

APPLICATION OF A MODEL OF REGULAR SOLUTIONS TO IONIC MELTS

Juraj LEŠKO^a, Jaroslav KALOUSEK^{a,b}, Jaroslav KUPČÁK^a and Radim BOCHŇÁK^a

^a *Institute of Metallurgical Process Theory,
Czechoslovak Academy of Sciences, 703 00 Ostrava 3 and*

^b *Institute of Mining and Metallurgy, 708 33 Ostrava 4*

Received June 20, 1988

Accepted January 23, 1989

1. Introduction	2287
2. Tyomkin's model of perfect ionic solutions	2288
3. Model of a regular solution in binary melts with a common ion	2289
4. Model of a regular solution in multicomponent systems with a common oxygen anion .	2291
4.1 Kozheurov's concept of regular ionic solutions.....	2291
4.2 Lumsden's concept of regular ionic solutions	2294
4.3 Discussion of experimental values of interaction parameters	2295
5. Model of regular solutions with arbitrary numbers of cations and anions	2298
6. Conclusions	2300
References	2300

The paper presents a review of applications of the model of regular solutions to ionic melts with regard to metallurgical slags. Various theoretical approaches to systems with a single common ion are discussed. A survey of experimentally determined interaction coefficients for basic metallurgical systems is given. Data for the model of regular solutions for arbitrary numbers of cations and anions are briefly discussed.

1. INTRODUCTION

Many metallurgical processes belong to the region of applied physical chemistry; for example, steel industry deals with a combination of selective oxidation and reduction at high temperatures. From the thermodynamic point of view, the most important parameters for controlling the pyrometallurgical reactions are the temperature, the partial pressure of oxygen, and the activities of the components in both condensed phases (in the slag and in the metal phase). Thermodynamic considerations have served metallurgists for a long time to estimate the possible reactions by using apparent equilibrium constants or changes of the Gibbs free energy (determination of the course of the process under study). This method is reliable in the case of binary or ternary slag systems. A survey of thermodynamic models of binary silicate melts was given by Gaskell¹. However, the thermodynamic properties of multicomponent

melts are determined either experimentally or by using the Tyomkin model and the model of regular solutions with a common oxygen anion (Sections 2 and 4).

The aim of this work is a critical evaluation of the present applications of the model of regular solutions, especially to systems with a common oxygen ion. The models of ideal solutions have already been discussed in detail². Therefore, only the basic facts concerning the Tyomkin's model and its relation with regular solutions will be discussed here.

2. TYOMKIN'S MODEL OF PERFECT IONIC SOLUTIONS

The theory of electrolytes elaborated by Debye, Hückel, and Falkenhagen and based on the concept of ionic atmosphere surrounding every ion meets with difficulties even in moderately concentrated solutions of both aqueous and nonaqueous electrolytes, where corrections must be introduced. It cannot be applied to melted electrolytes because of the close proximity of their ions.

Models of melted electrolytes are based on analogies with molecular solutions. A model of perfect ionic solutions was proposed by Tyomkin³, according to whom the cations and the anions are arranged in a quasicrystalline lattice. It is assumed that no other species are present. Thus, it follows that (i) the neighbours of every ion are ions with an opposite charge, (ii) interaction of ions of a given charge with their neighbours is independent of their nature, i.e. the cations among themselves and the anions among themselves are energetically equivalent. Replacement of an ion by another ion of the same sign does not lead to energetic changes in the solution.

The model requires to define molar fractions of the cations and of the anions. A completely dissociated electrolyte, which is electroneutral, consists formally of two individual solutions: one of the cations and one of the anions. Since ions of different sign in the quasicrystalline lattice cannot be interchanged, the calculation of the thermodynamic functions of the solution is restricted to the calculation of the entropy of mixing for the cations and for the anions separately. Their molar fractions are defined as

$$x_j^+ = \frac{n_j^+}{\sum n_i^+}, \quad \sum x_i^+ = 1, \quad (1)$$

$$x_j^- = \frac{n_j^-}{\sum n_i^-}, \quad \sum x_i^- = 1. \quad (2)$$

The superscripts + and - refer to cations and anions. The change of the entropy of mixing is given as $\Delta S = \Delta S^+ + \Delta S^-$, where

$$\Delta S^+ = k \ln W^+, \quad \Delta S^- = k \ln W^-. \quad (3)$$

Here, k is the Boltzmann constant; the thermodynamic probabilities for the cations, W^+ , and for the anions, W^- , are given by the equations

$$W^+ = \frac{(N_A \sum v_i^+ n_i^+)!}{\prod (N_A v_j^+ n_j^+)!}, \quad W^- = \frac{(N_A \sum v_i^- n_i^-)!}{\prod (N_A v_j^- n_j^-)!}, \quad (4)$$

where N_A denotes Avogadro's constant, n_i^+ etc. are molar fractions as above, v_i^- etc. are the corresponding stoichiometric coefficients for fully dissociated salts. By using the Stirling's approximation for factorials of large numbers

$$\ln N! \approx N \ln N - N \quad (5)$$

the following equation can be derived for the entropy of mixing, ΔS_{mix} , corresponding to the formation of a solution from n_1 moles of a salt, $M_{v_1^+}A_{v_1^-}$, and n_2 moles of $N_{v_2^+}B_{v_2^-}$:

$$\Delta S_{\text{mix}} = -R[n_1 \ln(x_M^{v_1^+} x_A^{v_1^-}) + n_2 \ln(x_N^{v_2^+} x_B^{v_2^-})]. \quad (6)$$

