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ON CALCULATIONS OF ACTIVITIES OF CHEMICAL INDIVIDUALS FROM DISORDER MODELS

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ABSTRACT

Assuming the validity of the law of mass action for particles, the relationships for the calculation of the activities of chemical individuals from the concentration of particles in a homogeneous system, are derived using the transformation of baricentric coordinates. These relationships can be applied to general disorder models, and they can serve for the selection of the correct and optimum methods for the comparison between disorder models and experimental data. Possible methods of application to binary and ternary systems are discussed.

INTRODUCTION

The disorder models (Fehlordungsmodellen) are, for the most part, derived under the assumption that the concentrations of the particles obey the law of mass action. According to this law the constancy of the product, K_L^X, in the equation

$$K_L^X = \prod_{j,L} X_j^{\nu_j} = \text{constant} \tag{1}$$

where X_j is the concentration, and ν_j is the stoichiometric coefficient of the jth type of particle (negative for "starting" particles), ought to be fulfilled for the reaction [L]

$$\prod_{j,L} \nu_j J = 0 \qquad [L]$$

between the different types of particle, J, for the system in equilibrium at a given temperature.

From the definition of the activity particle a_j, of the jth type of the constancy of the activity product results

$$K_L^a = \prod_{j,L} a_j^{\nu_j} = \text{constant} \tag{2}$$

Considering this fact, there is a parallel validity of the relationship between concentration and activity for every type of particle in the system, *i.e.*

$$a_j/X_j = \text{constant} \tag{3}$$

which is a sufficient condition for the validity of Eqn. 1.

As it is known from the statistical treatment, Eqn. 3 is valid for the following particular cases (where X_j means molar fraction): (*i*) the concentration of particles is near to zero (Henry's law); *(ii)* the pair interactions of particles are compensated* (Raoult's law); and *(iii)* for ionic substances, the pair interactions between ions of the same sign of charge are compensated (Tĕmkin[2]).

Although the more general and more precise statistical models do better justice to the real behaviour of substances, the application of disorder models as the first step of a quasi-chemical approach, is still important. Driessens[3] has shown, after thorough compilation, that numerous solid solutions obey the law of mass action for particles.

Driessens[4], comparing the disorder model of solid solutions of Mn_3O_4–Co_3O_4 with the literature data about the activities, has used the relationships $a_{Co_3O_4} = \frac{1}{4}[Co_A^{2+}]\cdot[Co_B^{3+}]^2$ and $a_{Mn_3O_4} = \frac{1}{4}[Mn_A^{2+}]\cdot[Mn_B^{3+}]^2$ (where the particle type in square brackets, $[J]$, means the number of particles per one spinel formula $A_xB_{3-x}O_4$), for the calculation of the activities of the chemical individuals Co_3O_4 and Mn_3O_4, as based on the assumption of strictly normal cation distributions in both of the pure components. Schmalzried and Treťjakov[5], among others, have calculated the activity of magnetite in Fe_3O_4–$NiFe_2O_4$ solid solutions, employing the correlation corresponding to the strictly inverse distribution in pure magnetite, *i.e.*, $a_{Fe_3O_4} = [Fe_B^{3+}]\cdot[Fe_B^{3+}]\cdot[Fe_A^{2+}]$

There arises the question of how to calculate the activity of chemical individuals when the more general assumptions are used. It can be seen from the available literature, that relations for the calculations of the activity of chemical individuals from particle concentrations, are performed only for the particular cases, but no general approach is reported. The establishing of more general relations is the aim of the present paper.

EXPERIMENTAL AND RESULTS

Homogeneous systems with chemical individuals as components

The Gibbs free energy of an *n*-component homogeneous system, in equilibrium, at constant temperature (*T*) and pressure (*P*), is given by

$$G = \sum_{i=1}^{n} \mu_i n_i \tag{4}$$

where $\mu_i = (\delta G/\delta n_i)_{T,P,n_{k\neq j}=\text{constant}}$ is the chemical potential, and n_i is the mole number of the *i*th component (chemical individual). When the total number of moles $n = \sum_{i=1}^{n} n_i$ and the mole fraction of the *i*th component $X_i = n_i/n$, then the integral molar Gibbs free energy G_m is given by

$$G_m = G/n = \sum_{i=1}^{n} \mu_i X_i \tag{5}$$

The chemical potential μ_i is commonly separated into two terms, *i.e.*

$$\mu_i = \mu_i^0 + RT \ln a_i \tag{6}$$

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* *e.g.*, for the system constituted from two sorts of particles A and B, compensation occurs if the relation $2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB} = 0$ is valid[1].

