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On Thermodynamic Models for Real Solutions

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Abstract—The thermodynamic consistency of modern models of nonideal aqueous solutions is evaluated. It was shown that the models of concentrated aqueous solutions used in current studies are thermodynamically incorrect. Criteria were proposed for the thermodynamic consistency of physicochemical models of the nonideality of real solutions. An example is given for the correct extension of the Debye–Hueckel equation.

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INTRODUCTION

In geochemistry, thermodynamic models are commonly understood as various means of simulating a stable state of a chemical system or a process of its evolution in response to a change in the external or other imposed (for example, by the dynamics) conditions. In any event, the process of simulation, in fact, is the single or multistep calculation of the equilibrium composition of the system at its specified parameters. The parameters of state that are the most convenient for thermodynamic simulations are temperature and pressure, which are thus most often utilized for these purposes. In this situation, the thermodynamic potential of the system is its Gibbs free energy, which reaches its minimum in the state of equilibrium. In this publication, the considerations are limited to isobaric–isothermal conditions and the free energy as the only thermodynamic potential.

As has been demonstrated by J.W. Gibbs [1], the tendency of the free energy of a system to assume its minimum value (at constant temperature and pressure) immediately follows from the second law of thermodynamics, and thus, the most general means of simulating equilibria in a complex chemical system is the numerical search for the minimum point of this potential. However, because of the universal character of this method, in application to simple systems, it can turn out to be less efficient than the method involving the solution of systems of equations for the law of mass action. In his publication quoted above, Gibbs has also demonstrated that the law of mass action (this is its modern name) follows from the principle of the minimum of the free energy at the equilibrium point. Hence, the law of mass action can also be applied to determine the compositions of the phases, although only if it is known that these phases are present in the system at equilibrium. The overwhelming majority of thermodynamic models utilized in geochemistry describe systems that always contain an aqueous solution and, hence, computer programs based on "equilibrium constants" are currently used most widely.

The input data of these programs for the minimization of the free energy of a system are the standard potentials of all compounds possible in the system (free energy values for pure compounds in their standard state). For programs relying on the law of mass action, the input thermodynamic parameters are the equilibrium constants of all (independent) chemical reactions. Each equilibrium constant can be expressed through the standard potentials of compounds participating in the reaction. Conversely, if the complete set of the equilibrium constants is known, they can be used to calculate the standard potentials of the compounds (although the scale of standard potentials calculated in this "inverse" manner cannot be unambiguously reproduced) sufficient for the calculation of equilibrium by the minimization technique. Because of this, the results yielded by both types of computer programs should be identical if the program makes use of input data consistent in this sense.

Both types of programs for calculating equilibrium compositions are underlain by the concept of chemical potential. The chemical potentials of compounds are explicitly contained in expressions for the free energy of the system and, implicitly, in expressions for the law of mass action. At a constant temperature and pressure, the chemical potential of a compound depends only on the composition of the phase (solution) that contains it. An expression for this dependence can be derived theoretically, if only the changes in the entropy during the mixing of components are taken into consideration (these solutions are referred to as ideal). This dependence is of general character, but individual features of the interactions of components in real solutions also affect (sometimes fairly significantly) the chemical potentials. The nonideality of real solutions is

accounted for in expressions for the chemical potential of compounds by means of multiplying their concentrations by correction coefficients. In practice, these coefficients, which are referred to as *activity coefficients*, can be calculated in several manners depending on the assumed nonideality model. Obviously, for the modeling results obtained with two different programs to be equivalent, it is necessary that both programs make use of the same nonideality models.

It is commonly thought that, if the aforementioned conditions are fulfilled, i.e., when the same thermodynamic properties of the compounds and the same nonideality models are used, the calculation results of equilibrium by the free energy minimization method and by using equilibrium constants should coincide. We will consider this discussion starting with considering an example demonstrating that this is not always the case.

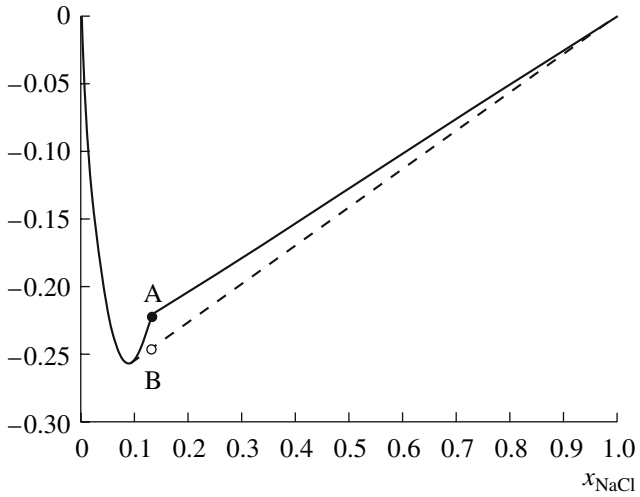

Fig. 1. Reduced "free energy" of mixing G^{mix}/RT for the "equilibrium" H_2O–NaCl system.

