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EMPIRICAL METHODS OF PREDICTING AND REPRESENTING THERMODYNAMIC PROPERTIES OF TERNARY SOLUTION PHASES

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ABSTRACT. Various empirical methods of predicting the properties of a ternary system from its binary components are reviewed and their generalization to higher systems is discussed. The methods are compared by applying the subregular solution model and expressions are derived which allow a direct comparison.

For symmetric treatments, a numerical method and equivalent analytical methods are recommended for universal usage. For asymmetric treatments, a numerical method is recommended but the possibility of treating such cases by transforming an asymmetric ternary system into a reciprocal system and using a formally symmetric description is emphasized.

Introduction

There is a considerable need to predict the thermodynamic properties of a ternary solution phase from the properties of its binary components and a large number of methods have been suggested. They have been reviewed by Ansara [1], for instance. Some are based upon theoretical models and others may be characterized as empirical. The present communication will only concern the empirical methods and their physical justifications will not be discussed. They may be divided into two groups. One group of methods can be applied directly to numerical information on the binary systems. They will here be called numerical methods although they treat the binary numerical information analytically. They are sometimes described as geometrical methods [2] because they can be illustrated by geometrical constructions. Another group requires that the binary information first be approximated by certain analytical expressions. They will here be called analytical methods although it has become very common also to apply the numerical methods to cases where the binary information has first been put in analytical form [3]. In such cases it is possible to make a direct comparison between the different methods. Such a comparison will now be made of the methods most commonly used for metallic systems.

Experience shows that the analytical expressions, given by the various methods of predicting ternary properties from binary ones, will also be used for the representation of experimental data. It is thus important to choose the method of prediction with this purpose in mind, as well. In particular, it would be a great advantage if a general agreement could be reached and only a few methods be used.

Analytical Methods

A large number of expressions have been proposed for the analytical representation of thermodynamic properties of solution phases in binary systems [2,4,5,6]. There is also a need to represent the properties of higher systems with such formulae. It may thus be advantageous to use a method which can easily be generalized to higher systems. Expressions, which are based upon some power series expansion using mole fractions, lend themselves to this purpose and will be used in the present work. The use of a power series expansion was first proposed

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by Margules [7]. For the excess Gibbs energy of a binary solution phase one can formulate the expression in two ways

$$^{E}G = x_1(1-x_1)P_{12} \tag{1a}$$

$$^{E}G = x_1x_2P_{12} \tag{1b}$$

The regular solution model is defined by P_{12} being a constant, which will here be denoted by $^{o}A_{12}$. The two expressions are completely equivalent in the binary case where $x_1+x_2=1$ but they yield different results when used to predict the properties of a ternary phase where $x_1+x_2=1-x_3$.

It is common to predict the properties of a ternary solution phase by a simple summation of the binary expressions, as given by eq. 1b, when they obey the regular solution model,

$$^{E}G = x_1x_2{}^{o}A_{12} + x_2x_3{}^{o}A_{23} + x_3x_1{}^{o}A_{31} \tag{2}$$

This expression has the attractive property of being gradually reduced to the expression for a binary system if two of the components could be made more and more similar. For example, when 2 and 3 become identical, one has $^{o}A_{12} = {}^{o}A_{31}$ and $^{o}A_{23} = 0$ and one thus obtains

$$^{E}G = x_1(x_2+x_3){}^{o}A_{12} \tag{3}$$

which is equivalent to eq. 1b when the components 2 and 3 are identical.

As already mentioned, a different result would be obtained if the ternary expression was constructed by using the form given by eq. 1a,

$$^{E}G = x_1(1-x_1){}^{o}A_{12} + x_2(1-x_2){}^{o}A_{23} + x_3(1-x_3){}^{o}A_{31} \tag{4}$$

This expression does not reduce to the expression for a binary system if two components become identical. It is thus less attractive and there seems to be universal agreement that eq. 2 represents a more natural way of predicting the properties of the ternary system. In fact eq. 2 can be justified by a nearest neighbor model with random mixing.

As soon as the P_{12} parameter is allowed to vary with the composition, there is a large number of alternatives which are equivalent in the binary case but not in the ternary. One may for instance write P_{12} as a symmetric function in x_1 and x_2 or as a function of only x_1, only x_2 or only the combination x_1-x_2. None of these expressions will yield the same attractive property as eq. 2. As a consequence, other criteria must now be used in order to choose between the alternatives. The remainder of this section will be concerned with various alternatives.