The first term, μ_i^0, is called the standard chemical potential, and is equal to the molar Gibbs free energy of the pure ith component; it is independent of composition. The second term includes the activity as a function of the molar fractions X_i. Then from Eqns. 5 and 6

$$G_m = \sum_{i=1}^{n} X_i(\mu_i^0 + RT \ln a_i) \tag{7}$$

The integral Gibbs free energy of mixing is defined as

$$\Delta G^{\text{mix}} = RT \sum_{i=1}^{n} X_i \ln a_i \tag{8}$$

On considering point R of the homogeneous region of the system which corresponds to the composition expressed by the molar fractions X_i^R, then the Gibbs free energy of mixing at this point is given by

$$\Delta G_R^{\text{mix}} = RT \sum_{i=1}^{n} X_i^R \ln a_i^R \tag{9}$$

where a_i^R are the activities of the components at the composition point R.

A system of this composition represents a pure chemical substance R, which need not be a chemical individual in the ordinary sense. It is not erroneous to determine the molar Gibbs free energy at the point R as the standard chemical potential of substance R, *i.e.*

$$G_m^R = \sum_{i=1}^{n} \mu_i^0 X_i^R + RT \sum_{i=1}^{n} X_i^R \ln a_i^R = \mu_R^0 \tag{10}$$

In addition, the original n-component system can be divided into n sub-systems, in which one of the original components is always substituted by the new component, the chemical substance R. Then for a sub-system, where the nth component is substituted, we have

$$G_m = \sum_{i=1}^{n-1} \mu_i Y_i - \mu_R Y_R \tag{11}$$

where Y_i and Y_R are the molar fractions corresponding to the new choice of components. According to the transformation of baricentric coordinates, it can be found that

$$Y_i = X_i - X_i^R \times X_n/X_n^R \text{ and } Y_R = X_n/X_n^R \tag{12}$$

The chemical potential of substance R, μ_R can be introduced symmetrically to Eqn. 6

$$\mu_R = \mu_R^0 + RT \ln a_R \tag{13}$$

using the quantity a_R, which can be called the activity of the substance R. From

Eqns. 9–13, the following relations are obtained

$$\ln a_R = \sum_{i=1}^{n} X_i^R \ln(a_i/a_i^R)$$
$$\ln a_R = \Delta G_R^{\text{mix}}/RT - \sum_{i=1}^{n} X_i^R \ln a_i \tag{14}$$

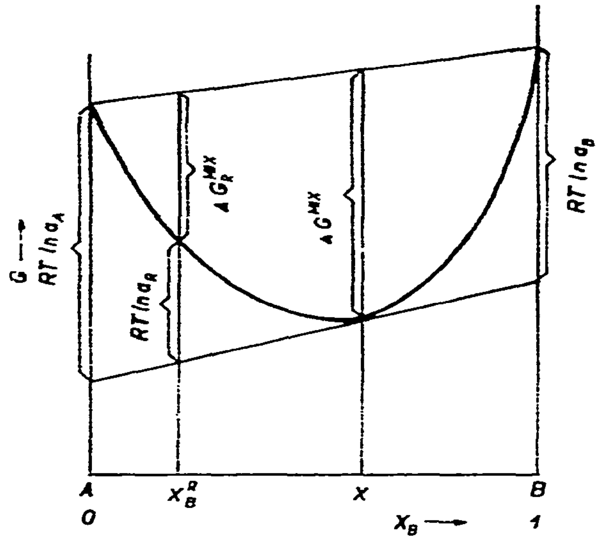

Fig. 1. The geometrical representation of the relationship between Gibbs free energy of mixing and the activity of components (a_A and a_B), and the activity (a_R) of the intermediate member of the solid solutions A–B.

The geometrical representation of the relationships between a_R, a_i, X_R, X_i, ΔG_R^{mix}, ΔG_R^{mix} in the binary system is given in Fig. 1.

Homogeneous systems with particles as components

Considering the same homogeneous system as above in equilibrium, but with particles as components, the number of particle types, m, is usually greater than n. The Gibbs free energy of the system is given by

$$G = \sum_{j=1}^{m} N_j \mu_j \tag{15}$$

where N_j is the mole number and $\mu_j = (\delta G/\delta N_j)_{T,P,N_{k \neq j}=\text{constant}}$ is the chemical potential of the jth type of particle.

