

A REGULAR SOLUTION MODEL FOR PHASES WITH SEVERAL COMPONENTS AND SUBLATTICES, SUITABLE FOR COMPUTER APPLICATIONS

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Abstract—A thermodynamic model, based on the regular solution approximation is presented and a formalism, suitable for phases with an arbitrary number of sublattices, is developed. A new concept, the component array, is introduced in order to simplify the analytical expressions for the integral Gibbs energy. The definition of the component array allows a straightforward procedure for the derivation of expressions describing the Gibbs energy for any kind of phase. Expressions for the partial Gibbs energy are derived. The implementation of the model on a computer is discussed.

1. INTRODUCTION

The term regular solution was introduced by Hildebrand[1] to describe mixtures, whose behaviour show some experimental regularities. Later Guggenheim[2] proposed the term "strictly-regular-solutions" to cover mixtures that show an ideal entropy of mixing but have a non-zero interchange energy. The enthalpy of mixing was obtained by counting the number of nearest neighbours of different kinds. As long as the various species, atoms or molecules, are sufficiently similar in size, shape, electronegativity etc., it may be a good approximation to assume random mixing. If the species are more different, they will not mix randomly and as a consequence the solution will not have an ideal entropy of mixing. If they are sufficiently different, they may even occupy different sublattices and only those which are similar go into the same sublattice. It may then be possible to use a regular-solution model which assumes random mixing within each sublattice. Recently, Hillert and Staffansson[3] proposed a model that describes mixing in two different sublattices. In the first version the model covered the case with 4 components that mixed pair-wise in two sublattices. An extended version, capable of treating an arbitrary number of components on both sublattices, was later presented by Harvig[4]. More recently, Hillert and Waldenström[5] introduced concentration dependent interaction parameters. In the future there may be a need for further extensions, e.g. by the introduction of more sublattices and higher-order interaction parameters. The mathematical description of the model grows more complex as more components and more sublattices are added. However, very complex systems can be handled by the application of computer techniques. As such techniques are now being developed for the purpose of calculating phase equilibria, it is interesting to generalize the regular solution model to an arbitrary number of sublattices and components. This will be done in the present report. The result will be presented in such a form that it can be

applied to any special case without further mathematical derivations. Furthermore, a fully automatic, computer-operated procedure will be described which can handle all such cases.

2. THE MODEL

2.1 Definition of site fractions

The mole fractions in a phase are generally defined by the following relation

$$x_i = n_i / \sum_{j=1}^c n_j = n_i/n \quad (1)$$

where n_i and n_j are the number of moles of component i and j respectively and n is the total number of moles in the phase. The number of components is c . It is convenient to introduce a similar composition parameter for each sublattice if the phase is composed of two or more sublattices and to include the number of moles of vacant sites, n_{v_s} , in the summation

$$y_i^s = n_i^s / (n_{v_s}^s + \sum_j n_j^s) \quad (2)$$

The superscript s denotes the sublattice under consideration. y_i^s thus represents the site fraction of component i on sublattice s . One can then define the site fraction of vacant sites and obtain the relation

$$y_{v_s}^s = 1 - \sum_j y_j^s \quad (3)$$

It is often convenient to regard the vacant sites in a sublattice as a component and include them in the summation for the sublattice in eqn (2) but not in the summation for the whole phase in eqn (1). We also introduce a^s as the number of sites on the sublattice s per mole of formula units of the phase.

The site fractions can be arranged in a $l \times c$ matrix if

there are l sublattices and c components

$$Y = \begin{matrix} y_1^1 & y_2^1 & y_3^1 & \dots & y_c^1 \\ y_1^2 & y_2^2 & y_3^2 & \dots & y_c^2 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ y_1^l & y_2^l & y_3^l & \dots & y_c^l \end{matrix} \quad (4)$$

Each row represents a sublattice and each column a component. Since most components do not enter into all sublattices, many components y_i^s are zero. It is always possible to calculate the mole fraction from a given Y matrix as

$$x_i = \frac{\sum_s a^s y_i^s}{\sum_s a^s (1 - y_{v_a}^s)} = \frac{\sum_s a^s y_i^s}{\sum_s a^s \sum_j y_j^s} \quad (5)$$