The subregular solution model is obtained by allowing P_{12} in eq. 1 to vary linearly with the composition. There are a number of ways to write the binary expression which should now contain two independent parameters. A rather common expression is the following symmetric one,

$$^{E}G = x_1x_2[A^{1}_{12}x_1 + A^{2}_{12}x_2] \tag{5}$$

which reduces to the regular solution model when $A^{1}_{12} = A^{2}_{12} = {}^{o}A_{12}$. However, if ternary properties are predicted by a simple summation of binary expressions like eq. 5, an expression results which does not reduce to the regular solution model, eq. 2. For instance, the first term will not be $x_1x_2{}^{o}A_{12}$ but $x_1x_2(x_1+x_2){}^{o}A_{12}$ i.e. $x_1x_2(1-x_3){}^{o}A_{12}$. One should thus avoid using eq. 5. However, it can easily be modified in such a manner that it reduces to the regular solution model if use is made of the relation $x_1+x_2=1$ in an appropriate way. A method which will give the desired result when applied to any expression is based upon the following parameters.

$$v_{12} = (1+x_1-x_2)/2 \tag{6a}$$

$$v_{21} = (1+x_2-x_1)/2 \tag{6b}$$

In the binary system they are equal to x_1 and x_2 but their sum is unity even in higher systems.

$$v_{12} + v_{21} = 1 \tag{6c}$$

The required modification of eq. 5 can thus be accomplished by simply replacing x_1 by v_{12} and x_2 by v_{21} inside the bracket,

$$E_G = x_1x_2[A^1_{12}v_{12}+A^2_{12}v_{21}] \quad (7)$$

In view of eq. 6c this expression always reduces to $x_1x_2{}^oA_{12}$ when $A^1_{12} = A^2_{12} = {}^oA_{12}$.

It is interesting that the procedure which was applied to eq. 5 would have no effect if it is again applied to eq. 7, since the bracket only contains v_{12} and v_{21} which are equal to $(1+x_1-x_2)/2$ and $(1+x_2-x_1)/2$. By replacing x_1 by v_{12} and x_2 by v_{21} one thus obtains the expressions $(1+v_{12}-v_{21})/2$ and $(1+v_{21}-v_{12})/2$ which are always equal to v_{12} and v_{21} in view of eq. 6c. It would thus be possible to construct a computer-operated procedure which could accept any analytical expression for P_{12} and by the substituion of x_1 and x_2 with $(1+x_1-x_2)/2$ and $(1+x_2-x_1)/2$, respectively, it would make all those expressions equivalent in higher-order systems which are equivalent in the binary system.

Eq. 7 can be rearranged in the following two ways,

$$E_G = x_1x_2[{}^oA_{12}+{}^1A_{12}(x_1-x_2)] \quad (8a)$$

$$E_G = x_1x_2[{}^oA_{12}+{}^1A_{12}x_1+{}^1A_{21}x_2] \quad (8b)$$

where ${}^oA_{12} = (A^2_{12})/2$ and ${}^1A_{12} = -{}^1A_{21} = (A^1_{12}-A^2_{12})/2$. Of course, these expressions are quite equivalent to eq. 7 and it is only a matter of convenience what expression is chosen. It is then worth noting that eqs. 8a and b should be accompanied by the information that ${}^1A_{12} + {}^1A_{21} = 0$ where ${}^1A_{21}$ is the parameter to be used in eq. 8a if the order of the two components is reversed. Eq. 7 requires no such information. This fact can be used as an argument in favour of eq. 7. It is not a strong argument and eq. 8a may be the most attractive alternative because of its simplicity. However, as shown later, the argument in favour of the v parameters grows stronger when one goes from binary interactions to ternary ones.

If the ternary properties are predicted by a summation of binary expressions like eq. 8a the result takes the following form

$$E_G = x_1x_2[{}^oA_{12}+{}^1A_{12}(x_1-x_2)] + x_2x_3[{}^oA_{23}+{}^1A_{23}(x_2-x_3)] + x_3x_1[{}^oA_{31}+{}^1A_{31}(x_3-x_1)] \quad (9)$$

As already mentioned, this reduces to the regular solution expression, eq. 2, when ${}^1A_{12} = {}^1A_{23} = 0$. However, it should be noticed that this attractive property may be retained even if one adds a term $x_1x_2x_3 \cdot f$ where f is some function which goes to zero when ${}^1A_{12}$, ${}^1A_{23}$ and ${}^1A_{31}$ go to zero. As a consequence, there is no formal way to justify why a simple summation of binary expressions like eqs. 7, 8a or 8b should be used for predicting ternary properties from binary information. Other alternatives will be discussed in the next sections.