EXAMPLE: H_2O–NACl SYSTEM

Let us assume that we decided to examine the water–halite binary system at a temperature of 25°C and a pressure of 1 bar. For this purpose, let us calculate a series of equilibrium compositions of this system ranging from pure water to pure halite with a certain step in terms of NaCl fraction. The calculations will be carried out with regard for the possibility of the existence of only two phases in the system: crystalline sodium chloride and its aqueous solution. The latter will be described based on a model of complexation, i.e., under the assumption that the aqueous solution contains the following species (along with water itself): H^+, OH^-, Na^+, Cl^-, $NaOH^0$, HCl^0, and $NaCl^0$. The equilibrium compositions will be calculated by the method of constants. The equilibrium constants needed for this will be derived from the standard free energy values, which can be compiled from some available database (for example, [2]). To account for the nonideality of the aqueous solution (we expect its fairly high concentrations), let us use the "extended" Debye–Huckel equation (i.e., that with an additional term, which is linear with respect to the ionic strength). The water activity is assumed to be equal to its mole fraction in the solution.

Upon completing the whole simulation set, we will see that the results show nothing unexpected. Early in the series ($x_{NaCl} < 0.13$), homogeneous aqueous solution is produced, in which an increase in the NaCl mole fraction is associated with a monotonous increase in the concentrations of all species with Na and Cl. The same pertains to their chemical potentials μ_i, which are calculated in a conventional manner with the use of the corresponding activity values. At $x_{NaCl} = 0.13$, the solution reaches saturation with respect to halite, and a solid phase appears. A further increase in x_{NaCl} is not associated with changes in the concentrations (and, hence, the potentials) of all aqueous species remain constant and, as can be expected, only with an increase in the amount of halite in the system. [1]

Having now complete information on the equilibrium compositions of the system, we are able to calculate the free energy at any point by the formula $G = \sum \mu_i n_i$ (sum for all species, n_i is their mole amounts) and plot the values in a diagram. For the sake of better demonstrativeness, it is more convenient to operate not with the whole free energy but with the "energy of mixing" $G^{mix} = G - (\mu^0_{NaCl} x_{NaCl} + \mu^0_{H_2O} x_{H_2O})$. However, the results turn out to be surprising.

Figure 1 shows the plot of the obtained function (solid line). To the left of point A (solid circle), the line corresponds to unsaturated homogeneous aqueous solution of NaCl, point A itself shows saturated solution, and the right-hand part of the line displays both coexisting phases. Note that the law of mass action remains valid for all points of the line for all possible reactions. Nevertheless, from the viewpoint of thermodynamics, no such plot can exist because the curve is *not convex*.

Indeed, let us draw a tangent line (shown as a dashed line) to the curve at the point of pure halite and consider point B on this tangent line having an abscissa $x = 0.13$ (shown as an open circle). Evidently, points A and B correspond to the same bulk composition of the system. It can be easily demonstrated (for example, by solving a linear system of two equations) that the composition of the system corresponding to point B can be represented

[1] In this publication, I do not consider the problem of the "accuracy" of the simulations in the context of the correspondence of the simulation results to the observed values of solubility, concentrations, etc. These issues do not pertain to thermodynamics but to the "parametrization" of empirical models. Our task was the analysis of the accuracy of the models from the standpoints of thermodynamics and mathematics.

as the sum of positive amounts of halite and NaCl aqueous solution of the composition $x = 0.1$, with the sum of the free energies being lower than for solution A (this can also be seen from the plot). In other words, the obtained "equilibrium" composition (point A) does not correspond to the minimum of the free energy! At the same time, analyzing this equilibrium (at $x = 0.13$) with the use of a computer program for free energy minimization, we should have obtained point B as the solution, at which, however, the solid phase coexists with unsaturated solution, i.e., the law of mass action is violated. Thus, in calculating the equilibrium composition of the same system (moreover, in doing this based on the same input thermodynamic information and utilizing the same nonideality model) by two different methods, we obtained two distinct results, both of which are erroneous.

As was mentioned above, the user of the program "based on constants" cannot note that the result contradicts thermodynamics, until the user calculates the minimum free energy value for the simulated system. It is interesting that, analogously, the user of the "minimizing" program will not discern any indications of the erroneousness of the results, until/if he or she tests the validity of the law of mass action. Indeed, the dashed straight line in Fig. 1 passes through the multiplicity of "minimized" solutions, each of which includes a solution of the same (maximum) concentration, thus creating the illusion of saturation!

The example presented above is not of my devising. Although this is impossible, [2] a nonconvex "surface of free energy" can be obtained by anyone eager to reproduce the calculation presented above, of course, within the scope of the same thermodynamic model.