2.2 The ideal entropy of mixing

The assumption of random mixing on each sublattice yields an expression for the ideal molar entropy of mixing in the phase. It can be written in the following way

$$-S_m^{ideal}/R = \sum_s a^s \sum_i y_i^s \ln y_i^s \quad (6)$$

Sometimes it is possible to express all the y values in terms of the x values and thus to express the ideal entropy as a function of the x parameters. However, such an expression is not always possible to formulate and when possible it is always more complicated.

2.3 The state of reference for the Gibbs energy

We need to define a frame of reference for the Gibbs energy of a solution which contains two or more sublattices. This problem was considered by Hillert and Staffansson[3]. For the simple case where there are two sublattices and two components on each one, A, B and C, D respectively, they suggested the following expression

$$G_m^{ref} = y_A y_C {}^0G_{A_1 C_2} + y_B y_C {}^0G_{B_1 C_2} + y_A y_D {}^0G_{A_1 D_2} + y_B y_D {}^0G_{B_1 D_2} \quad (7)$$

where ${}^0G_{A_1 C_2}$ is the Gibbs energy of one mole of formula units of the pure compound $A_1 C_2$ and the other quantities have an equivalent definition.

An alternative notation of these quantities would be ${}^0G_{ij}^{st}$ where i is the component on the s sublattice and j the component on the t sublattice. More sublattices can easily be added. When eqn (7) is generalized, the principle suggested by Hillert and Staffansson makes it necessary to consider every possible compound and multiply its Gibbs energy by the fraction of that compound, i.e. the product of the corresponding site fractions, e.g. $y_i^s y_j^t$ in the case of two sublattices.

As another alternative the information contained in the

superscript and subscript can be represented by a component array I , which defines one component for each sublattice. Using this notation one can write eqn (7) in the following generalized form

$$G_m^{ref} = \sum_I P_I(Y) \cdot {}^0G_I \quad (8)$$

0G_I represents the Gibbs energy of the compound defined by I which may of course depend on temperature and pressure, and $P_I(Y)$ represents the corresponding product of site fractions from the Y matrix. The frame of reference defined by eqn (8) is composed of up to c^l terms if there are l sublattices and c components and this would yield a maximum number of 16 terms for the case of 4 components and 2 sublattices. However, only 4 terms were included in eqn (7) because A and B only entered the first sublattice and C and D the second. Four y values were thus zero and a large number of hypothetical compounds could be omitted.

2.4 The excess Gibbs energy

It is now possible to define an excess Gibbs energy, ${}^E G_m$, of a solution from the following expression

$$G_m = G_m^{ref} - TS_m^{ideal} + {}^E G_m \quad (9)$$

${}^E G_m$ is mainly composed of the interaction energies between different components in the same sublattice. The interactions between neighbouring atoms in different sublattices are essentially described by the G_m^{ref} terms. According to the original regular solution model the contribution from the pair-wise interaction between atoms of different components can be expressed by the terms

$${}^E G_m = \frac{1}{2} \sum_s \sum_t x_s x_t K_{st} \quad (10)$$

where K_{st} represents the interaction energies. By generalizing this model to phases with two or more sublattices we obtain the following expression

$${}^E G_m = \frac{1}{2} \sum_s \sum_t \sum_j y_i^s y_j^t K_{ij}^{st} \quad (11)$$

By definition $K_{ii}^{st} = 0$. The values of the K quantities should normally depend upon what components are present in the other sublattices and Hillert and Staffansson suggested the following expression for the case of two sublattices,

$${}^E G_m = \frac{1}{2} \sum_s \sum_t \sum_j \sum_k y_i^s y_j^t y_k^u L_{ijk}^{st} \quad (12)$$

where s denotes one sublattice and t the other. The superscript st gives the sublattices where the components i, j and k are located. Each such L quantity can be identified by giving a component array I , which tells that the components i and k are in the sublattices s and t , respectively, and in addition giving the information that there is another component j in the s sublattice. The

