

Short Communication

On the *Abraham Equation* for Salt Activities in Concentrated Solutions

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Summary. It is shown that the equations derived by *Voigt* and *Abraham* for the calculation of salt activities in concentrated solutions are equivalent and that they satisfy the *Gibbs-Duhem* equation.

Keywords. Activity coefficients; Aqueous electrolytes; *Gibbs-Duhem*, *Brunauer-Emmett-Teller* (BET), Adsorption isotherm.

Zur *Abraham*-Gleichung zur Berechnung der Aktivitäten von Salzen in konzentrierten Lösungen (Kurze Mitt.)

Zusammenfassung. Es wird gezeigt, daß die von *Voigt* und *Abraham* zur Berechnung der Aktivitäten von Salzen in konzentrierten Lösungen hergeleiteten Gleichungen äquivalent sind und die *Gibbs-Duhem*-Beziehung erfüllen.

Introduction

Voigt [1] has calculated phase equilibria in salt hydrate melts using an equation for the salt activity derived by *Gibbs-Duhem* integration of the water activity equation obtained from the *Stokes-Robinson-BET* model. *Voigt's* equation for the salt activity appears to differ in its form from that derived by *Abraham* [2] and used by *Ally* and *Braunstein* [3] for the evaluation of excess properties and phase equilibria, and is considerably more cumbersome to apply. *Voigt* states that “the assumptions introduced with the statistical treatment by *Abraham* are more restrictive than the *BET* model.”

In this paper, we demonstrate that the equations derived by *Abraham* and verified by us do – and in fact must – satisfy the *Gibbs-Duhem* equation and that *Voigt's* assertion to the contrary and his statement, quoted above, is incorrect. We show that the equation for the solute activity derived by *Abraham* is identical to the expression obtained by *Voigt* through *Gibbs-Duhem* integration of the water activity equation derived from the *Stokes-Robinson-BET* model. Although the expressions of *Abraham* and of *Voigt* appear different, we prove that they are equivalent. We exemplify this point by numerically calculating the activity of CaCl_2 using *Abraham's* and *Voigt's* equations, and demonstrate that they yield exactly the same

Table 1. Identical numerical value of activities of CaCl_2 in aqueous solutions at CaCl_2 in aqueous solutions at 450 K from *Abraham's* and *Voigt's* derivation of solute activities from the *BET* model

molality	Activity of CaCl_2 (a_s)		Water Activity (a_w)
	Abraham ^a (<i>BET</i> Model)	Voigt ^b (<i>BET</i> Model) (Reference [1], Eq. 14)	(<i>BET</i> Model)
10	6.334×10^{-4}	6.333×10^{-4}	0.4231
12	0.001810	0.001810	0.3438
14	0.004354	0.004354	0.2800
16	0.008974	0.008974	0.2304
18	0.016180	0.016180	0.1924
20	0.026120	0.026120	0.1634

^a Abraham, M., *Jornal de Chimie Physique* (1981), vol. 78, p. 57; ^b the *BET* parameters r and ε used to calculate the solute activities in the above Table were obtained from *Voigt's* paper [1]; it is pointed out that *Voigt's* expression for the parameter ε does not consider the data of *Stokes* and *Robinson* [8]

values (see Table 1). Although *Voigt's* paper is interesting, we show convincingly that there is no new information contained in his expression for the salt activity, and thus his claim of a “restriction” in *Abraham's* derivation is invalid.