The reasonable questions are which of the two approaches to the calculation of equilibrium is preferable in this situation, and which of the solutions is more accurate. The answer is none of them, of course, because both of the solutions contradict thermodynamics and, hence, the problem is not the selection of the simulating program but the correction of the model itself. Moreover, inasmuch as the model is inaccurate, we cannot regard the results obtained with it even as a certain approximation, because we are unable to assay the accuracy of the simulations even at the intuitive level. However, the latter consideration is often not regarded, because it is thought that the comparison of simulation results with observations (or the results of experiments) provides a sufficient verification of the model, even if it is inaccurate.

Because of this, it is pertinent to present another argument for the use of noncontradictory models. Assume that some hypothetical computer program was developed for calculating equilibria of the "combined" type. The program (1) calculates equilibrium for a system of specified phase composition by minimizing the free energy; (2) then, proceeding from the saturation indices, corrects the phase composition (mineral association); and (3) returns to step (1) if the phase composition has changed. Obviously, such a program (which is flawless from the standpoint of thermodynamics) will not be able to solve the problem considered above: the program will cycle when trying to choose between points A and B. The problem faced by our hypothetical program can be readily surmounted by appending the program with a criterion for selection of the two (both erroneous!) solutions, but analogous situations can arise when real, much more complicated programs operate. As was mentioned above, programs for calculation equilibria in systems of general form (i.e., systems with any number of solutions of any type, each of which can contain any components and are not necessarily present at equilibrium) make use of the principle of the free energy minimum. At certain phases of the simulations, these programs can calculate the equilibrium composition of the system or its subsystem (to increase the efficiency) based on the law of mass action. At the same time, it was demonstrated in [3] that the universal numerical criterion of equilibrium requires the knowledge of the minimum free energy value of the subsystem to accurately select the equilibrium set of phases. Because of this, the contradictory character of the thermodynamic model for any of the phases can make the solution of the problem (even an erroneous one) impossible.

The aforesaid is, hopefully, enough to convince the reader of the importance of the use of only thermodynamically accurate models for physicochemical simulations. In any event, the thermodynamic coherence of the models undoubtedly simplifies both the simulation process itself and the interpretation of its results.

The obvious reasons for the inconsistencies are as follows. Both equilibrium criteria—the minimum of the free energy and the law of mass action that follows from it—are undoubtedly valid because they were derived rigorously mathematically. Hence, the calculated G function is not the free energy and, correspondingly, the values of μ_i are not the chemical potentials.

PRINCIPAL RELATIONS

In order to elucidate the roots of our worries, we have to turn to [1] to recall how J.W. Gibbs defined free energy.

First J.W. Gibbs considered the first law of thermodynamics to derive the general criteria of thermodynamic equilibrium (in the absence of external forces and other complicating phenomena) in terms of inner energy and entropy of the system and demonstrated that all phases of a system in equilibrium have the same values of temperature T, pressure P, and the chemical

[2] It is known from experience that real solutions of any state can have a nonconvex configuration of their free energy surface, but the free energy of the system must likely always be convex, because these solutions can be exsolved in nature and, thus, decrease their free energy and level off its surface.

potential of components μ_i. The latter are defined as partial derivatives of the inner energy with respect to the quantities of the compounds $\mu_i = \partial U/\partial n_i$ (although Gibbs himself expressed the quantities of compounds in mass units, we will use moles).

Then J.W. Gibbs defined the free energy of a homogenous phase (in modern notation)

$$G = U - TS + PV, \quad (1)$$

where U is the internal energy of the phase, S is its entropy, V is the volume, T is the absolute temperature, and P is the pressure. It is known from experience that internal energy, entropy, and volume are additive functions (i.e., their values in a system are equal to the sums of the values from discrete phases or any other subsystems), and, hence, at T and P equal throughout the system, definition (1) can be extended over the whole system. Thus, the function G is also additive. Finally, Gibbs demonstrated that, in a system at constant temperature and pressure, the function G is independent of the entropy and volume and is determined solely by the composition (amounts of various compounds composing phases) and reaches a minimum at equilibrium.

In a differential form, the dependence of free energy only on the composition of the system (at constant T and P) is written as

$$dG = \sum \mu_i dn_i, \quad (2)$$

where

$$\mu_i = \frac{\partial G}{\partial n_i} \quad (3)$$

and n_i denotes the amount of component i. Expression (3) is valid: internal energy is a function of entropy S, volume V, and the amounts n_i of components, which are regarded as independent variables. Because of this, the partial derivatives of the functions U and G with respect to n_i are equal. In expressions (2) and (3), components are understood as any compounds through which the composition of the system can be defined, with the only requirements of their independent derivatives. The latter condition is sometimes understood incorrectly by regarding it as the requirement of the chemical independence of the compositions composing the system, i.e., the impossibility of expressing the chemical composition of some compounds through others. In fact, Gibbs did not impose these constraints and used the term in its mathematical meaning, thus emphasizing that components are independent variables (but not functions), and the possible transformations of components in one another are accounted for in equations for additional equilibrium conditions.