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The partial Gibbs energy with respect to a component array is defined as

$$G_{i0} = \left(\frac{\partial G}{\partial n_{i0}} \right)_{T, P, n_{j0}} \quad (A3)$$

We now derive some useful quantities that will be used to formulate eqn (A3) in terms of derivatives of G_m . First we express the number of moles of component i on sublattice s

$$n_i^s = a^s \sum n_{i0} \quad (A4)$$

This summation is taken over all $i0$ with i in sublattice s . Of course, the following relation holds between the quantities for all the components

$$\sum n_i^s = a^s n_i \quad (A5)$$

and for all the component arrays we obtain

$$\sum_{i0} n_{i0} = n_i \quad (A6)$$

From (A6) we find

$$\frac{\partial n_i}{\partial n_{i0}} = 1 \quad (A7)$$

and from (A5)

$$\frac{\partial n_i^s}{\partial n_{i0}} = a^s \quad (A8)$$

Equation (2) in combination with (A4) yields

$$\frac{\partial y_i^s}{\partial n_j^s} = (\delta_{ij} - y_j^s) / n_j \cdot a^s \quad (A9)$$

where δ_{ij} is unity if $i = j$ and zero otherwise. We now return to eqn (A3). By combination with (A1)

$$\begin{aligned} G_{i0} &= \frac{\partial n_i}{\partial n_{i0}} \cdot G_m + n_i \cdot \frac{\partial G_m}{\partial n_{i0}} \\ &= G_m + n_i \sum \frac{\partial G_m}{\partial n_i^s} \cdot \frac{\partial n_i^s}{\partial n_{i0}} \\ &= G_m + n_i \sum \frac{\partial G_m}{\partial n_i^s} \cdot a^s \\ &= G_m + n_i \sum a^s \sum_j \frac{\partial G_m}{\partial y_j^s} \cdot \frac{\partial y_j^s}{\partial n_i^s} \\ &= G_m + \sum_j \left(\frac{\partial G_m}{\partial y_{i0}^s} - \sum_j y_j^s \frac{\partial G_m}{\partial y_j^s} \right) \end{aligned} \quad (A10)$$

We now apply (A10) on the expression of G_m given by eqn (18). First we define "the partial operator"

$$D_{i0} = 1 + \sum_j \left\{ \frac{\partial}{\partial y_{i0}^s} - \sum_j y_j^s \frac{\partial}{\partial y_j^s} \right\} \quad (A11)$$

Thus

$$G_{i0} = D_{i0} G_m \quad (A12)$$

We first examine how D_{i0} will operate on the sum of interaction terms of an arbitrary order Z .

$$\begin{aligned} D_{i0} \sum_{KZ} P_{KZ}(Y) L_{KZ} &= \sum_{KZ} \left[P_{KZ}(Y) L_{KZ} + \sum_j \left\{ P_{KZ}(Y) \delta_{KZi}^s \right. \right. \\ &\quad \left. \left. \times \left(\frac{L_{KZ}}{y_i^s} + \frac{\partial L_{KZ}}{\partial y_i^s} \right) - \sum_j P_{KZ}(Y) \delta_{KZi}^s y_j^s \left(\frac{L_{KZ}}{y_j^s} + \frac{\partial L_{KZ}}{\partial y_j^s} \right) \right\} \right] \end{aligned} \quad (A13)$$

The quantity δ_{KZi}^s was defined in connection with eqn (22). We have used

$$\frac{\partial}{\partial y_j^s} P_{KZ}(Y) = \delta_{KZi}^s \frac{P_{KZ}(Y)}{y_j^s} \quad (A14)$$

Notice that if L_{KZ} is composition dependent, it can only depend on the components given by KZ . If we assume that L_{KZ} is composition independent, then eqn (A13) can be simplified by the observation that the last term will run through all components j in all sublattices. As the component array contains $l + Z$ components, this term will be non zero $l + Z$ times and its value will be $P_{KZ}(Y) L_{KZ}$ each time.