Discussion

We first outline briefly the procedure used in the statistical thermodynamic treatment of the *Stokes-Robinson-BET* model. This treatment is analogous to that for a lattice model in which one mixes vacant and occupied (by water) sites and free and bound water. This provides the combinatorial factor or number of distributions, Ω [2, 4, 5]

$$\Omega = \frac{(rs)!}{x!(rs-x)!} \cdot \frac{h!}{x!(h-x)!} \quad (1)$$

in terms of the number of sorption sites provided by the salt (rs), and the number of free ($h-x$) and bound (x) water molecules; the energy is given by the number of sorbed water molecules (x) and a sorption energy (ε):

$$E = x\varepsilon \quad (2)$$

The most probable distribution is found in the usual way [6] by applying *Stirling's* approximation and the *Lagrange* undetermined multipliers to Eqs. 1 and 2. The statistical thermodynamic definition of the entropy $\mathcal{S} = k \ln \Omega$, where k is the *Boltzmann* constant, combined with the thermodynamic definition of the *Helmholz* energy, leads to the *Gibbs* free energy equation presented by *Abraham*. Differentiation of the free energy equation with respect to the mole numbers leads unequivocally to the chemical potentials of salt and of water, and to the activities of salt and of water as presented by *Abraham*.

From the form of the combinatorial factor as presented in Eq. 1 and the resulting free energy equation,

$$G/RT \simeq A/RT = rS \ln \left(\frac{rS - X}{rS} \right) + H \ln \frac{H - X}{H} \quad (3)$$

where G is the *Gibbs* free energy of adsorption, $S = (s/N)$ and $H = (h/N)$ ($N = Avogadro$'s number) are the numbers of moles of salt and water, respectively, r is the number of moles of sorption sites per mole of salt, and $X = (x/N)$ is the number of moles of sorbed water (sorbed with energy ε), it is evident that the free energy equation is a homogeneous function of first degree in the mole numbers of salt and water. Consequently, the chemical potentials must satisfy the *Gibbs-Duhem* Eq. [7]. Although no further proof should be needed, we verify the *Gibbs-Duhem* consistency below.

Differentiation of the free energy function yields the chemical potentials and activities:

$$\begin{aligned} \left(\frac{\partial G/RT}{\partial S} \right)_H = \mu_s/RT = \ln a_s = r \ln \left(\frac{rS - X}{rS} \right) \\ + \left(r \frac{X}{rS - X} - \left(\frac{\partial X}{\partial S} \right)_H \left(\frac{rS}{rS - X} + \frac{H}{H - X} \right) \right) \end{aligned} \quad (4)$$

$$\begin{aligned} \left(\frac{\partial G/RT}{\partial H} \right)_S = \mu_H/RT = \ln a_H = \ln \left(\frac{H - X}{H} \right) \\ + \left(\left(\frac{X}{H - X} \right) - \left(\frac{\partial X}{\partial H} \right)_S \left(\frac{rS}{rS - X} + \frac{H}{H - X} \right) \right) \end{aligned} \quad (5)$$

The partial derivatives of X can be eliminated by making use of the relation which maximizes the probability of the distribution in Eq. 1 subject to the condition of Eq. 2 and which was used in the derivation of Eq 2.

$$\ln \frac{X^2}{(rS - X)(H - X)} = \frac{-\varepsilon}{kT} = \frac{-N\varepsilon}{RT} = c \quad (6)$$

Differentiating Eq. 6 with respect to S and to H , multiplying by X and collecting terms yields

$$\frac{rX}{rS - X} = \left(\frac{\partial X}{\partial S} \right)_H \left(2 + \frac{X}{rS - X} + \frac{X}{H - X} \right) = \left(\frac{\partial X}{\partial S} \right)_H \left(\frac{rS}{rS - X} + \frac{H}{H - X} \right) \quad (7a)$$

$$\frac{rX}{rS - X} = \left(\frac{\partial X}{\partial H} \right)_S \left(2 + \frac{X}{rS - X} + \frac{X}{H - X} \right) = \left(\frac{\partial X}{\partial H} \right)_S \left(\frac{rS}{rS - X} + \frac{H}{H - X} \right) \quad (7b)$$

Hence, the bracketed terms for the chemical potentials, vanish in Eqs. 4 and 5 yielding

$$\ln a_s = r \ln \left(\frac{rS - X}{rS} \right); \quad a_s = \left(\frac{rS - X}{rS} \right)^r \quad (8a)$$

and

$$\ln a_{\text{H}} = \ln\left(\frac{H-X}{H}\right); \quad a_{\text{H}} = \left(\frac{H-X}{H}\right) \quad (8b)$$

The water activity is thus the fraction of unbound water, as postulated by *Stokes* and *Robinson*, and the salt activity is that published by *Abraham* and used by *Ally* and *Braunstein* [3] to derive the excess properties and phase equilibria.