It is important to mention that (2) and (3) cannot be regarded as definitions of the free energy of the system because, as is known from mathematical analysis, these relations are satisfied by any differentiable function. In other words, free energy possesses some additional characteristics that are not reflected in these relations. There are at least two such characteristics.

The first and obvious one is the continuous differentiability of the function G for the necessary number of times, a characteristic usually implied in thermodynamics. We will adhere to this assumption with a single comment. According to the physical meaning, the domain of definition of the function G is all nonnegative values of the mole quantities of the components of the system $n_i \geq 0$ (or, in the vector form, $\mathbf{n} \geq \mathbf{0}$). However, in the situation when some component is characterized by a constant chemical potential independent of the composition of the system (for example, a mineral of constant composition or a perfectly mobile component [4]), the domain of definition of the function G can be extended at negative values of this component, which is fairly convenient and useful [5]. At other boundary points of the definition domains, the function G either has infinite partial derivatives with respect to some variable or does not have them at all [3]. This, however, does not pose any insurmountable problems but should nevertheless be borne in mind. Hence, let us consider the function G to be continuous throughout its definition domain and doubly continuously differentiable within this domain.

The other characteristic of free energy, which was mentioned above, is its additiveness, which implies, for example, that, for any $\alpha > 0$, the expression $G(\alpha\mathbf{n}) = \alpha G(\mathbf{n})$ is valid. Written in its vector form, the equality indicates that, when the amounts of all components are changed proportionally, the free energy of the system also changes in the same proportion. Such functions are referred to as homogeneous.

Definition: Function n of variables $f(\mathbf{x})$ is called homogeneous of degree r, if for any $\alpha > 0$ $f(\alpha\mathbf{x}) = \alpha^r f(\mathbf{x})$. The Euler theorem for homogeneous functions reads: if $f(\mathbf{x})$ is a continuously differentiable function of degree r, then $\sum x_i \frac{\partial f}{\partial x_i} = rf(\mathbf{x})$.

Hence, free energy G is a first-order homogeneous function, and hence, the Euler theorem implies that this function can be represented in the form

$$G(\mathbf{n}) = \sum \mu_i n_i, \quad (4)$$

where the chemical potential μ_i is also defined by formula (3). It follows from the definition of chemical potentials that they are functions of the same independent variables n_i. It can be readily demonstrated that all $\mu_i(\mathbf{n})$ are zero-order homogeneous functions, i.e., they do not change during a proportional change in the composition of the system. In other words, chemical potentials depend not on the amounts of components but on their concentrations.

In contrast to relation (3), which is valid for any differentiable function, formula (4) reflects a principally important feature of the function G: its homogeneity. It is thus tempting to utilize this expression to define free energy (which is sometimes done, as in [6]). Indeed, this "definition" is convenient, for example, for developing a thermodynamic model of a real solution when

the chemical potentials of all of its components are known. Let us consider the possible consequences of this. Let each component i of the solution have an empirical function φ_i describing the results of the measurements of its chemical potential depending on the composition of the solution. Our idea is to construct the function $\Phi(\mathbf{n}) = \sum \varphi_i n_i$ and use it as the "free energy" of the solution in numerical simulations. At first glance the idea seems to be quite attractive because the function $\Phi(\mathbf{n})$ thus constructed is an obviously homogeneous first-order function (as must the free energy function be), and the independent variables are multiplied by their chemical potentials (as they also should be). Let us, however, first consider the properties of the function $\Phi(\mathbf{n})$.

First of all, it is pertinent to recall that free energy should be at least two times continuously differentiable (at $\mathbf{n} > \mathbf{0}$). These conditions can be readily tested, because it is known that the second-order mixed derivatives of such a function should be equal. We believe to already have the first-order derivatives: these are the φ_i functions. Thus, the condition

$$\frac{\partial \varphi_i}{\partial n_j} = \frac{\partial \varphi_j}{\partial n_i} \tag{5}$$

should be fulfilled for any $i \neq j$. Inasmuch as our functions φ_i are empirical and were most probably constructed independently, conditions (5) can sometimes not be met. [3] In this situation, the model should be rapidly corrected to become consistent with (5).

Now when our function $\Phi(\mathbf{n})$ meets the requirements of the Euler theorem, we can apply this theorem to it and write $\Phi(\mathbf{n}) = \sum (\partial \Phi / \partial n_i)\, n_i$. We will be completely satisfied if $\partial \Phi / \partial n_i = \varphi_i$ (for all i). This is, however, not always the case.

Let us consider the "actual" free energy function written in form (4) and take its complete differential $dG = \sum \mu_i dn_i + \sum n_i d\mu_i$. Comparing this expression with (2), we immediately arrive at $\sum n_i d\mu_i = 0$, which is referred to as the Gibbs–Duhem relations (it is sometimes named equation, although, in fact, it is an identity, which holds for any possible values of the differentials of the independent variables). Because of this, it can be written for each independent variable n_i as $\sum_k n_k \frac{\partial \mu_k}{\partial n_i} = 0$.