For an ideal solution, we have

$$\Delta S_{\text{mix}}^* = -R(n_1 \ln x_1 + n_2 \ln x_2) \quad (7)$$

A perfect ionic solution and an ideal solution differ only by the expression for the entropy of mixing. For systems with a common anion, the molar fraction of the anion is equal to 1 and the molar fractions of the cations are equal to those of the components for $v_1^+ = v_2^+ = 1$. If we define the components so that each one contains only one cation (e.g. for the system $\text{FeO} + \text{Al}_2\text{O}_3 + \text{SiO}_2$ we define the components FeO , $\text{AlO}_{3/2}$, and SiO_2), then Tyomkin's perfect ionic solution is formally identical with an ideal solution.

Although Tyomkin did not consider the presence of complex particles, some authors⁴ have attempted to generalize this model for ideal mixtures of O^{2-} and SiO_4^{4-} anions.

Tyomkin's model has been used mainly in metallurgy (determination of activities in melted metallurgical slags, reactions in them, reactions between melted slag and melted metal, evaluation of phase diagrams, etc.). However, the weak point of the model is the assumption of energetic equivalence of ions of the same sign, which is not satisfied in real systems.

3. MODEL OF REGULAR SOLUTIONS IN BINARY MELTS WITH A COMMON ION

A real solution for which the entropy of mixing and the volume of mixing are ideal and the enthalpy of mixing is non-ideal is called a "strictly regular solution". In the

text below, we shall use the notion "regular solution" introduced by Hildebrand⁵.

The theory of regular solutions was first applied to ionic melts by Hildebrand and Salstrom⁶. By using statistical thermodynamics, they derived the following equation for a binary system with a common ion (e.g. anion):

$$\Delta G_1^E = x_2^2(2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22}) - T \Delta S_1^E - p \Delta V_1^E. \quad (8)$$

Here, ΔG_1^E , ΔS_1^E and ΔV_1^E denote changes of additional functions, ε_{11} , ε_{22} , and ε_{12} are partial molar energies characterizing the bond between the cations of the components (e.g. in the system AgBr–MBr the bonds $\text{Ag}^+ - \text{Ag}^+$, $\text{M}^+ - \text{M}^+$, and $\text{Ag}^+ - \text{M}^+$), T denotes absolute temperature and p pressure.

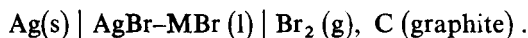
From the definition of regular solutions and from Eq. (8) it follows that

$$\Delta G_1^E = RT \ln \gamma_1 = \alpha_{12} x_2^2, \quad (9)$$

where γ_1 is the activity coefficient and α_{12} interaction parameter.

Since α_{ij} is not equal to zero in real solutions, the activity of species i is not equal to its molar fraction ($a_i \neq x_i$). The standard state corresponds mostly to the pure liquid species i at the temperature and pressure of the system.

The linear dependence of G_1^E on x_2^2 was first experimentally verified in binary liquid melts⁶ AgBr–MBr ($M = \text{Li}, \text{Na}, \text{K}, \text{Rb}$) by using the galvanic cell



At standard pressure of Br_2 and in the standard state of Ag, Eq. (9) and the Nernst equation can be combined to give

$$\Delta G_1^E = nF(E - E^0) - RT \ln x_1(\text{AgBr}) = \alpha_{12} x_2^2(\text{MBr}). \quad (10)$$

For AgBr–MBr ($M = \text{L}, \text{Na}, \text{K}, \text{Rb}$) the values of α_{12} were determined as 7 870 4 400, –6 200, and –10 800 J mol^{-1} , respectively. Based on these results, Hildebrand and Salström⁶ assumed that all the mentioned systems have the properties of regular solutions. However, later it turned out that the difference between the calorimetric enthalpy of mixing and the value of ΔG_1^E obtained from electrochemical measurements in the AgBr–RbBr system is not equal to zero⁷. Thus, the linear dependence of ΔG_1^E on x_2^2 is a necessary, but not sufficient condition from the point of view of regular behaviour. This was not taken into account (as shown below on examples of metal-lurgical slags) and the values of α_{ij} according to different authors are considerably different.