As before, l is the number of sublattices. Thus

$$\begin{aligned} D_{i0} \sum_{KZ} P_{KZ}(Y) L_{KZ} &= \sum_{KZ} P_{KZ}(Y) L_{KZ} + \sum_{KZ} \sum_j P_{KZ}(Y) \delta_{KZi}^s \\ &\quad \times \frac{L_{KZ}}{y_i^s} - (l + p) \sum_{KZ} P_{KZ}(Y) L_{KZ} \\ &= \sum_{KZ} P_{KZ}(Y) L_{KZ} \left\{ 1 + \sum_j \frac{\delta_{KZi}^s}{y_i^s} - (l + Z) \right\} \end{aligned} \quad (A15)$$

This simplification can be applied to any case where L_{KZ} is composition independent. An important case is $Z = 0$ where L_{KZ} is replaced by ${}^0G_{i0}$ which is composition independent by definition. We now let D_{i0} operate on the ideal entropy of mixing, eqn (6)

$$\begin{aligned} S_{i0}^{ideal} &= D_{i0} S_m^{ideal} = -RD_{i0} \left(\sum_j a^s \sum_j y_j^s \ln y_j^s \right) \\ &= -R \left\{ \sum_j a^s \sum_j y_j^s \ln y_j^s + \sum_j a^s (1 + \ln y_i^s) \right. \\ &\quad \left. - \sum_j a^s \sum_j (y_j^s + y_j^s \ln y_j^s) \right\} \\ &= -R \sum_j a^s \left\{ \left(1 - \sum_j y_j^s \right) + \ln y_i^s \right\} \end{aligned} \quad (A16)$$

By using $\sum_j y_j^s = 1$ we obtain

$$S_{i0}^{ideal} = -R \sum_j a^s \ln y_i^s \quad (A17)$$

By combining (A13) and (A17) the general expression for the partial Gibbs energy can be obtained. For the simpler case composition independent interaction parameters we combine (A15) and (A17) to

$$\begin{aligned} G_{i0} &= \sum_{j0} P_{j0}(Y) {}^0G_{i0} \left(1 + \sum_j \frac{\delta_{KZi}^s}{y_i^s} - 1 \right) \\ &\quad + RT \sum_j a^s \ln y_i^s + \sum_{Z>0} \sum_{jZ} P_{jZ}(Y) L_{jZ} \left(1 + \sum_j \frac{\delta_{jZi}^s}{y_i^s} - (l + Z) \right) \end{aligned} \quad (A18)$$

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(A2)

following notation could be used Isj . However, this notation is slightly arbitrary since one could just as well include the j component in the component array instead of i and add the further information that there is another component i on the s sublattice. This can be avoided by simply generalizing the component array by allowing more than one component to be given for each sublattice.

From now on, we shall refer to a component array, that in one sublattice contains two components but only one in each of the remaining sublattices, as a component array of the first order and it will be denoted by $I1$. The type of component array that was introduced when defining the reference state could then be denoted $I0$ and be referred to as a component array of the zeroth order. Using this notation we could write eqn (12) as

$${}^E G_m = \sum_{I1} P_{I1}(Y) \cdot L_{I1} \quad (13)$$

where the summation is taken over all different $I1$. It is easy to extend to higher order interaction by simply introducing higher order component arrays IZ . However, in order to make the definition of the interaction parameters unambiguous, we must impose the restriction that a component array must not contain any component more than once in each sublattice. In this way we automatically exclude parameters such as L_{iik}^{iii} in eqn (12).

The excess Gibbs energy can then be written

$${}^E G_m = \sum_{Z>0} \sum_{IZ} P_{IZ}(Y) \cdot L_{IZ} \quad (14)$$

The interaction parameters L_{IZ} may of course depend on temperature and pressure. As an example of this formalism one may consider a term used by Blander [6] for the interaction between all four components in a reciprocal system, i.e. two components A and B on sublattice 1 and C and D on sublattice 2

$$y_A^1 y_B^1 y_C^2 y_D^2 L_{A,B,C,D} \quad (15)$$

which is included in eqn (14) for $Z=2$. Notice that a component array is written with a comma “,” between components in different sublattices and a colon “:” between components in the same sublattice.