There are many ways to formulate the power series for a binary system when higher powers are included. By generalizing eqs. 7 and 8a one obtains

$$E_G = x_1x_2 \sum_{k=0}^{n} A^{k+1}_{12} v^{n-k}_{12} v^k_{21} \quad (10a)$$

$$E_G = x_1x_2 \sum_{k=0}^{n} {}^kA_{12}(x_1-x_2)^k \quad (10b)$$

These expressions are completely equivalent since v_{12} and v_{21} only contain x_1 and x_2 in the combination x_1-x_2. The relations between the two sets of parameters in eqs. 10a and b are presented in Table 1.

Another method is to use the Legendre polynomials, which have the advantage that the addition of a new higher term has only a small effect or none at all on the values of the lower terms. This has been discussed in detail by Bale and Pelton (6) who also discussed other orthogonal functions. They chose to express the Legendre polynomials in terms of x_1 and obtained the following equation,

$$E_G = x_1x_2[{}^0B_{12}+{}^1B_{12}(2x_1-1)+{}^2B_{12}(6x_1^2-6x_1+1)+{}^3B_{12}(20x_1^3-30x_1^2+12x_1-1)$$
$$+ {}^4B_{12}(70x_1^4-140x_1^3+90x_1^2-20x_1+1)+.....] \qquad (11a)$$

TABLE I

Coefficients for the Conversion between the Sets of Parameters in Eqs. 10a and b. For Example, at n=2, $A^2=2{}^0A-2{}^2A$ and $4{}^1A=2A^1-2A^3$

n		$^0A/A^1$	$^1A/A^2$	$^2A/A^3$	$^3A/A^4$	$^4A/A^5$	$^5A/A^6$	$^6A/A^7$	$^7A/A^8$
0	$A^1/{}^0A$	1							
1	$A^1/2{}^0A$	1	1						
	$A^2/2{}^1A$	1	-1						
2	$A^1/4{}^0A$	1	1	1					
	$A^2/4{}^1A$	2	0	-2					
	$A^3/4{}^2A$	1	-1	1					
3	$A^1/8{}^0A$	1	1	1	1				
	$A^2/8{}^1A$	3	1	-1	-3				
	$A^3/8{}^2A$	3	-1	-1	3				
	$A^4/8{}^3A$	1	-1	1	-1				
4	$A^1/16{}^0A$	1	1	1	1	1			
	$A^2/16{}^1A$	4	2	0	-2	-4			
	$A^3/16{}^2A$	6	0	-2	0	6			
	$A^4/16{}^3A$	4	-2	0	2	-4			
	$A^5/16{}^4A$	1	-1	1	-1	1			
5	$A^1/32{}^0A$	1	1	1	1	1	1		
	$A^2/32{}^1A$	5	3	1	-1	-3	-5		
	$A^3/32{}^2A$	10	2	-2	-2	2	10		
	$A^4/32{}^3A$	10	-2	-2	2	2	-10		
	$A^5/32{}^4A$	5	-3	1	1	-3	5		
	$A^6/32{}^5A$	1	-1	1	-1	1	-1		
6	$A^1/64{}^0A$	1	1	1	1	1	1	1	
	$A^2/64{}^1A$	6	4	2	0	-2	-4	-6	
	$A^3/64{}^2A$	15	5	-1	-3	-1	5	15	
	$A^4/64{}^3A$	20	0	-4	0	4	0	-20	
	$A^5/64{}^4A$	15	-5	-1	3	-1	-5	15	
	$A^6/64{}^5A$	6	-4	2	0	-2	4	-6	
	$A^7/64{}^6A$	1	-1	1	-1	1	-1	1	
7	$A^1/128{}^0A$	1	1	1	1	1	1	1	1
	$A^2/128{}^1A$	7	5	3	1	-1	-3	-5	-7
	$A^3/128{}^2A$	21	9	1	-3	-3	1	9	21
	$A^4/128{}^3A$	35	5	-5	-3	3	5	-5	-35
	$A^5/128{}^4A$	35	-5	-5	3	3	-5	-5	35
	$A^6/128{}^5A$	21	-9	1	3	-3	-1	9	-21
	$A^7/128{}^6A$	7	-5	3	-1	-1	3	-5	7
	$A^8/128{}^7A$	1	-1	1	-1	1	-1	1	-1

In order to treat the two components in a symmetric way, the following modification of the Legendre polynomials may be chosen

$$E_G = x_1x_2[{}^0B_{12}+{}^1B_{12}(x_1-x_2) + {}^2B_{12}(x_1^2-4x_1x_2+x_2^2)$$
$$+ {}^3B_{12}(x_1^3-9x_1^2x_2+9x_1x_2^2-x_2^3)+..... + {}^nB_{12}\sum_{k=0}^{n}\left(\frac{n!}{k!(n-k)!}\right)^2 x_1^{n-k}x_2^k(-1)^k] \qquad (11b)$$