4. MODEL OF A REGULAR SOLUTION IN MULTICOMPONENT SYSTEMS WITH A COMMON OXYGEN ANION

4.1 Kozheurov's concept of regular ionic solutions

Kozheurov⁸ started from older works^{3,6} and elaborated first a theory for melted electrolytes with a single common cation or anion. The theory is based on statistical thermodynamics. In the first approximation, the theory of ionic regular solutions assumes that the thermal effect during formation of a ionic solution is due to the different character of the bonds of different cations with the same anion or of different anions with the same cation. The inner energy of the system is expressed as⁸

$$U = \sum_{i=1}^k x_i U_i + \sum_{i=1}^{k-1} \sum_{j=i+1}^k x_i x_j \alpha_{ij}. \quad (11)$$

Here, U_i (J mol⁻¹) denotes inner molar energy of species i (compound), k is the number of cationic (or anionic) species in the completely dissociated electrolyte, x_i and x_j are molar fractions of the corresponding ions. The quantity α_{ij} is, according to Kozheurov, the energy of mixing defined as

$$\alpha_{ij} = N_A [(\varepsilon_{ij} - \varepsilon_{ii}) - (\varepsilon_{jj} - \varepsilon_{ji})]. \quad (12)$$

The terms in parentheses correspond to energetic changes during replacement of an ion of a pure component (ε_{ii}) by another sort of ion (ε_{ij}), and analogously for ε_{jj} and ε_{ji} .

The definition of the configuration entropy is in agreement with the Tyomkin's model of perfect ionic solutions. The inner energy of a regular solution and the entropy of a perfect solution thus represent a starting point for the derivation of the Helmholtz or Gibbs energy of the solution, the corresponding partial molar quantities, additional thermodynamic quantities, activities, and activity coefficients of the solution constituents.

If the volume changes are neglected, the additional thermodynamic quantities of an ionic solution are expressed by the second term on the right-hand side of Eq. (11)

$$\Delta U^E = \Delta H^E = \Delta G^E = \sum_{i=1}^{k-1} \sum_{j=i+1}^k x_i x_j \alpha_{ij}. \quad (13)$$

On multiplying Eq. (13) by the total number of moles of cations (or anions) in solution, we obtain

$$\Delta G^E \sum_{i=1}^k v_i n_i = \sum_{i=1}^{k-1} \sum_{j=i+1}^k n_i v_i n_j v_j \alpha_{ij} / \sum_{i=1}^k v_i n_i. \quad (14)$$

According to thermodynamics, we have for ion species l

$$\frac{\partial}{\partial n_l} (\Delta G^E \sum_{i=1}^k v_i n_i) = RT \ln \gamma_l. \quad (15)$$

On introducing here Eq. (14) we obtain

$$\begin{aligned} RT \ln \gamma_l = & \left[v_l \left(\sum_{i=1}^{l-1} v_i n_i \alpha_{il} + \sum_{i=l+1}^k v_i n_i \alpha_{il} \right) \sum_{i=1}^k v_i n_i - \right. \\ & \left. - v_l \sum_{i=1}^{k-1} \sum_{j=i+1}^k v_i n_i v_j n_j \alpha_{ij} \right] / \left(\sum_{i=1}^k v_i n_i \right)^2. \end{aligned} \quad (16)$$

The ionic fraction is defined as

$$x_i = v_i n_i / \sum_{i=1}^k v_i n_i. \quad (17)$$

From Eqs (16) and (17) we obtain

$$RT \ln \gamma_l = v_l \left(\sum_{i=1}^{l-1} x_i \alpha_{il} + \sum_{i=l+1}^k x_i \alpha_{il} - \sum_{i=1}^{k-1} \sum_{j=i+1}^k x_i x_j \alpha_{ij} \right). \quad (18)$$

The chemical potential is then given as

$$\mu_l = \mu_l^0 + RT \ln \gamma_l. \quad (19)$$

Here, μ_l^0 denotes chemical potential of a perfect ionic solution according to the Tyomkin's model

$$\mu_l^0 = v_l (F_l^0 + RT \ln x_l), \quad (20)$$

$F_l^0 = G_l^0$ denotes Gibbs (Helmholtz) energy, v_l number of ions of species l formed by complete dissociation.