Let us now return to the problem of the conditions at which the equality $\partial \Phi / \partial n_i = \varphi_i$ is fulfilled. Let us differentiate our function $\Phi(\mathbf{n}) = \sum \varphi_i n_i$ with respect to n_i: $\frac{\partial \Phi}{\partial n_i} = \varphi_i + \sum_k n_k \frac{\partial \varphi_k}{\partial n_i}$. This equality obviously implies that the necessary and sufficient condition of the thermodynamic validity of our empirical model is the fulfillment of conditions analogous to Gibbs–Duhem relations for μ_i for the function φ_i, that is

$$\sum_k n_k \frac{\partial \varphi_k}{\partial n_i} = 0 \tag{6}$$

for any i.

Although our considerations always pertained to a system, conditions (6) should hold not only for it as a whole but also for any of its discrete phases because any phase is a particular case of a system. Thus, summing in (6) may (and must) be conducted only over components (labeled with the k index) of the phase that also contains component i.

For the sake of completeness, let us utilize criteria (5) and (6) to test the accuracy of the model for an ideal solution. This will also allow us to simplify the further analysis of real solutions by considering only their deviations from ideality.

As is known, the chemical potential of component i of an ideal solution is $\mu_i = g_i^0 + \ln x_i$, where x_i is the mole fraction of this component. [4] Let us denote $N = \Sigma n_i$, then $x_i = n_i/N$. Let also $\varphi_i = \mu_i$. We can now test the fulfillment of conditions (5)

$$\frac{\partial \varphi_i}{\partial n_j} = \frac{\partial \ln x_i}{\partial n_j} = \frac{1}{x_i}\frac{\partial x_i}{\partial n_j}$$

$$= \frac{N}{n_i}\frac{\delta_{ij} N - n_i}{N^2} = \frac{\delta_{ij}}{n_i} - \frac{1}{N},$$

where the δ_{ij} is the Kronecker delta. Since $\delta_{ij} = 0$ at $i \neq j$, all the cross derivatives are equal, i.e., condition (5) is valid.

Let us now test condition (6)

$$\sum_k n_k \frac{\partial \varphi_k}{\partial n_i} = \sum_k n_k \frac{\partial \ln x_k}{\partial n_i}$$

$$= \sum_k n_k \left(\frac{\delta_{ik}}{n_k} - \frac{1}{N} \right) = 1 - \sum_k x_k = 0.$$

Thus, the model of ideal solution was proved not to contradict thermodynamic relations, so that it is sufficient for the analysis of models for real solutions, whose nonideality is described using activity coefficients ($\mu_i = g_i^0 + \ln x_i + \ln \gamma_i$), to test relations (5) and (6) only for the functions $\varphi_i = \ln \gamma_i$.

Note that conditions (5) and (6) must be tested when empirical dependences are introduced directly into the

[3] The necessity of the fulfillment of equalities (5) for the thermodynamic correctness of a model is self-evident, but, nevertheless, these conditions are often ignored. Note that the models for magmatic melt discussed in [7] do not fulfill these conditions (which are referred to as Maxwell's generalized relations) and are simply rejected from the analysis.

[4] For simplicity, hereafter we will use the reduced free energy in place of free energy $g = G/RT$, and the concentrations of components of all solutions (including the aqueous one) will be expressed in mole fractions. Correspondingly, we will consider rational activity coefficients.

expressions (or at least one of them) for the chemical potentials of the components of a solution. If an empirical model for a solution is specified by an expression for the free energy as a composition function (of course, only homogeneous and of the first order), and the chemical potentials of components are then derived by differentiation of this expression, there is no need to verify conditions (5) and (6) because their validity is ensured in this situation automatically.

DEBYE–HUCKEL MODEL

One of the modern models of nonideal aqueous solutions of electrolytes is the Debye and Huckel electrostatic theory. The so-called second approximation of the Debye–Huckel law makes it possible to calculate the activity coefficients of individual ions by the formula [5]

$$\ln\gamma_i = -\frac{Az_i^2\sqrt{I}}{1+\mathring{a}B\sqrt{I}}, \quad (7)$$

where A and B are constants under given conditions, $\mathring{a}$ is an empirical parameter, z is the charge of the ion, and $I = \frac{1}{2}\sum z_k^2 m_k$ is the ionic strength of the solution. [6]

Formula (7) and all of its parameters were derived theoretically, but the theory does not permit determining the value of the parameter $\mathring{a}$, which has the sense of the effective size of the solvated ion. This value can be determined empirically.

Debye and Huckel derived their law for the average activity coefficient for a diluted solution of a strong electrolyte. It was, however, established empirically that formula (7) can be successfully enough applied in determining the activity coefficients of individual ions, in solutions of mixed electrolytes, and even at elevated concentrations. It was also determined that various electrolytes can be "well" described with various values of the parameter $\mathring{a}$. This provided the basis for an empirical model in which the size of the solvated ion is taken to be different for various ions. It was also recommended (see, for example, [8]) to substitute the parameter $\mathring{a}$ in formula (7) for $\mathring{a}_i$.