Rand (8) has pointed out that it may be advantageous to express the Legendre polynomials in

terms of the concentration parameter $z_{12}=x_1-x_2$,

$$E_G = x_1x_2[{}^0B_{12}+{}^1B_{12}z_{12}+{}^2B_{12}(3z_{12}^2-1)/2 + {}^3B_{12}(5z_{12}^3-3z_{12})/2 + {}^4B_{12}(35z_{12}^4-30z_{12}^2+3)/8 + {}^5B_{12}(63z_{12}^5-70z_{12}^3+15z_{12})/8 + {}^6B_{12}(231z_{12}^6-315z_{12}^4+105z_{12}^2-5)/16 + {}^7B_{12}(429z^7-693z^5 + 315z^3-35z)/16+.....] \quad (11c)$$

The coefficients in all these equations using Legendre polynomials are identical and they are directly related to the coefficients in eqs. 10a and b as shown in Table II. However, when used

TABLE II

Coefficients for the Conversion between the Sets of Parameters in Eq. 10b and the Equations using Legendre Polynomials. For each n Value read up to the corresponding Parameter. For Example, at n=3 or 4, ${}^1A={}^1B-\frac{3}{2}{}^3B$ and at n=5 and 6, ${}^1A={}^1B-\frac{3}{2}{}^3B+\frac{15}{8}{}^5B$.

	${}^0B$	${}^1B$	${}^2B$	${}^3B$	${}^4B$	${}^5B$	${}^6B$	${}^7B$
${}^0A$	1		$-\frac{1}{2}$		$\frac{3}{8}$		$-\frac{5}{16}$	
${}^1A$		1		$-\frac{3}{2}$		$\frac{15}{8}$		$-\frac{35}{16}$
${}^2A$			$\frac{3}{2}$		$-\frac{15}{4}$		$\frac{105}{16}$	
${}^3A$				$\frac{5}{2}$		$-\frac{35}{4}$		$-\frac{315}{16}$
${}^4A$					$\frac{35}{8}$		$-\frac{315}{16}$	
${}^5A$						$\frac{63}{8}$		$-\frac{693}{16}$
${}^6A$							$\frac{231}{16}$	
${}^7A$								$\frac{429}{16}$

	${}^0A$	${}^1A$	${}^2A$	${}^3A$	${}^4A$	${}^5A$	${}^6A$	${}^7A$
${}^0B$	1		$\frac{1}{3}$		$\frac{1}{5}$		$\frac{1}{7}$	
${}^1B$		1		$\frac{3}{5}$		$\frac{3}{7}$		$\frac{1}{3}$
${}^2B$			$\frac{2}{3}$		$\frac{4}{7}$		$\frac{10}{21}$	
${}^3B$				$\frac{2}{5}$		$\frac{4}{9}$		$\frac{14}{33}$
${}^4B$					$\frac{8}{35}$		$\frac{24}{77}$	
${}^5B$						$\frac{8}{63}$		$\frac{8}{39}$
${}^6B$							$\frac{16}{231}$	
${}^7B$								$\frac{16}{429}$

to predict ternary properties, only the type of equations, where the bracket is composed of the combination x_1-x_2, only, give the same result. These are eqs. 10a and b and 11c. The other equations yield different results because they can be derived from the first type of equations by the use of the relation $x_1+x_2=1$ which is only true in the binary case. These equations can easily be transformed to the first type by substituting x_1 and x_2 with v_{12}, respectively. For

example, eq. 11b is thus transformed as follows

$$E_G = x_1x_2[{}^oB_{12}+{}^1B_{12}(v_{12}-v_{21})+{}^2B_{12}(v_{12}^2-4v_{12}v_{21}+v_{21}^2) + {}^3B_{12}(v_{12}^3-9v_{12}^2v_{21}+9v_{12}v_{21}^2-v_{21}^3)+{}^4B_{12}(v_{12}^4-16v_{12}^3v_{21}+36v_{12}^2v_{21}^2 -16v_{12}v_{21}^3+v_{21}^4)+.....] \quad (11d)$$

By this transformation it becomes completely equivalent to eqs. 10a and b. As already pointed out, the same transformation would have no effect when applied to an equation which is already composed of the combination x_1-x_2.