The first approximation of the theory of regular ionic solutions involves only the first coordination sphere of different ions around a central cation. The coordination number is considered the same for all cation species, usually $z = 12$. Systems with a common cation are analogous. Kozheurov⁸ developed further the quasichemical approximation for binary and ternary systems with regard to different sorts of cations or anions in the system, and discussed the influence of other coordination spheres on the thermodynamic functions of the melted electrolyte. His approach to the definition of the mean activity coefficient of a constituent is new. In aqueous solu-

tions, the mean activity coefficient is usually defined⁸ as

$$\gamma_{\pm} = [a/(x_+^{v_+} x_-^{v_-})]^{1/(v_+ + v_-)}. \quad (21)$$

Here, a denotes the activity, x_+ and x_- are molar fractions of cations and anions of a dissociated salt, v_+ and v_- are their stoichiometric numbers. This definition cannot be applied to systems with a common anion, and according to Kozheurov⁸ it is necessary in such a case to set $v_- = 0$, since this quantity does not occur in the definition of the chemical potential (Eqs (19, 20)). Similarly, for systems with a common cation we have⁸ $v_+ = 0$. A general definition of the activity coefficient cannot be given; it depends on the expression for the chemical potential in the given ionic solution.

The mixing energies α_{ij} occurring in Kozheurov's theory in the expressions for the chemical potential are, according to experimental data, temperature-dependent. The author gave a semiquantitative explanation for this dependence based on statistical thermodynamics (i.e. on an approximate expression for the partition function of a melted electrolyte).

The Kozheurov's model is represented by a strictly regular solution with an entropy of mixing identical to the Tyomkin's model. Deviations from ideality, represented by the latter, are manifested by non-zero values of additional enthalpy and Gibbs energy in the Kozheurov's model. The mathematical formulation of this model implies formally its transition into the Tyomkin's model when all mixing energies are equal to zero.

From the theoretical point of view, different interaction energies between different species lead not only to changes of the additional enthalpy and Gibbs energy; they also disturb the random statistical arrangement and lead to non-zero values of additional entropy. The model of a strictly regular solution can be accepted on the assumption that the entropy changes are small compared with the enthalpy changes. It should be noted that the same considerations apply to non-ionic melts, e.g. melted metal alloys.

The possibility of an experimental evidence depends on the method and accuracy of the determination of mixing energies in melted electrolytes. Experimental methods in the region of medium temperatures are demanding and their accuracy is lower compared to measurements in aqueous electrolytes at usual temperatures. The determination of mixing energies will be dealt with in Section 4.3.

In applying the theory to melted metallurgical slags with a high content of SiO_2 (acidic slags), Kozheurov admits the possibility of a preferential (not statistically random) grouping of oxygen anions around the silicium ions and polymeration of silicate ions. This situation is taken into account by a semiempirical correction of the thermodynamic functions represented by additional energy of mixing⁸. The correction was verified by calculation of the limited solubility in binary silicate melts.

4.2 Lumsden's concept of regular ionic solutions

Lumsden^{9,10} contributed significantly to extending the model of regular solutions to metallurgical melts. He used first the model to describe binary metal alloys⁹. In deriving a model for oxide systems he used, by analogy to Kozheurov⁸, statistical thermodynamics. He proved theoretically that binary systems of the type $XO-YO_{1.5}$ containing cations in the second and third oxidation state have the properties of a regular solution. He assumed that the system $FeO-Fe_2O_3-SiO_2$ forms a regular solution and contains cations Fe^{2+} , Fe^{3+} and Si^{4+} which are randomly distributed in the quasicrystalline lattice of oxygen anions. The author considers FeO , $FeO_{1.5}$ and SiO_2 as formal components of the system with a common oxygen anion, hence the coefficient ν expressing the number of cations formed by dissociation of an oxide molecule need not be introduced.

Lumsden derived the dependence of the activity coefficients of species i, j, k on the composition and temperature as follows. The change of the additional enthalpy ΔH^E in a ternary regular solution is given as

$$\Delta H^E = (\alpha_{ij}n_i n_j + \alpha_{ik}n_i n_k + \alpha_{jk}n_j n_k) / (n_i + n_j + n_k). \quad (22)$$

Partial differentiation of Eq. (22) with respect to the content of the particular species on the assumption that $\Delta S^E = 0$ leads to the following expression for the activity coefficient of species i :

$$RT \ln \gamma_i = (x_j + x_k) (\alpha_{ij}x_j + \alpha_{ik}x_k) - \alpha_{jk}x_j x_k. \quad (23)$$

Analogous expressions hold for species j and k . Generalization of this procedure for a polycomponent system gives

$$RT \ln \gamma_i = \sum_j \alpha_{ij} x_j^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) x_j x_k. \quad (24)$$

This general expression can only be used if no strong interactions exist between the components of the polycomponent system.

According to Lumsden¹⁰, the activity coefficient in the binary system $CaO-SiO_2$ can be calculated as

$$RT \ln \gamma_i = \alpha_{ij} x_j^2 - x_i x_j^2 (3x_i - 1) \alpha_{ij}^2 / 13 RT. \quad (25)$$

It can be shown that Eqs (18) and (24) are identical. To this end, the formal content of the oxides must be expressed in an analogous way ($\nu_i = 1$) and the molar fraction x_i in Eq. (18) must be expressed as

$$1 - \sum_{i \neq l} x_i = x_l. \quad (26)$$

Since Lumsden¹⁰ started from the same theoretical assumptions and arrived at the same conclusions as Kozheurov⁸, the priority belongs to the latter, although Lumsden's work has been more widely acknowledged.