Let us now test whether condition (5) is met by this empirical form of the Debye–Huckel model by assuming $\varphi_i = -\frac{Az_i^2\sqrt{I}}{1+\mathring{a}_iB\sqrt{I}}$. Differentiating the logarithm of the activity coefficient of aqueous species i with respect to the amount of species j, we obtain

$$\frac{\partial\varphi_i}{\partial n_j} = -\frac{Az_i^2z_j^2}{(1+\mathring{a}_iB\sqrt{I})^2 4\sqrt{I}}\frac{55.51}{n_0},$$

where n_0 is the molar amount of water (solvent), and 55.51 denotes the value of $1000/M_w$ (where M_w is the molar mass of water). The value for the "cross" derivative can be obtained from this formula by means of simple permutation of indices. Thus, condition (5) yields $\mathring{a}_i = \mathring{a}_j$ for all pairs of i and j. Because of this, below we will consider the Debye–Huckel second approximation only in its original form (7). Note that in the HKF model [9], which is the most popular now and accounts for complexation, the parameter $\mathring{a}$ is assumed universal for all aqueous species. [7]

Experiments with more concentrated solutions demonstrate that, as the concentrations of electrolytes are increased, the activity coefficients of ions begin to increase starting at a certain point, which is not predicted by the Debye–Huckel theory. It was established empirically that this increase can be satisfactorily described by introducing a summand bI into (7), where I is, as before, the ionic strength, and b is an empirical constant depending on the electrolyte. Analogous relations were established for neutral species, whose empirical dependence $\ln\gamma = bI$ is referred to as the Sechenov equation. It was also reliably established that the parameter b in the Sechenov equation is individual for any neutral species [10], which is also applicable to ions, although this parameter in the HKF model is assumed to be the same for all solute species, and its value is determined by the type of the background (predominant) electrolyte. It should be generally admitted that the parameter b depends on both the solute species (either neutral or charged) and the predominant electrolyte. Because of this, in considering the "third approximation" of the Debye–Huckel formula in a more general form, we will write it in the form

$$\ln\gamma_i = -\frac{Az_i^2\sqrt{I}}{1+\mathring{a}B\sqrt{I}} + b_iI. \quad (8)$$

Since the first summand of this formula has already been tested using criterion (5) and has been proved to satisfy it, it is sufficient to verify these conditions for $\varphi_i = b_iI$. Differentiating yields $\frac{\partial\varphi_i}{\partial n_j} = b_i\frac{z_j^2}{2}\frac{55.51}{n_0}$ (here the square of the charge of species j appeared during the differentiation of the ionic strength). Rearranging the indices and equalizing the results, we obtain an equation for the consistency of model (8) in the form $b_iz_j^2 =$

[5] Formula (7) is commonly written with a common logarithm of the activity coefficients, but we will write it with a natural logarithm for the sake of universality, bearing in mind that the transition module has already been taken into account in the value of the constant A. Recall that expression (7) presents a rational activity coefficient.

[6] The Debye–Huckel law was introduced when molar ionic strength was used, whereas the more convenient molal scale is more often used in practice in hope that this transition will not impair the validity of the law and that the possible deviations can be compensated by the selection of empirical coefficients.

[7] When formally applied to neutral species, formula (7) yields $\gamma = 1$ for them, which is consistent with the idea that neutral species do not participate in electrostatic interactions. Because of this, the Debye–Huckel second approximation can be regarded as an universal law applicable to all solute species.

$b_j z_i^2$. These equalities should be fulfilled for all pairs of solute species, including neutral ones. Evidently, this is possible only if $b_i = 0$ for all ions. Hence, expression (8) is in conflict with thermodynamics and cannot be utilized in thermodynamic simulations. This equally pertains to the situation when the value of the parameter b is the same for all species of a solution.

In order to surmount this contradiction, some researchers proposed to replace the term bI in formula (8) by $bz_i^2 I$, which should have made it possible to equalize the results of cross differentiating, because they now would have contained products of the squared charges of both species. However, this modification also requires the use of one common coefficient b for all species and, moreover, makes it impossible to specify the activity coefficients for neutral species. These considerations lead us to the conclusion that it is undesirable to use ionic strength in empirical summands introduced into the Debye–Huckel law (at least in simple expressions like "virial expansion in ionic strength").

It would be optimal to find an empiric expansion of formula (7) ensuring the following:

* the possibility of simulating electrolyte solutions at elevated concentrations;

* consistency with relations reliably established for aqueous solutions of electrolytes;

* the possibility of individual accounting for the characteristics of solute species;

* the introduction of the minimum number of empirical parameters; and

* mathematical consistency in terms of criterion (5).