The expressions involving Legendre polynomials have the disadvantage of taking slightly longer to compute and from a practical point of view eq. 10b seems to be the best expression. On the other hand, the Legendre expressions have an advantage when the parameters are to be evaluated from experimental information because they can in principle be determined one after the other due to the orthogonality. In practice one must allow a small correction to the previously evaluated parameters when a new one is included unless the experimental data are closely and regularly spaced (6). Furthermore, the standard deviation for each parameter, which is obtained from the data fitting procedure, is meaningful and can be judged separately when one works with the Legendre expressions but not when one works with the non-orthogonal power series expressions. In addition, the Legendre expressions allow approximate expressions to be constructed by simply dropping any higher order terms. It may thus be concluded that both types of expressions should be used where appropriate and a conversion can be made by means of Table II whenever it is needed.

Once it has been decided what analytical expression should be used for the representation of the binary information and what method should be used for the construction of the ternary expression, e.g. the simple summation of the binary expressions, it is possible to compare the prediction with experimental information from the ternary system. To what extent the difference is due to a real ternary effect, depends upon how well the physical justification for the method of constructing the ternary expression applies to the system under consideration. Such aspects will not be discussed in the present work. In any case, it is convenient to represent the difference by an expression of the follwing form

$$E_G = x_1x_2x_3P_{123} \quad (12)$$

where P_{123} is some power series expansion using mole fractions. In the simplest case, P_{123} can be put equal to a constant ${}^oA_{123}$. If the next higher order terms are needed, there will be three parameters and the following symmetric expression can be used

$$E_G = x_1x_2x_3[A_{123}^1x_1+A_{123}^2x_2+A_{123}^3x_3] \quad (13)$$

This expression reduces to the previous one when $A_{123}^1=A_{123}^2=A_{123}^3={}^oA_{123}$. However, it is not suitable for predictions of quaternary properties from ternary information because $A_{123}^1=A_{123}^2=A_{123}^3={}^oA_{123}$ will then yield $x_1x_2x_3(x_1+x_2+x_3){}^oA_{123}$, i.e. $x_1x_2x_3(1-x_4){}^oA_{123}$. On the other hand, it can be modified by the method used on eq. 5. Introduce the following quantities

$$v_{123} = (1+2x_1-x_2-x_3)/3 \quad (14a)$$

$$v_{231} = (1+2x_2-x_3-x_1)/3 \quad (14b)$$

$$v_{312} = (1+2x_3-x_1-x_2)/3 \quad (14c)$$

In the ternary system, v_{123}, v_{231} and v_{312} are identical to x_1, x_2 and x_3, respectively, but their sum is unity even in higher systems,

$$v_{123} + v_{231} + v_{312} = 1 \quad (14d)$$

The required modification of eq. 13 can thus be accomplished by replacing x_1 by v_{123}, x_2 by

v_{231} and x_3 by v_{312} inside the bracket,

$$E_G = x_1x_2x_3[A^1_{123}v_{123}+A^2_{123}v_{231}+A^3_{123}v_{312}] \quad (15)$$

If the same procedure is repeated it would have no effect since the bracket only contains v_{123}, v_{231} and v_{312} and, for instance, v_{123} is equal to $(1+2x_1-x_2-x_3)/3$ which will be modified to $(1+2v_{123}-v_{231}-v_{312})/3$ which is always equal to v_{123} in view of eq. 14d. Equivalent relations hold for v_{231} and v_{312}.

As expected, eq. 15 reduces to $x_1x_2x_3{}^oA_{123}$ when $A^1_{123}=A^2_{123}=A^3_{123}={}^oA_{123}$. It can be rearranged in the following two ways,

$$E_G = x_1x_2x_3[{}^oA_{123}+{}^1A_{123}(x_1-x_2)+{}^1A_{231}(x_2-x_3)+{}^1A_{312}(x_3-x_1)] \quad (16a)$$

$$E_G = x_1x_2x_3[{}^oA_{123}+{}^1C_{123}x_1+{}^1C_{231}x_2+{}^1C_{312}x_3] \quad (16b)$$

where ${}^1C_{123}={}^1A_{123}-{}^1A_{312}$; ${}^1C_{231}={}^1A_{231}-{}^1A_{123}$; ${}^1C_{312}={}^1A_{312}-{}^1A_{231}$ and ${}^1A_{123}+{}^1A_{231}+{}^1A_{312}=0$. These two equations are quite equivalent to eq. 15 but they must be accompanied by the information that the sum of the three ^1A or ^1C parameters is zero. This fact makes eq. 15 more preferable although it is more complex because it contains v instead of x. If even higher order terms are needed, it is advisable to use a generalization of eq. 15 similar to eq. 10a.

It is possible to extend this treatment to higher systems by simply taking the summation of the contribution from all the binary components, expressed by means of eq. 10a, all the ternary components, expressed by means of a generalization of eq. 15, and all the higher components, expressed by similar equations.