4.3 Discussion of experimental values of interaction parameters

The interaction parameter α_{ij} expresses quantitatively the deviation from Tyomkin's model of perfect ionic solutions. The model of regular solutions assumes equal values of α_{ij} for the same combinations of ions i and j regardless of the composition.

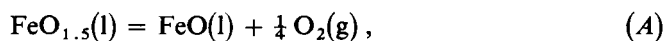
A theoretical calculation of the interaction parameters α_{ij} is a problem of quantum mechanics. Its solution is not known and there is only little hope that it will be known in the future. Since the interaction parameters are determined by experimental methods, the model under discussion is semiempirical in substance.

The interaction parameters α_{ij} can be determined by

- measurement of the electromotive force of galvanic cells⁶,
- from the liquidus curves of phase diagrams¹¹,
- by measurement of physical properties (viscosity, surface tension)¹²,
- from combined chemical and phase equilibria for reactions of gases with liquids^{13,14}.

The values of α_{ij} are then determined by regression methods based on the corresponding model.

The last of the mentioned methods will serve us to demonstrate some inadequacies in the determination of α_{ij} especially in multicomponent systems. Shim and Bayn-ya¹³ determined the interaction parameters from the redox equilibrium between Fe^{2+} and Fe^{3+} . They determined the interactions ($\text{Fe}^{2+}-\text{Si}^{4+}$) and ($\text{Fe}^{3+}-\text{Si}^{4+}$) in the system $\text{FeO}-\text{FeO}_{1.5}-\text{SiO}_2$ (subscripts 1, 2, 3) as follows. The equilibrium constant for the reaction



$$\Delta G^0 = -126\,820 - 53.01 T \quad (\text{J mol}^{-1}) \quad (27)$$

is given by the equation

$$\begin{aligned} RT \ln K &= RT \ln [x(\text{FeO})/x(\text{FeO}_{1.5})] + 0.25 RT \ln p(\text{O}_2) + \\ &+ RT \ln [\gamma(\text{FeO})/\gamma(\text{FeO}_{1.5})]. \end{aligned} \quad (28)$$

From the general equation (24) we express $\gamma(\text{FeO})$ and $\gamma(\text{FeO}_{1.5})$ as

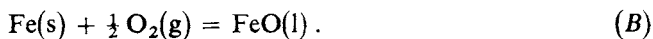
$$\begin{aligned} RT \ln \gamma(\text{FeO}) &= \alpha_{12}x^2(\text{FeO}_{1.5}) + \alpha_{13}x^2(\text{SiO}_2) + \\ &+ (\alpha_{12} + \alpha_{13} - \alpha_{23}) x(\text{FeO}_{1.5}) x(\text{SiO}_2), \end{aligned} \quad (29)$$

$$RT \ln \gamma(\text{FeO}_{1.5}) = \alpha_{12}x^2(\text{FeO}) + \alpha_{23}x^2(\text{SiO}_2) + \\ + (\alpha_{12} + \alpha_{23} - \alpha_{13})x(\text{FeO})x(\text{SiO}_2). \quad (30)$$

By combining Eqs (27–30) and using the known value of $\alpha_{12}(\text{Fe}^{2+}-\text{Fe}^{3+}) = -18\,660 \text{ J}$ (ref.¹⁰) we obtain

$$(\alpha_{23} - \alpha_{13})x(\text{SiO}_2) = 18\,660[x(\text{FeO}) - x(\text{FeO}_{1.5})] + \\ + RT \ln [x(\text{FeO})/x(\text{FeO}_{1.5})] + 0.25 RT \ln p(\text{O}_2) + \\ + 126\,820 - 53.01 T = Y. \quad (31)$$

The difference of $\alpha_{23} - \alpha_{13}$ is determined from the slope of the dependence of Y on $x(\text{SiO}_2)$. The value of $\alpha_{13}(\text{Fe}^{2+}-\text{Si}^{4+})$ is found in an analogous way from the equation



The interaction parameters thus found are used in calculating other values of α_{ij} in quaternary or multicomponent oxide systems, but always on the basis of the chemical reactions (A) and (B).

This approach certainly enlarged our knowledge of the interaction parameters; however a considerable uncertainty arises from the fact that all the found values of α_{ij} are based on the value of $\alpha(\text{Fe}^{2+}-\text{Fe}^{3+}) = -18\,660 \text{ J}$, on the value of ΔG^0 for reactions (A) and (B), and on the ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and value of $p(\text{O}_2)$ at high temperatures (compare Eq. (31)). The authors^{13,15} themselves arrived later at more accurate values of α_{ij} , which differ appreciably from the original ones (Table I). Thus, it seems that these interaction parameters have the character of regression coefficients for the given set of experiments and the melt need not have the properties of a regular solution (cf. Section 3).