These requirements are likely met by the expression $Cb_i\Sigma b_k m_k$ (the constant C is introduced to account for the temperature and pressure dependences). Indeed,

* ionic strength is regarded in practice as a measure of the bulk concentration of solute species, particularly in application to strong electrolytes, for which these values are proportional;

* the Harned rule (for mixed electrolytes with a common ion) immediately follows from the proposed formula, which evidently is an analogue of the Sechenov formula for neutral species;

* the values of empirical coefficients b_j can be specified independently, with the thermodynamic consistency of the model preserved at any of their values;

* each solute species is characterized only by one parameter; and

* testing of condition (5) yields $\dfrac{\partial \varphi_i}{\partial n_j} = Cb_i b_j \dfrac{55.51}{n_0} = \dfrac{\partial \varphi_j}{\partial n_i}$.

The form of the model proposed for the nonideality of solute species resembles that of the Pitzer model [11] constrained by the sum of the second virial coefficients, but these similarities are only semblant. First, the parameters b_i are constants but not functions of ionic strength. Second, these constants do not describe pairwise interactions, and the effects of complexation and ionic pairs are accounted for by the model of complexation.

The practical utilization of the model may at first face certain difficulties, because the values of its empirical parameters are not determined. However, when solutions with a single strong background electrolyte are simulated, the parameters b_γ of the HKF model can be used in it, for which it is sufficient to assume $b_i = 1$ for all solute species and let $C = b_\gamma/2$.

WATER ACTIVITY

In the previous section, we tested the consistency of expressions for the chemical potentials of solute species but did not touch upon the predominant component of aqueous solution: water itself. The reason for this was the fact that the Debye–Huckel model does not provide an expression for the activity (or an activity coefficient) of a solvent but instead assumes it to be close to unity. This assumption can be considered justified in the Debye–Huckel theory, because formula (7) was derived for fairly diluted solutions. However, the "third approximation" can be applied to the description of fairly concentrated solutions, whose water activity coefficients notably differ from unity.

Of course, all modern models for aqueous solutions include formulas for evaluating water activity as functions of solution composition. Nevertheless, we did not even try to test conditions (5) for any pair of a solute species and water: the result of this test is easily predictable and evident. The activity of water is usually expressed through the osmotic coefficient, whose values are calculated for simulations based on the model assumed for the nonideality or by functions approximating experimental data for certain systems. The former approach is, of course, more preferable because it does not depend on the specifics of the modeled system. However, we cannot use the estimate of the water activity on the basis of another model of nonideality because of the absence of reasons to believe that conditions (5) in which water is involved remain valid.

Inasmuch as conditions (5) do not hold for the whole set of components of our aqueous solution, neither will hold more "rigorous" conditions (6) for it. At the same time, if conditions (6) were valid for the aqueous solution, then all equalities (5) would also hold true for it. In view of these considerations, let us utilize the Gibbs–Duhem relations to calculate the activity of water in aqueous solution.

We will take into account only deviations from ideality, i.e., assume that $\varphi_i = \ln \gamma_i$ (index 0 is assigned to water). For solute species, we assume the nonideality model

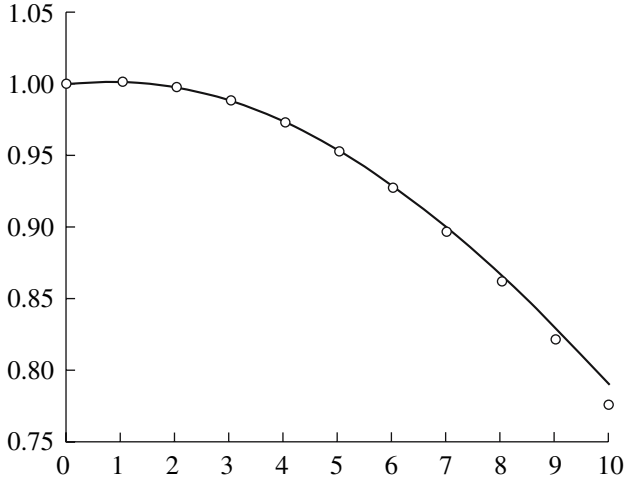

Fig. 2. Activity coefficient of water in equilibrium aqueous NaCl solution depending on the ionic strength. Symbols: open circles—calculated by the HKF model; solid line—calculated by formula (10).