Verification of *Gibbs-Duhem* consistency follows by differentiation of Eqs. 8a and 8b, yielding

$$\begin{aligned} S\left(\frac{\partial \ln a_{\text{s}}}{\partial S}\right)_{\text{H}} + H\left(\frac{\partial \ln a_{\text{H}}}{\partial S}\right)_{\text{H}} &= \frac{rX}{rX-X} - \left(\frac{\partial X}{\partial S}\right)_{\text{H}} \left(\frac{rS}{rS-X}\right) - \frac{H}{H-X} \left(\frac{\partial X}{\partial S}\right)_{\text{H}} \\ &= \left(\left(\frac{rX}{rS-X}\right) - \left(\frac{\partial X}{\partial S}\right)_{\text{H}} \left(\frac{rS}{rS-X} + \frac{H}{H-X}\right)\right) \quad (9) \end{aligned}$$

However, it was shown above that the right hand side of Eq. 9 vanishes (Eqs. 7a and 7b), thereby satisfying the *Gibbs-Duhem* relation and making the *Gibbs-Duhem* integration of *Voigt* redundant.

An analogous result is found for the partial derivatives with respect to H . Hence also

$$S\left(\frac{\partial \ln a_{\text{s}}}{\partial H}\right)_{\text{s}} + H\left(\frac{\partial \ln a_{\text{H}}}{\partial H}\right)_{\text{s}} = 0$$

and

$$Sd \ln a_{\text{s}} + Hd \ln a_{\text{H}} = 0$$

It should be understood that, regardless of other possible merits or deficiencies of a model, if its mathematical form provides a free energy function which is extensive and homogeneous in the mole numbers, its chemical potentials satisfy the *Gibbs-Duhem* relation automatically.

Finally, we need to resolve the discrepancy between the analytical expression for the salt activity derived from the *BET* model and that obtained by *Voigt* through *Gibbs-Duhem* integration by proving that they are the same. From the *BET* model, $a_{\text{s}} = ((rS-X)/rS)^f$ and from *Voigt's* integration of the *Gibbs-Duhem* equation, $a_{\text{s}} = ((1-a_{\text{H}})/(c-1)a_{\text{H}}+1)^f$. We now prove that the two expressions for a_{s} are indeed equivalent.

From Eq. 6

$$\begin{aligned} \frac{X^2}{(rS-X)(H-X)} &= e^{\beta\varepsilon} = c = \left(\frac{X}{rS-X}\right)\left(\frac{X}{H-X}\right) = \left(\frac{X-rS+rS}{rS-X}\right)\left(\frac{X-H+H}{H-X}\right) \\ &= \left(\frac{rS}{rS-X} - 1\right)\left(\frac{H}{H-X} - 1\right) \end{aligned}$$

Rearranging Eqs. 8a and 8b and combining with the above,

$$c = \left(\frac{1}{a_{\text{s}}^{1/f}} - 1\right)\left(\frac{1}{a_{\text{H}}} - 1\right)$$

$$c = \left(\frac{1}{a_s^{1/r}} - 1 \right) \left(\frac{1 - a_H}{a_H} \right)$$

$$\frac{1}{a_s^{1/r}} - 1 = \frac{ca_H}{1 - a_H}$$

$$\frac{1}{a_s^{1/r}} = 1 + \frac{ca_H}{1 - a_H} = \frac{1 - a_H + ca_H}{1 - a_H} = \frac{(c - 1)a_H + 1}{1 - a_H}$$

$$a_s = \left(\frac{1 - a_H}{(c - 1)a_H + 1} \right)^r$$

This is equivalent to *Voigt's* Eq. 14 and is a simple way to calculate a_s once a_H and c are evaluated.

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