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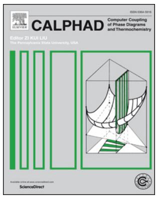

CALPHAD aqueous solution model based on the BET approach: General theory

Risto Pajarre*, Pertti Koukkari

VTT Technical Research Centre of Finland Ltd, Biologinkuja 7, P.O. Box 1000, FI-02044 VTT, Finland

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ABSTRACT

The Brunauer–Emmett–Teller (BET) model for adsorption has found extensive use in modelling of adsorption, surfaces and concentrated solutions. We present here a Gibbs energy minimiser based application of a BET and related GAB model, implemented using the ChemApp program library via ChemSheet. The basic model is constructed using solely ideal mixture phases. The use of a free energy minimiser readily enables various extensions, such as multicomponent adsorption and interactions between lattice sites. While the method presented is applicable to BET model problems in general, the emphasis in this work is on applications related to concentrated aqueous solutions.

1. Introduction

Most approaches to explaining the activity data of aqueous electrolytes include the extension of dilute solution models to moderate concentrations of the solute species. However, in highly concentrated solutions these extensions of the dilute solution models tend to be quite unsuccessful. Thus, it remains still a challenge to develop models for very concentrated solutions that would be further applicable in conjunction with an appropriate dilute solution model. The lack of both adequate property data and models for concentrated aqueous solutions hampers both the design of primary extraction processes for many metals and minerals, as well as the development of hydrometallurgical recycling technologies. In this context the Brunauer–Emmett–Teller (BET), and related models applicable to highly concentrated solutions, could be used to shed light on the general problem.

The BET model [1] was originally presented for the adsorption of gases on solids surfaces. Later Stokes and Robinson [2] proposed the use of the BET adsorption isotherm for representing the water activities of very concentrated salt solutions, and demonstrated its application to a series of pure electrolyte solutions. Since its introduction, the aqueous BET equation has been extended to common-ion mixtures with a number of proposed mixing rules [3–5], and expressions for salt activities have been determined [6–8]. By using a different assumption regarding the adsorption energy, the related Guggenheim – Anderson – De Boer (GAB) equations can be derived and have also been applied to salt solutions, already first by Stokes and Robinson [2]

The method of using immaterial surface sites as additional components in Gibbs energy minimisation, originally developed by Pajarre et al. [9] as one of the key applications of the Constrained Gibbs Free energy (CFE) method, makes it possible to apply the Gibbsian method to various surface systems. Since its development, the CFE method has been applied to various systems including surface and interfacial tensions of alloys [10,11], phase diagrams of surface and nanoparticle systems [12], as well as properties of steels and melts [13,14]. The technique of immaterial surface sites is, however, quite generic and can be applied to include adsorption sites in Gibbsian calculations in arbitrary well-defined systems. With the prospect of achieving a consistent model for highly concentrated aqueous systems applicable in computational thermodynamics, it is of interest to apply the CFE technique for the properties of concentrated aqueous solutions by implementing the BET adsorption theory to the Gibbs energy minimisation calculation.

The example models, presented in the following, have been implemented using the ChemSheet program [15], which applies the ChemApp program library [16] for the thermochemical equilibrium calculations.

2. Theory

The Brunauer–Emmett–Teller (BET) approach is based on the Langmuir model of surface equilibria, with the assumption that the first layer of molecules adsorbing to the surface has a constant energy of adsorption and that there are no interactions between the adsorbing molecules. When applied to gaseous species, the adsorption energy of

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* Corresponding author.
E-mail address: risto.pajarre@vtt.fi (R. Pajarre).

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the subsequent layers after the first one is assumed to be equal to the heat of liquefaction of the adsorbing gas, so that the adsorbed molecules after the first layer behave like liquid

A practical equation that based on experimental data enables to fit the model parameters was derived by Brunauer et al. [1] as

$$\frac{p}{v(p_0-p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c}\frac{p}{p_0} \tag{1}$$

where v is the total volume of the adsorbed gas, v_m the volume of the adsorbed gas in a unimolecular layer covering the surface, p is the pressure, p_0 the saturation pressure and c is a constant that approximately equals

$$c = \exp((E_1 - E_l)/RT) \tag{2}$$

Here E_1 is the heat of adsorption of the gas on the surface for the first monolayer and E_l is the heat of liquefaction of the gas. When the left hand side of the Eq. (1) is plotted as a function p/p_0, within the validity range of the BET model, a straight line giving values of $1/v_m c$ and $c - 1/v_m c$, and consequently c and v_m , is obtained.