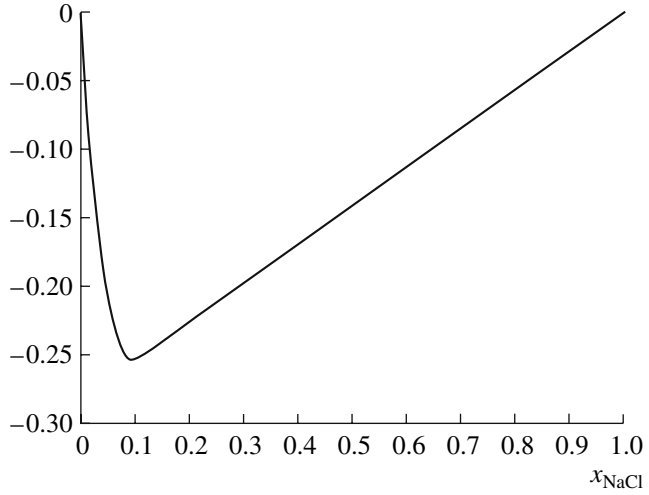

Fig. 3. Reduced free energy of mixing G^{mix}/RT for the equilibrium H_2O–NaCl system (corrected model).

$$\ln\gamma_i = -\frac{Az_i^2\sqrt{I}}{1+\mathring{a}B\sqrt{I}} + Cb_i\sum b_j m_j \qquad (9)$$

and modify equalities (6) by expressing φ_0 through φ_k for solute species

$$\frac{\partial\varphi_0}{\partial n_i} = -\sum_k \frac{n_k}{n_0}\frac{\partial\varphi_k}{\partial n_i}.$$

Upon solving this system of equations, we obtain an expression for the logarithm of the water activity coefficients in solution of given composition

$$\ln\gamma_0 = -\frac{A}{\mathring{a}B}\frac{2}{55.51}\left[\frac{I}{1+\mathring{a}B\sqrt{I}} - \frac{2\sqrt{I}}{\mathring{a}B} + \frac{2}{(\mathring{a}B)^2}\ln(1+\mathring{a}B\sqrt{I})\right] - C\frac{(\sum b_j m_j)^2}{2\times 55.51}, \qquad (10)$$

where the first summand is defined by the Debye–Huckel law (second approximation), and the second one is defined by the additional empirical term.

The application of formula (10) in the calculation of water activity during thermodynamic simulations guarantees that the model for the aqueous solution remains thermodynamically self-consistent at any variations in the composition of this solution. This does not, however, mean that formula (10) enables the calculation of the "actual" activity of water in an aqueous solution and thus eliminates the necessity of its experimental determining. [8] Conversely, the comparison of the calculation results obtained with this formula and the actual values of the water activity obtained experimentally for the same solutions should serve as a good criterion for assaying the quality of the empirical description of the characteristics of solute species by relation (9).

Let us now compare the values of activity coefficients obtained for water by formula (10) and calculated with the use of the osmotic coefficient within the framework of the HKF model. Let us assume that the modeled system is NaCl solution at a temperature of 25°C and a pressure of 1 bar. The HKF parameters of this model have the following values: $\mathring{a}$ = 3.72 and b_γ = 0.064. Because of this, let all b_i values in (9) and (10) to be equal to 1 and C = 0.032 ln 10 (see footnote [5]). The calculation results are presented as functions of the ionic strength (Fig. 2). [9] Circles in Fig. 2 show the evaluations made by the HKF model (under the assumption of the complete dissociation of the electrolyte: see formula (193) in [9]), and the line corresponds to calculations by formula (10). Thus, the quality of the thermodynamic description of this system with formulas (9) and (10) can be acknowledged as acceptable.

CONCLUSIONS

With regard for the facts and considerations presented above, we can repeat the attempt to simulate the H_2O–NaCl system. Let us assume relation (9) as a model for the nonideality of the solute species, and the nonideality of the solvent will be accounted for by formula (10). As before, the equilibrium composition will be calculated by the method of equilibrium constants. Figure 3 shows the plot of the free energy of the system obtained with this model at $\mathring{a}$ and b_γ values recommended by the HKF model for NaCl.

The following general conclusions can be drawn from the facts and considerations presented above.

[8] If the Debye–Huckel law is valid for diluted electrolyte solutions, the first summand in formula (10) yields a "theoretical" activity coefficient of water for these conditions.

[9] Note that saturation with respect to halite is reached under these conditions at I = 6.2.

1. The internal inconsistency of the thermodynamic model for a real solution can result in simulation results obviously contradicting thermodynamic laws and even sometimes make impossible the simulation process itself.

2. This inconsistency can arise when the empirical dependences or values of empirical parameters are introduced immediately into expressions for the activity coefficients of components of a real solution.

3. A necessary (but not sufficient) condition on the internal consistency of empirical expressions for the chemical potentials is the equality of cross partial derivatives (5) for these expressions.

4. The necessary and sufficient conditions of the consistency of empirical expressions for the chemical potentials is the fulfillment of the Gibbs–Duhem relations for them in the form (6).

In application to a nonideality model for an aqueous solution, these general statements lead to the following particular conclusions:

1. The parameter *å* in the Debye–Huckel formula should always be the same for all solute species.

2. The empirical expansion (additional summand) of the Debye–Huckel formula should not be a function of the ionic strength. An acceptable variant is a polynomial of the concentrations of aqueous species satisfying condition (5). An example of this expansion is (9).

3. A model for the nonideality of the solvent (water) should be consistent with the nonideality model for the solute species, i.e., the aqueous solution should meet condition (6). An example of this agreement is (10).

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