The total mole number N and the molar fractions X_j are then, respectively,

$$N = \sum_{j=1}^{m} N_j \text{ and } X_j = N_j/N \tag{16}$$

and the molar Gibbs free energy G_m introduced by Eqn. 5 is given by

$$G_m = G/n = \xi \times G/N = \sum_{j=1}^{m} \mu_j X_j \tag{17}$$

where $\xi = N/n$ (18)

and $\mu_j = \mu_j^0 + RT \ln a_j$ (19)

so that

$$G_m = \sum_{j=1}^{m} X_j(\mu_j^0 + RT \ln a_j) \tag{20}$$

For the point R of the system

$$G_m^R = \xi_R \sum_{j=1}^{m} X_j^R(\mu_j^0 + RT \ln a_j^R) = \mu_R^0 \tag{21}$$

is obtained, where ξ_R means the ratio of the total mole number of particles at the point R to the total mole number of chemical individuals at the same point.

We now introduce "average" particles r, one mole of which is identical with a mixture of m sorts of particles j, in amounts corresponding to the molar fractions X_j^R, and with a standard chemical potential of

$$\mu_r^0 = \sum_{j=1}^{m} X_j^R(\mu_j^0 + RT \ln a_j^R) \tag{22}$$

It should be noted that ξ_R moles of the average particles, r, are identical with one mole of the substance R, so that

$\mu_R^0 = \xi_R \times \mu_r^0$ and $\mu_R = \xi_R \times \mu_r$ (23)

The original m-component system can be divided into m sub-systems, in which one original particle component (mth type) is substituted by the "average" type of particle r, so that for the molar Gibbs free energy G_m we have

$$G_m = \sum_{j=1}^{m-1} \mu_j^0 Y_j - \mu_r Y_r \tag{24}$$

where $Y_j = X_j - X_j^R \times X_m/X_m^R$, $Y_r = X_m/X_m^R$, and $\mu_r = \mu_r^0 + RT \ln a_r$.

Then from Eqns. 13, and 20–24

$$\ln a_R = \xi_R \sum_{j=1}^{m} X_j^R \ln(a_j/a_j^R) \tag{25}$$

the equation expressing the relations between the activity of the chemical substance R and the activities of the particles. Eqn. 25 could be used for calculations in the case of a known function of $a_j = a_j(X_j)$, which can be obtained from the models based on the regular or ideal behaviour of particles.

Further, using Eqn. 14, the general correlations between the activity of the chemical individuals and the activity of the particle types, the following equations are obtained.

$$\sum_{i=1}^{n} X_i^R \ln(a_i/a_i^R) = \xi_R \sum_{j=1}^{m} X_j^R \ln(a_j/a_j^R)$$

$$\sum_{i=1}^{n} X_i^R \ln a_i - \Delta G_R^{mix}/RT = \xi_R \sum_{j=1}^{m} X^R \ln(a_j/a_j^R) \qquad (26)$$

For disorder models, where the relationship in Eqn. 3 is assumed to be valid for every particle type, the following equation can be written

$$a_j/a_j^R = X_j/X_j^R \qquad (27)$$

Then Eqn. 25 becomes

$$\ln a_R = \sum_{j=1}^{m} X_j^R \ln(X_j/X_j^R) \qquad (28)$$

The last equation after the substitution of X_j as a function of composition X_i, as it appears from the disorder model, permits us to express the activity a_R (using values of X_j^R) in the whole composition range in which the validity of the disorder model is assumed.

DISCUSSION

As a first point of the discussion, the comparison of the relationships used in the literature with those derived in the present paper, is attempted. As seen from the above derivation, one can consider the composition R, on the perifery of a homogeneous region, to be identical with one of the pure chemical individuals which form the end members of a solid solution series. Then, it can easily be seen that the expressions for the calculation of the activities of Co_3O_4, Mn_3O_4 and Fe_3O_4 used in the literature[4,5] (see Introduction), correspond to Eqn. 28 for the applied assumptions of cation distribution in the pure substances. For example, if the pure Mn_3O_4 is chosen as a reference substance, with the cation distribution assumed to be strictly normal (*i.e.*, $[Mn_A^{2+}] = 1$; $[Mn_B^{3+}] = 2$), and considering the relation between particle molar fractions, X_j and number of particles per spinel formula, $[J] = 7\ X_j$, the relationship

$$a_{Mn_3O_4} = [Mn_A^{2+}]\cdot[Mn_B^{3+}]^2/4 \qquad (29)$$

is easily obtained from Eqn. 28.