Numerical methods

All the numerical methods as well as the analytical ones give different results for different choices of concentration parameter. The choice of mole fraction is almost universally preferred.

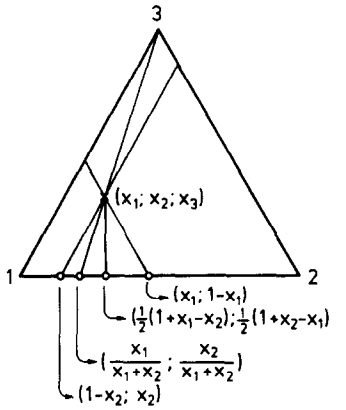

FIG. 1

Various methods of selecting the point on a binary side whose value will be used as a contribution to the value of a ternary alloy

In the discussion of the numerical methods, the numerical values of the excess Gibbs energy on the binary 1-2 side will be denoted by ${}^EG_{12}(x_1;x_2)$ where $x_1+x_2=1$. The question is from what point on the binary side one should take the numerical value which will be allowed to contribute to the value in a ternary alloy. Figure 1 illustrates the geometrical constructions which have been used to illustrate the different methods. In addition each method uses a weight factor which is constructed in such a way that the final expression can be reduced to the regular solution model. In particular, three methods deserve special mention [9,10,11]. They yield the following expressions.

Kohler $$E_G = \Sigma(x_1+x_2)^2 \cdot {}^EG_{12}(x_1/(x_1+x_2);x_2/(x_1+x_2)) \quad (17)$$

$$\underline{\text{Colinet}} \qquad {}^{E}G = \Sigma\left[\frac{x_2/2}{1-x_1}\,{}^{E}G_{12}(x_1;1-x_1) + \frac{x_1/2}{1-x_2}\,{}^{E}G_{12}(1-x_2;x_2)\right] \tag{18}$$

$$\underline{\text{Muggianu}} \qquad {}^{E}G = \Sigma\,\frac{x_1x_2}{v_{12}v_{21}}\,{}^{E}G(v_{12};v_{21}) \tag{19}$$

The summations are taken over all the binary components. The three methods have here been defined with expressions which allow an extension to higher systems by simply adding terms for the new binary components. In addition, ternary contributions should be added in the following way.

$$\underline{\text{Kohler}} \qquad {}^{E}G = \Sigma(x_1+x_2+x_3)^3\,{}^{E}G_{123}(x_1/(x_1+x_2+x_3);x_2/(x_1+x_2+x_3);x_3/(x_1+x_2+x_3)) \tag{20}$$

$$\underline{\text{Colinet}} \qquad {}^{E}G = \Sigma\left[\frac{x_3/3\cdot{}^{E}G_{123}(x_1;x_2;(1-x_1-x_2))}{1-x_1-x_2} + \frac{x_1/3\cdot{}^{E}G_{123}((1-x_2-x_3);x_2;x_3)}{1-x_2-x_3} + \frac{x_2/3\cdot{}^{E}G_{123}(x_1;(1-x_3-x_1);x_3)}{1-x_3-x_1}\right] \tag{21}$$

$$\underline{\text{Muggianu}} \qquad {}^{E}G = \Sigma\,\frac{x_1x_2x_3}{v_{123}v_{231}v_{312}}\,{}^{E}G_{123}(v_{123};v_{231};v_{312}) \tag{22}$$

The summations are taken over all the ternary components. Expressions for higher components can be constructed in a similar way.

The numerical methods are often applied to cases where the binary information has already been put in analytical form [3]. It is then possible to make a direct comparison with the analytical methods. Such a comparison will now be made for the subregular solution model written in the form given by eq. 7 or 8a. The following results are obtained.

$$\underline{\text{Kohler}} \qquad {}^{E}G = \Sigma(x_1+x_2)^2\cdot\frac{x_1}{x_1+x_2}\cdot\frac{x_2}{x_1+x_2}\left[{}^{o}A_{12}+{}^{1}A_{12}\,\frac{x_1-x_2}{x_1+x_2}\right]$$

$$= \Sigma x_1x_2\left[{}^{o}A_{12}(x_1-x_2+\frac{x_1-x_2}{x_1+x_2}\cdot x_3)\right] \tag{23}$$

$$\underline{\text{Colinet}} \qquad {}^{E}G = \Sigma\left[\frac{x_2/2}{1-x_1}\cdot x_1(1-x_1)\;[{}^{o}A_{12}+{}^{1}A_{12}(2x_1-1)]\right.$$

