - R \ln P \right). \quad (18)$$

Here $s_j^{\text{Id},*}(T)$ simply is the temperature integral of $C_p(T)/T$.

The ideal Gibbs free energy is,

$$g^{\text{Id}}(\mathbf{e}, T, P) = h^{\text{Id}}(\mathbf{e}, T) - T s^{\text{Id}}(\mathbf{e}, T, P). \quad (19)$$

The ideal chemical potential therefore becomes,

$$\mu_i = \frac{\partial g^{\text{Id}}}{\partial e_i} = h_i^{\text{Id}} - T \left(s_i^{\text{Id},*} - R \ln \frac{e_i}{e_T} - R \ln P \right), \quad (20)$$

$$= h_i^{\text{Id}} - T s_i^{\text{Id},*} + RT \ln(x_i P). \quad (21)$$

Since the $\ln(x_i P)$ is accounted for in the fugacity coefficient, we only need to account for $h_i^{\text{Id}} - T s_i^{\text{Id},*}$.

References

- [1] B. Maribo-Mogensen. *Development of an Electrolyte CPA Equation of state for Applications in the Petroleum and Chemical Industries*. PhD thesis, Technical University of Denmark, 2014.
- [2] Michael L. Michelsen and Jørgen M. Møllerup. *Thermodynamic models: Fundamentals & computational aspects*. Tie-Line Publication, second edition, 2007.