It must be pointed out, that Eqn. (28) was only derived for the one reference substance in the system. In the Driessens treatment, there are two reference substances Mn_3O_4 and Co_3O_4, for the system used. In the case of the simple model, neglecting the existence of vacancies and interstitials, the same value of $a_{Co_3O_4}$ is obtained through

$$a_{Co_3O_4} = [Co_A^{2+}]\cdot[Co_B^{3+}]^2/4 \qquad (30)$$

as by expressing $a_{Mn_3O_4}$ by Eqn. (29) and then integrating according to the Gibbs–Duhem equation

$$\ln a_{Co_3O_4} = \int_{a_{Mn_3O_4}=0}^{a_{Mn_3O_4}} (X_{Mn_3O_4}(1 - X_{Mn_3O_4}))\, d \ln a_{Mn_3O_4} \tag{31}$$

However, when the model involves *e.g.*, vacancies, the concentration of which are different in pure Co_3O_4 than in pure Mn_3O_4, the value X_j^R for the vacancies is ambiguous. So the activity of Co_3O_4 obtained through a method similar to that using Eqn. 30, is different from that obtained using Eqn. 31 through an equation similar to Eqn. 29.

A more serious mistake would occur in the case of $Fe_3O_4-ZnFe_2O_4$ solid solutions if the activity of $ZnFeO_4$ was calculated by means of

$$a_{ZnFe_2O_4} = [Zn_A^{2+}]\cdot[Fe_B^{3+}]^2/4$$

starting from a strictly normal cation distribution in zinc ferrite, and (at the same time) the activity of magnetite, Fe_3O_4, was calculated from the expression

$$a_{Fe_3O_4} = [Fe_A^{2+}]\cdot[Fe_A^{3+}]\cdot[Fe_B^{3+}]$$

based on a strict inverse cation distribution in pure magnetite. For the activities calculated by this way, the Gibbs–Duhem equation is invalid.

Therefore, the activity of only one chemical component could generally be calculated directly from a disorder model using Eqn. (28). The activity of the second component in binary systems must then be calculated by means of the Gibbs–Duhem equation only.

Similarly in ternary systems, if one component is chosen as a reference substance, the Schuhmann's integration procedure[6] derived from the Gibbs–Duhem

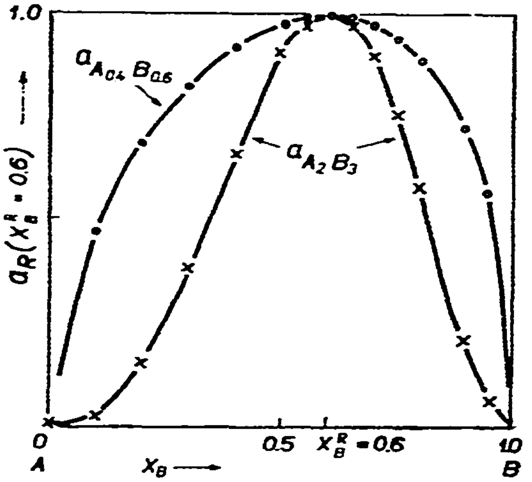

Fig. 2. The concentration dependence of the activity of $A_{0.4}B_{0.6}$ and A_2B_3, as the intermediate member of ideal (Raoult's) solutions A–B.

equation for ternary systems, must be used for the evaluation of the activity of the remaining two components.

When available information about the cation distribution exists for any composition inside the solid solution range, it is preferable to choose this intermediate composition as the reference substance for the system. The concentration dependence of the activity a_R can then be calculated from the model using Eqn. 28.

The concentration dependence of a_R, in the case of an ideal solid solution consisting of particles A and B only, and with the composition $A_{0.4}B_{0.6}$, chosen as reference substance, is represented in Fig. 2). Evaluation of the activity of chemical components from a_R is than based on the Gibbs–Duhem equation, and on the relationship given by Eqn. 14.