As IZ must not contain a component more than once for the same sublattice, the value of Z is limited. A binary system with one sublattice and no vacancies will thus have just one interaction parameter. Such systems are by far the most commonly investigated [7] and it is a general experience that a single parameter usually is not sufficient to represent the experimental data. A composition dependency is often introduced. However, if more than one sublattice is used to describe the system, the number of parameters may be large enough even if the L_{IZ} parameters are composition independent. As an example, consider an $A-B$ system first having only one sublattice and then two with A and B mixing randomly on each one but not between them. The Gibbs energy for

the binary $A-B$ solution with only one sublattice is

$$G_m = y_A^0 G_A + y_B^0 G_B + RT[y_A \ln y_A + y_B \ln y_B] + y_A y_B L_{A:B} \quad (16a)$$

For the case with two sublattices with a^1 and a^2 sites respectively the model gives

$$\begin{aligned} G_m = & y_A^1 y_A^{20} G_{A,A} + y_A^1 y_B^{20} G_{A,B} + y_B^1 y_A^{20} G_{B,A} \\ & + y_B^1 y_B^{20} G_{B,B} \\ & + RT\{a^1(y_A^1 \ln y_A^1 + y_B^1 \ln y_B^1) \\ & + a^2(y_A^2 \ln y_A^2 + y_B^2 \ln y_B^2)\} \\ & + y_A^1 y_B^1 y_A^2 L_{A:B,A} + y_A^1 y_B^1 y_B^2 L_{A:B,B} \\ & + y_A^1 y_A^2 y_B^2 L_{A:A,B} + y_B^1 y_A^2 y_B^2 L_{B:A,B} \\ & + y_A^1 y_B^1 y_A^2 y_B^2 L_{A:B,A:B} \end{aligned} \quad (16b)$$

In order to be able to handle the currently available data on binary systems, interaction parameters may be given different kinds of composition dependency. The most common expression for binary systems is

$$L_{I1}(Y) = \sum_{b=0} (y_i^s - y_i^{s'})^b \cdot {}^b G_{I1} \quad (17)$$

where i_s' and i_s'' are the two components which occupy sublattice s according to the component $I1$. The number b is called the degree of the parameter ${}^b G_{I1}$.

Any such expression can be incorporated in the model. We can now write the Gibbs energy per mole

$$\begin{aligned} G_m = & \sum_{I0} P_{I0}(Y) \cdot {}^0 G_{I0} + RT \sum_i a^i \sum_j y_j^i \ln y_j^i \\ & + \sum_{Z>0} \sum_{IZ} P_{IZ}(Y) \cdot L_{IZ} \end{aligned} \quad (18)$$

3. THE PARTIAL GIBBS ENERGY

The partial Gibbs energy with respect to a component i is defined in any textbook as

$$G_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \quad (19)$$

For a phase with several sublattices one can define the following partial energy with respect to a component array of zeroth order, $I0$

$$G_{I0} = \left(\frac{\partial G}{\partial n_{I0}} \right)_{T,P,n_{j0}} \quad (20)$$

where n_{I0} is the number of moles of formula units of $I0$. This quantity is, in contrast to the partial Gibbs energy for the individual components, always possible to formulate explicitly.

In the appendix it is shown that the well-known expression for the calculation of partial quantities can be generalized as follows

$$G_{I0} = G_m + \sum_i \left(\frac{\partial G_m}{\partial y_i^s} - \sum_j y_j^s \frac{\partial G_m}{\partial y_j^s} \right) \quad (21)$$

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where i_s is the component in sublattice s of the component array IO . By applying eqn (18) for G_m , the partial derivatives are obtained as follows,

$$\frac{\partial G_m}{\partial y_i^s} = \sum_{IO} P_{IO}(Y) \cdot \frac{\delta_{IOi_s}}{y_i^s} \cdot {}^0G_{IO} + RT \cdot a^s \cdot (1 + \ln y_i^s) + \sum_{Z>0} \sum_{JZ} P_{JZ}(Y) \cdot \frac{\delta_{JZi_s}}{y_i^s} \left(L_{JZ} + y_i^s \frac{\partial L_{JZ}}{\partial y_i^s} \right) \quad (22)$$