$$\left. + \frac{x_1/2}{1-x_2}\cdot(1-x_2)x_2[{}^{o}A_{12}+{}^{1}A_{12}(1-2x_2)]\right] = \Sigma x_1x_2[{}^{o}A_{12}+{}^{1}A_{12}(x_1-x_2)] \tag{24}$$

$$\underline{\text{Muggianu}} \qquad {}^{E}G = \Sigma\frac{x_1x_2}{v_{12}v_{21}}\cdot v_{12}v_{21}\left[A^1_{12}v_{12}+A^2_{12}v_{21}\right]$$

$$= \Sigma x_1x_2\left[A^1_{12}v_{12}+A^2_{12}v_{21}\right] = \Sigma x_1x_2[{}^{o}A_{12}+{}^{1}A_{12}(x_1-x_2)] \tag{25}$$

The summations are taken over all the binary components. The three methods are illustrated in Figure 2. The Colinet and Muggianu methods both yield the same result as the analytical method, eq. 7. The Kohler method yields a similar result but it contains an extra term of the form $x_1x_2x_3\cdot f$ where

$$f = {}^{1}A_{12}\,\frac{x_1-x_2}{x_1+x_2} + {}^{1}A_{23}\,\frac{x_2-x_3}{x_2+x_3} + {}^{1}A_{31}\,\frac{x_3-x_1}{x_3+x_1} \tag{26}$$

It may thus be regarded as a modification of eq. 9. The factor f is zero at the center of the ternary system where $x_1=x_2=x_3$ and it has always a low value in comparison with the total value given by eq. 9.

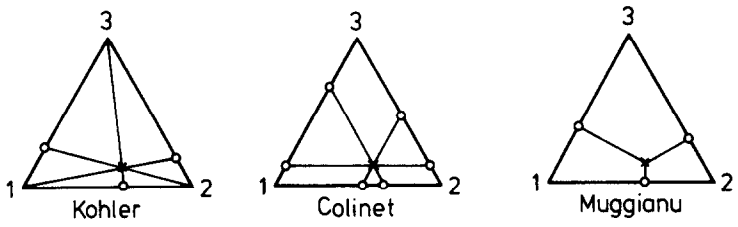

FIG. 2

Illustration of the character of some symmetric numerical methods of predicting ternary properties from binary ones. The properties of the alloy, marked with a cross, are given by some average of the properties of the binary alloys marked with circles.

The results will generally be more complicated if higher order terms are included in the analytical description of the binary properties. An exception is Muggianu's method, eq. 19. When applied to eq. 10a or b $^{(12)}$, it recreates the binary expression. In the case of eq. 10a this is because it contains v_{12} and v_{21} which are equal to $(1+x_1-x_2)/2$ and $(1+x_2-x_1)/2$. By substituting v_{12} and v_{21} for x_1 and x_2, according to eq. 19, and applying eq. 6c one obtains for instance,

$$(1+v_{12}-v_{21})/2 = v_{12} \tag{27a}$$

In the case of eq. 10b it is because it contains the combination x_1-x_2 and by substituting v_{12} and v_{21} for x_1 and x_2 according to eq. 19, one obtains,

$$v_{12} - v_{21} = (1+x_1-x_2)/2 - (1+x_2-x_1)/2 = x_1 - x_2 \tag{27b}$$

Muggianu's method as well as the analytical method thus yields the following expression if eq. 10a or b is chosen,

$$E_G = \Sigma\left[x_1x_2 \sum_{k=0}^{n} A_{12}^{k+1} v_{12}^{n-k} v_{21}^{k}\right] = \Sigma\left[x_1x_2 \sum_{k=0}^{n} {}^{k}A_{12}(x_1-x_2)^k\right] \tag{28}$$

where the first summations are taken over all the binary components. When applied to the Legendre polynomials in the forms given by eqs. 11c and d, Muggianu's method also recreates the binary expressions. The generalized version of Muggianu's method has the same property if applied to eq. 15 or a generalized version of it. For instance, the bracket contains v_{123} which is equal to $(1+2x_1-x_2-x_3)/3$. When replacing x_1, x_2 and x_3 by v_{123}, v_{231} and v_{312}, according to eq. 22, and applying eq. 14d, one obtains

$$(1+2v_{123}-v_{231}-v_{312})/3 = v_{123} \tag{29}$$

The expression inside the bracket is thus recreated.