A survey of the interaction parameters α_{ij} of the components of metallurgical slags is given in Table I. There are considerable differences between the data of different authors. On comparing the values of α_{ij} according to Kozheurov⁸ and Ban-ya¹³⁻¹⁵ for the basic metallurgical system $\text{FeO}-\text{FeO}_{1.5}-\text{CaO}-\text{MgO}-\text{MnO}-\text{SiO}_2$ it turns out that none of them is in agreement. It is apparent that the assumption⁸ of ideal behaviour in the system $\text{CaO}-\text{MgO}-\text{MnO}$ ($\alpha_{ij} \neq 0$) is not fulfilled, since other authors give values of α_{ij} up to about -10^5 J (Table I).

Similarly, the values of $\alpha(\text{Fe}^{2+}-\text{Fe}^{3+})$ determined from the same experimental data¹⁶ by different authors^{8,10} differ by more than 250%. Interestingly enough, this parameter was used to construct the whole ensemble of α_{ij} .

At present, ensembles of α_{ij} values are derived on the assumption that the melted electrolyte shows regular behaviour. There is a tendency to confirm this situation

TABLE I
Published values of interaction energies

Couple	α_{ij} , J mol ⁻¹	Ref.	Couple	α_{ij} , J mol ⁻¹	Ref.		
Fe ²⁺ -Fe ³⁺	-48 530 ^a	8	Fe ³⁺ -P ⁵⁺	14 640 ± 6 000	28		
	-18 660	10		Na ⁺ -Si ⁴⁺	-111 290	18	
	0	17			Na ⁺ -P ⁵⁺	-50 210	31
	-6 230	21				Mg ²⁺ -Ca ²⁺	18 830 ± 8 000
Fe ²⁺ -Na ⁺	19 250	18			-100 420		15
	Fe ²⁺ -Mg ²⁺	0	8	Mg ²⁺ -Mn ²⁺	-23 850, 38 900	30	
		12 850 ± 8 000	13			61 920	32
	33 470	15	Mg ²⁺ -Si ⁴⁺	-113 040, -188 400	8		
Fe ²⁺ -Ca ²⁺	0	8			-66 950	15	
	-31 380	14			-127 600 ± 8 000	13	
	-14 650	15, 21		Mg ²⁺ -P ⁵⁺	-37 660	15	
	-50 210 ± 12 000	19	Ca ²⁺ -Al ³⁺		-83 680	21	
-48 120	20			-48 120 ± 10 000	33		
Fe ²⁺ -Mn ²⁺	0	8, 17, 23-26			33		
	7 110	22	Ca ²⁺ -Ti ⁴⁺	-167 360	20		
Fe ²⁺ -Al ³⁺	-16 740	21		Ca ²⁺ -Si ⁴⁺	-112 970, -37 680	8	
	-1 760	24, 27			-133 900	15	
Fe ²⁺ -Ti ⁴⁺	-41 840	17		-138 500	17		
	-37 660 ± 8 000	19	Ca ²⁺ -P ⁵⁺	-272 000 ± 8 000	19		
Fe ²⁺ -Si ⁴⁺	0	8			-167 360	21	
	-41 840	10, 24, 27			-125 500 ± 12 000	34	
	-28 030, -21 750	17		Mn ²⁺ -P ⁵⁺	-201 000	8	
	-41 804 ± 8 000	19			-251 000	15	
	-35 500	21	Mn ²⁺ -Ca ²⁺	0	8		
Fe ²⁺ -P ⁵⁺	-31 380 ± 4 000	28			-16 740	20	
	Fe ³⁺ -Na ⁺	-74 890		18		-92 050	35
-156 900		29	Mn ²⁺ -Al ³⁺	-20 920	24, 27		
Fe ³⁺ -Mg ²⁺	-23 510 ± 8 000	13		Mn ²⁺ -Ti ⁴⁺	-66 950	24	
	-2 930	15	Mn ²⁺ -Si ⁴⁺		0, -41 868	8	
Fe ³⁺ -Ca ²⁺	-95 810, -102 500	15			-65 270	17	
	-64 850	21			-100 400	20	
	-114 650 ± 20 000	19					

TABLE I
 (Continued)

Couple	α_{ij} , J mol ⁻¹	Ref.	Couple	α_{ij} , J mol ⁻¹	Ref.
Fe ³⁺ -Mn ²⁺	-56 480	22		-75 310	22
	-12 550	30		-76 820	24, 27
Fe ³⁺ -Al ³⁺	25 100	21	Mn ²⁺ -P ⁵⁺	-108 800	30
Fe ³⁺ -Ti ⁴⁺	1 260 ± 16 000	19	Al ³⁺ -Si ⁴⁺	-62 760	21
	17 570	23		-52 300	24, 27
Fe ³⁺ -Si ⁴⁺	13 390	10	Si ⁴⁺ -P ⁵⁺	83 680	31
	24 270	17			
	32 640 ± 16 000	19			
	20 200	21			

in complicated systems by the choice of suitable, experimentally not evidenced and, eventually, adapted interaction parameters. This may lead to a formal agreement of the model with experimental data, but not to elucidation of the nature of the interaction parameters.