The quantity $\delta_{JZi_s}^s$ is a special form of the Kronecker delta. $\delta_{JZi_s}^s$ is unity if i is one of the components in sublattice s , of the component array JZ and zero otherwise. It is shown in the appendix that in the case of composition independent interaction parameters we obtain by inserting eqn (22) into eqn (21),

$$G_{IO} = \sum_{IO} P_{IO}(Y) {}^0G_{IO} \left(1 - l + \sum_i \frac{\delta_{IOi_s}^s}{y_i^s} \right) + RT \sum_i a^s \ln y_i^s + \sum_{Z>0} \sum_{JZ} P_{JZ}(Y) L_{JZ} \left(1 - (l+z) + \sum_i \frac{\delta_{JZi_s}^s}{y_i^s} \right) \quad (23)$$

where l is the number of sublattices.

4. IMPLEMENTATION OF THE MODEL ON COMPUTER

There is a considerable need for thermodynamic evaluations in many types of calculations relating to problems of chemical equilibrium or kinetics. In order to simplify such calculations on computer it would be helpful to have a library of subroutines for the evaluation of the various thermodynamic quantities involved. In order to keep the number of such subroutines at a minimum, it is necessary to make such subroutines as general as possible. It was thus felt that the present thermodynamic model should be programmed in a general way, such that the person working on an application program could always use the same subroutine and would only have to specify the phase by giving the number of components and sites on each sublattice. Such a program has now been constructed in the FORTRAN language for a Nord-10 minicomputer. It can be modified for usage on other computers.

Since there may be a need for calculating various quantities from the integral molar Gibbs energy G_m , it was necessary to structure the data in some special way. The method chosen was inspired by the monograph, "The Art of Computer Programming" by Knuth [8]. Some programming languages like PL/I, PASCAL and SIMULA are designed to handle structural data. However, it turned out to be quite straight-forward to implement dynamic storage allocation and list processing for the present purpose in FORTRAN. The data was structured in such a way that both G_m and partial derivatives with respect to fractions can be calculated by the same subroutine. This is achieved by using the same techniques as in programs for symbolic manipulations of formulas, but in the present case the procedure is taken one step further and a numerical value rather than a formula is the final result. Another benefit of this tech-

nique is that only non-zero parameter values need to be stored which reduces the space required for storage.

As an extra feature the possibility of evaluating the molar volume and its derivatives was included in the program, as well as a composition dependent ferromagnetic contribution to the Gibbs energy.

The program has an interactive command monitor written as a separate subroutine. With this monitor the user can, from his terminal, specify his system and give all the necessary data and also inspect it and obtain listings. There is a special Users Guide for this monitor [9].

The program has been tested in several applications. At present there are two different application programs available for phase diagram calculations, one for optimizing parameters in the thermodynamic model to fit experimental tie-lines or activities and one for simulating diffusion controlled transformations in solid or solid-liquid systems. Some results from the application programs have been reported [10, 11].

The experience has shown that the program has some advantages in addition to saving time for the person writing the application program. In particular, it yields safer application programs since the highly structural data storage eliminates many errors. In view of the fact that the program derives all quantities analytically from the integral quantities, it is not possible for the user to make logical errors in his handling of thermodynamics. Among the drawbacks of the program it should be mentioned that it yields execution times which are unnecessary long for very simple cases. Furthermore, it uses a rather large part of the primary memory of the Nord-10 minicomputer. It may thus be necessary to segment an application program or to use overlay techniques. On the other hand, such drawbacks will grow less and less important due to the rapid progress of computer hardware.

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APPENDIX

Calculation of partial quantities

Gibbs energy for n_i molar of formula units is

$$G = n_i \cdot G_m \quad (A1)$$

where G_m is a function of temperature, pressure and the fractions of all components given by the Y matrix

$$G_m = G_m(T, P, Y) \quad (A2)$$

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