For a general binary system A–B, the activity a_A, in the sub-system A–R, can be calculated by the integration of an adequate Gibbs–Duhem equation

$$Y_A \, \mathrm{dln}\, a_A + Y_R \, \mathrm{dln}\, a_R = 0 \tag{32}$$

Substituting Y_A and Y_R from Eqn. 12, the integration

$$\ln a_A = \int_{X_A=1}^{X_A} [(1 - X_A)/(X_A - X_A^R)] \, \mathrm{dln}\, a_R \tag{33}$$

leads to the value of a_A. The activity a_B in the sub-system can be calculated from the values of a_R and a_A using Eqn. 14, *i.e.*

$$X_B^R \ln a_B = G_R^{mix} - X_A^R \ln a_A + \ln a_R \tag{34}$$

(The reverse procedure, *i.e.*, a_B from the Gibbs–Duhem equation, and a_A from Eqn. 14, is then used in the sub-system R–B).

For a ternary system A–B–C the Schuhmann integrations related to sub-systems, mentioned above, can be used. In the sub-system A–R–B, the activities, a_A and a_B, are calculated from

$$\left[\ln a_A = \ln a_A^s - \int_{\ln a_R^s}^{\ln a_R} \rho_{AB} \, \mathrm{dln}\, a_R \right]_{Y_A/Y_B = \mathrm{constant}}$$

$$\left[\ln a_B = \ln a_B^s - \int_{\ln a_R^s}^{\ln a_R} \rho_{BA} \, \mathrm{dln}\, a_R \right]_{Y_A/Y_B = \mathrm{constant}}$$

where the superscript s indicates the quantities at the starting point of the integration path, and ρ_{AB}, ρ_{BA} mean the ratios of the distances formed by the intersecting of the A–R and B–R lines, respectively, by the tangent line of the curve, $a_R = \mathrm{constant}$, at the point of the integration path (see Fig. 3). The activity a_C for this sub-system is then calculated from Eqn. 14.

It should be noted that, if the activity a_R is known from the model as an explicit function of composition, the analytical integrating, instead of the graphical one, could be used.

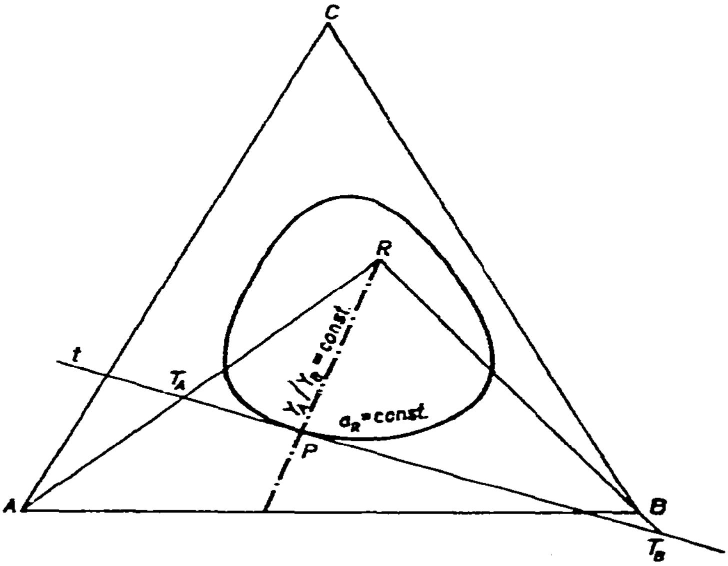

Fig. 3. The illustration for Schuhmann's procedure for a ternary system. t is the tangent line of the isoactivity curve (a_R = constant) at the point P; ρ_{AB} and ρ_{BA} (see text) are the ratios of the distances T_AA/RT_A and T_BB/RT_B, respectively.

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REFERENCES

1 E. A. Guggenheim, *Proc. Roy. Soc. Ser. A*, 148 (1935) 304.
2 M. Těmkin, *Acta Physicochim. U.S.S.R.*, 20 (1945) 411.
3 F. C. M. Driessens, *Ber. Bunsenges. Phys. Chem.*, 72 (1968) 1123.
4 F. C. M. Driessens, *Ber. Bunsenges. Phys. Chem.*, 72 (1968) 754.
5 H. Schmalzried and J. D. Tretjakov, *Ber. Bunsenges. Phys. Chem.*, 70 (1966) 180.
6 R. Schuhmann, Jr., *Acta Met.*, 3 (1955) 219.