5. MODEL OF REGULAR SOLUTIONS WITH ARBITRARY NUMBERS OF CATIONS AND ANIONS

Kozheurov and coworkers³⁶ developed further the model of regular ionic solutions: first for a melt consisting of two cationic and two anionic species, then for systems involving arbitrary numbers of cations and anions^{37,38}. The basic idea is that the energy of cation-anion interaction depends on the presence of all other ions in the melt. This concept is formulated mathematically by the series

$$\begin{aligned} \varepsilon_{ij} = & \varepsilon_{ij}^0 + \sum_{m=1}^{i-1} \frac{\partial \varepsilon_{ij}}{\partial x_m} x_m + \sum_{m=i+1}^k \frac{\partial \varepsilon_{ij}}{\partial x_m} x_m + \\ & + \sum_{n=1}^{j-1} \frac{\partial \varepsilon_{ij}}{\partial y_n} y_n + \sum_{n=j+1}^l \frac{\partial \varepsilon_{ij}}{\partial y_n} y_n \end{aligned} \quad (32)$$

$$E_{ij} = N_A Z \varepsilon_{ij}; \quad E_{ij}^0 = N_A Z \varepsilon_{ij}^0. \quad (33)$$

Here, E_{ij} denotes internal energy corresponding to one mole of cations formed by dissociation of a component of the melted electrolyte, E_{ij}^0 is the internal energy of the pure component defined similarly, Z is the coordination number of the quasicrystal-line lattice, which is the same for all components, k is the number of cationic species,

l the number of anionic species in the system, x_m and y_n denote molar fractions of cations and anions.

The configuration entropy is in accord with the Tyomkin's model. Equation (32) leads after a longer rearrangement to complicated expressions for the thermodynamic functions, activities, activity coefficients, and chemical potentials^{37,38}. The results were verified by studies of the solubility of hydrogen in slags containing FeO, FeS, CaO, and CaS, equilibrium between water vapour and slags consisting of CaO, Al₂O₃, and SiO₂, distribution of sulphur in the basic slag FeO, MnO, CaO, SiO₂, FeS etc.

A different approach to the thermodynamics of regular ionic solutions represented by melted electrolytes was used in ref.³⁹. The basic idea can be more simply formulated for a system of two cationic and two anionic species. If we consider, e.g., a cation K_1 in a quasicrystalline lattice with a coordination number Z , then the probability of occurrence of r cations K_1 and $Z-r$ cations K_2 as the closest neighbours of the cation K_1 mentioned can be expressed by the binomial distribution function

$$P_{K_1}(r) = \binom{Z}{r} x_1^r x_2^{Z-r}. \quad (34)$$

Here, x_1 and x_2 are molar fractions of cations K_1 and K_2 . A similar consideration applies to an anionic quasicrystalline lattice with a coordination number ξ , anion A_1 and ϱ neighbouring anions:

$$P_{A_1}(\varrho) = \binom{\xi}{\varrho} y_1^\varrho y_2^{\xi-\varrho}. \quad (35)$$

Since exchange of ions of different sign in the quasicrystalline lattice is not possible, both probabilities are considered as independent. Further it is assumed that the interaction energy of an ion depends linearly on the number of neighbouring ions of the same kind. After an involved mathematical procedure, the thermodynamic functions of the solution are derived. By using a multinomial distribution, the model was generalized for systems with arbitrary numbers of cationic and anionic species. The resulting equations are complicated and involve mixing energies defined in agreement with the Kozheurov's model. In limiting cases – a common anion or a common cation – the Kozheurov's model is obtained, and when the mixing energies are set equal to zero, the Tyomkin's model results. The criteria of thermodynamic consistency, published by Malinovský⁴⁰, were checked with the aim to calculate the liquidus curves of phase diagrams. The model satisfies also these criteria. The models of Kozheurov and of ref.³⁹ corresponding to systems with general numbers of cations and anions differ by the additional Gibbs energy. The configuration entropies are in mutual agreement.

6. CONCLUSIONS

The model of regular ionic solutions is at present a suitable tool permitting to interpret experimental data and – with some care – to predict some characteristics of melted electrolytes. It is probable that, in near future, the model will be defined with more precision, or possibly replaced by more elaborated models, which already have found application in the field of relatively simple systems of melted metals and salts.