Later Stokes and Robinson [2] applied the model for concentrated aqueous solutions of salts. For their formulation they made the substitutions

$$\frac{p}{p_0} = a_w \tag{3}$$

and

$$\frac{v_m}{v} = m\cdot \quad r/55.51\frac{mol}{kg} \tag{4}$$

where a_w, is the activity of the adsorbing water, m the molality of the salt solution and r the number of adsorption sites per salt molecule, resulting in Eq. (5)

$$m = \frac{55.51\frac{mol}{kg}\cdot(1-a_w)}{a_w}\left(\frac{1}{cr} + \frac{c-1}{cr}a_w\right) \tag{5}$$

The activities of salt and adsorbed water in a BET system were derived by Braunstein and Ally [7] as

$$a_s = \left(\frac{rn_S - n_{Ads}}{rn_S}\right)^r \tag{6}$$

for the salt and

$$a_{H_2O} = \frac{n_{H_2O} - n_{Ads}}{n_{H_2O}} \tag{7}$$

for the water, where n_S is the total molar amount of salt, n_{H_2O} the total molar amount of water, r the number of adsorption sites per salt species (generally not assumed to be an integer) and n_{Ads} the number of adsorbed water molecules. As an extension of the model corresponding to Eqs. (6) and (7) Ally and Braunstein [8] later further presented an analogous equation for the activity of a salt i in a salt mixture as

$$a_{s_i} = \frac{n_{s_i}}{\sum_j n_{s_j}}\left(\frac{r_i n_{s_i} - n_{Ads_i}}{r_i n_i}\right)^{r_i} \tag{8}$$

In Eq. (8) n_{s_i} is the molar amount of salt i, the number of adsorption sites per salt species i and n_{Ads_i} the number of water molecules adsorbed on salt i. In their paper, Stokes and Robinson [2] also described a modification of the BET equation derived by Anderson [17] (again, originally derived for adsorption of a gas on a solid, but applied by Stokes and Robinson for salt solutions), where the adsorption energy differs from the heat of liquefaction by a constant amount d. The same model was also derived by means of statistical mechanics by Guggenheim [18], who noted that it is really a general case of the adsorption model where the original BET equation is obtained when $d = 0$. The model, most commonly called the Guggenheim – Anderson – De Boer model, leads to an equation where the a_w in (5) is replaced by Ka_w [2]

$$m = \frac{55.51\frac{mol}{kg}\cdot(1-Ka_w)}{Ka_w}\left(\frac{1}{cr} + \frac{c-1}{cr}Ka_w\right) \tag{9}$$

where

$$K = e^{-\frac{d}{RT}} \tag{10}$$

The GAB equation, with one additional parameter, is also valid in somewhat more dilute solutions than the BET model. Stokes and Robinson [2] gave approximate maximum values for water activities of the respective applicability ranges as 0.3 for BET and 0.5 for GAB.

3. CALPHAD model

The original BET model with the water and salt (or gas and adsorption site) activities as described by Braunstein and Ally [7] (Eqs. (6) and (7)) is equivalent to a model with two ideal lattices (or phases), one for free and adsorbed water molecules, and one for salt sites that are either free or with adsorbed water. The total number of lattice sites is n_{H_2O} in the water lattice and rn_S in the salt site lattice. The two lattices are non-interacting otherwise, but the number of sites with water adsorbed on salt ,n_{Ads}, is the same in both. The standard state chemical potential difference between the free and occupied salt adsorption site is given by

$$\mu_{free}^{salt\ site,0} - \mu_{adsorbed}^{salt\ site,0} = RTlnc \tag{11}$$

equalling the energy of adsorption for the water (Eq. (2)). A stoichiometry corresponding to this is presented in Table 1.

Alternative stoichiometry for the same system, but more suitable for calculating equilibrium solubilities is given in Table 2

Here, the component 'salt' refers to the salt compound and not to an adsorption site on it, the stoichiometric coefficients related both to the free sites and those with adsorbed water are now $1/r$.

For a gas adsorption system stoichiometry can correspondingly be presented as shown in Table 3.

For systems with more than one salt, the two factors in Eq. (8) for activity (two terms in the corresponding chemical potential) can be split into two separate linked phases, one that is a mixture of the different salts in the system, and the other is a mixture of empty and filled adsorption sites. An example stoichiometry for the system $CaCl_2$-LiCl is presented in Table 4.

With the stoichiometric structure described in Table 4, the dissolution of a solid salt (increase of the amount of "aq-salt" phase) can only happen with the simultaneous increase of the corresponding adsorption sites, for example

$$LiCl{*}H_2O \Leftrightarrow LiCl^{aq-salt} + r(LiCl)\cdot free^{LiCl-site} + free^{water} \tag{12}$$

The chemical potential of the dissolved salt is correspondingly given by

$$\begin{aligned}\mu(LiCl) &= \mu(LiCl{*}H_2O) - \mu_{free}^{water} = \mu_{LiCl}^{aq-salt} + r(LiCl)\mu_{free}^{LiCl-site}\\ &= \mu_{LiCl}^{aq-salt,0} + r(LiCl)\mu_{free}^{LiCl-site,0} + RTln\left(x_{LiCl}^{aq-salt}\cdot(x_{free}^{LiCl-site})^{r(LiCl)}\right)\end{aligned} \tag{13}$$

There are extra degrees of freedom in setting the various standard state chemical potentials. The authors considered it simplest to set them

Table 1

Structure of the aqueous-salt BET model.

		salt site	water	adsorption
salt site	free	1	0	0
	adsorbed	1	0	1
water	free	0	1	0
	adsorbed	0	1	-1