REFERENCES

1. Gaskell D. R.: *Can. Met. Quart.* 20, 3 (1981).
2. Horsák I., Sláma I.: *Chem. Listy* 77, 1138 (1983).
3. Tyomkin M. I.: *Acta Physicochim. URSS* 20, 411 (1945).
4. Masson C. R.: *Can. Met. Quart.* 20, 27 (1981).
5. Hildebrand J. H.: *J. Am. Chem. Soc.* 51, 66 (1929).
6. Hildebrand J. H., Salström E. J.: *J. Am. Chem. Soc.* 54, 4257 (1932).
7. Markov B. F. in: *Termodinamika rasplavlennykh soleyevykh smesei*, p. 120. Naukova dumka, Kiev 1974.
8. Kozheurov V. A.: *Termodinamika metalluricheskikh shlakov*. Metallurgizdat, Sverdlovsk 1955.
9. Lumsden J.: *Thermodynamics of Alloys*. Inst. of Metals, London 1952.
10. Lumsden J. in: *Physical Chemistry of Process Metallurgy* (G. R. Pierre, Ed.), Vol. I, p. 165. Interscience Publishers, New York 1961.
11. Kalousek J., Kalousovká G.: *Chem. Papers* 41, 465 (1987).
12. Bochnák R., Kalousek J., Kupčák J.: *Silikáty* 31, 317 (1987).
13. Shim J. D., Ban-ya S.: *Tetsu-to-Hagane* 67, 1745 (1981).
14. Ban-ya S., Shim J. D.: *Can. Met. Quart.* 23, 319 (1983).
15. Ban-ya S., Hino M.: *Tetsu-to-Hagane* 73, 476 (1987).
16. Darken L. S., Gurry R. W.: *J. Am. Chem. Soc.* 68, 798 (1946).
17. Smith I. C., Bell H. B.: *Trans. Bull. Inst. Min. Metall.* 79, C 253 (1970).
18. Ban-ya S., Hino M., Takezoe H.: *Tetsu-to-Hagane* 71, 1765 (1985).
19. Ban-ya S., Chiba A., Hikosaka A.: *Tetsu-to-Hagane* 66, 1484 (1980).
20. Suito H., Inoue R.: *Trans. Iron Steel Inst. Jpn.* 24, 257 (1984).
21. Altman R.: *Trans. Bull. Inst. Min. Metall.* 87, C 23 (1978).
22. Ban-ya S., Hino M., Yuge N.: *Tetsu-to-Hagane* 71, 853 (1985).
23. Smith I. C., Bell H. B.: *Trans. Bull. Inst. Min. Metall.* 80, C 55 (1971).
24. Martin E., Bell H. B.: *Trans. Bull. Inst. Min. Metall.* 83, C 193 (1974).
25. Yavoiskii V. I.: *Teoriya protsesov proizvodstva stali*. Metallurgizdat, Moskva 1967.
26. Yesin O. A., Geld P. V.: *Fizicheskaya khimiya pirometallurgicheskikh protsesov*. Metallurgiya, Moskva 1968.
27. Ivanchev I., Bell H. B., Sommerville I. D.: *Rudobiv i Metall. (Bul.) No 1*, 34 (1974).
28. Ban-ya S.: *Tetsu-to-Hagane* 63, 1809 (1977).
29. Suito H., Inoue R.: *Tetsu-to-Hagane* 70, 553 (1984).
30. Lumsden J.: *Thermodynamics of Molten Salt Mixtures*. Academic Press, London 1966.
31. Ban-ya S., Hino M., Takezoe H.: *Trans. Iron Steel Inst. Jpn.* 25, 1122 (1985).
32. Banyan S.: *Tetsu-to-Hagane* 72, S 223 (1986).
33. Yavoiskii V. I., Savov P. Kh., Luzgin V. P., Ivanchev I., Yerinin Kh.: *Izv. Vyssh. Ucheb. Zaved., Chyorn. Metall.* 3, 27 (1976).

34. Maruhashi S.: *Trans. Iron Steel Inst. Jpn.* *12*, 197 (1972).
35. Ban-ya S.: *Tetsu-to-Hagane* *71*, 933 (1985).
36. Kozheurov V. A. in: *Termodinamika i stroenie rastvorov*, p. 186. Izd. Akad. Nauk SSSR, Moskva 1959.
37. Kozheurov V. A.: *Izv. Vyssh. Ucheb. Zaved., Chyorn. Metall.* *10*, 5 (1965).
38. Antonenko V. I., Kozheurov V. A.: *Izv. Vyssh. Ucheb. Zaved., Chyorn. Metall.* *11*, 14 (1965).
39. Kalousek J.: Report SPV IV-4-4/03-07. Institute of Mining and Metallurgy, Ostrava 1985.
40. Malinovský M.: *Chem. Zvesti* *28*, 489 (1974).

Translated by K. Micka.