Asymmetric methods

So far, all the methods that have been discussed treat the components in the same way and may thus be characterized as symmetric methods. However, sometimes there may be a physical reason to divide the component elements into different groups. For instance, if components 2 and 3 are similar to each other but differ markedly from component 1, then one should expect the binary systems 1-2 and 1-3 to be similar and it may be advantageous to describe the ternary 1-2-3 system in such a way that the expression would reduce to the binary expression if one could make 2 and 3 identical. This could be accomplished with the analytical method if eq. 9 is modified by the addition of a term $x_1x_2x_3({}^{1}A_{31}-{}^{1}A_{12})$,

$$E_G = x_1x_2[{}^{o}A_{12}+{}^{1}A_{12}(x_1-x_2)] + x_2x_3[{}^{o}A_{23}+{}^{1}A_{23}(x_2-x_3)]$$
$$+ x_3x_1[{}^{o}A_{31}+{}^{1}A_{31}(x_3-x_1)] + x_1x_2x_3({}^{1}A_{31}-{}^{1}A_{12}) \tag{30}$$

For 2 = 3 one has ${}^{o}A_{12}={}^{o}A_{31}$, ${}^{1}A_{12}={}^{1}A_{13}=-{}^{1}A_{31}$, ${}^{o}A_{23}={}^{1}A_{23}=0$ and one then obtains

$$E_G = x_1(x_2+x_3)[{}^0A_{12}+{}^1A_{12}(x_1-x_2-x_3)] \tag{31}$$

which is identical to eq. 6c for the binary system. In connection with eq. 2 it was shown that this attractive property is obtained for all possible pairs of components when the regular solution model holds. It was lost when higher order terms were introduced. We have now seen that it can be restored for a preselected pair of the components by the addition of an asymmetric term $x_1x_2x_3 \cdot f$.

A numerical method has been proposed by Toop [13], which also has this asymmetric property It is illustrated in Figure 3 and it yields the following equation,

$$\underline{\text{Toop}}\ E_G = \frac{x_2}{1-x_1} E_{G_{12}}(x_1;1-x_1) + \frac{x_3}{1-x_1} E_{G_{13}}(x_1;1-x_1)$$

$$+ (x_2+x_3)^2 \cdot E_{G_{23}}\left(\frac{x_2}{x_2+x_3}; \frac{x_3}{x_2+x_3}\right) \tag{32}$$

When Toop's method is applied to the subregular solution model, eq. 8a, the following result is obtained,

$$E_G = x_1x_2[{}^0A_{12}+{}^1A_{12}(x_1-x_2-x_3)] + x_1x_3[{}^0A_{13}+{}^1A_{13}(x_1-x_3-x_2)]$$

$$+ x_2x_3[{}^0A_{23}+{}^1A_{23}(x_2-x_3+\frac{x_2-x_3}{x_2+x_3} \cdot x_1)] \tag{33}$$

This expression contains all the terms in eq. 25 and in addition a term of the form $x_1x_2x_3 \cdot f$ where

$$f = {}^1A_{23}\frac{x_2-x_3}{x_2+x_3} \tag{34}$$

This term comes from the last term in Toop's equation which has been borrowed from Kohler's method From the previous discussion of Kohler's, Colinet's and Muggianu's methods it is evident that the extra term can be avoided if Toop's method is modified by taking the last term from Colinet's or Muggianu's method. These new methods are illustrated in Figure 3. In particular, the "new method 2" is very attractive because it yields fairly simple expressions when applied to higher power descriptions of the binary components, eq. 10a or b. Its formulation for a ternary system is as follows,

$$\underline{\text{New asymmetric model}}\ E_G = \frac{x_2}{1-x_1} E_{G_{12}}(x_1;1-x_1) + \frac{x_3}{1-x_1} E_{G_{13}}(x_1;1-x_1)$$

$$+ \frac{x_2x_3}{v_{23}v_{32}} E_{G_{23}}(v_{23};v_{32}) \tag{35}$$

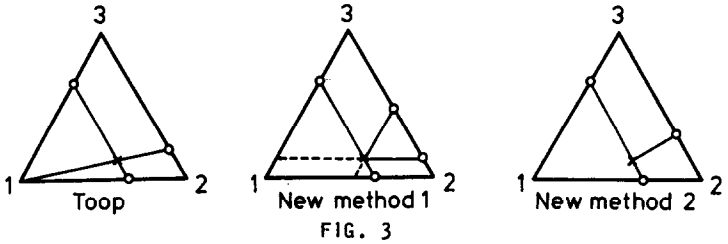

FIG. 3

Illustration of the character of some asymmetric, numerical methods of predicting ternary properties from binary ones. The properties of the alloy, marked with a cross, are given by some average of the properties of the binary alloys, marked with circles.

The generalization of the asymmetric models to higher systems yields a large number of alternatives depending upon how the component elements are divided into separate groups. This will not be discussed further in the present work but it may be emphasized that such cases might be better handled by the introduction of real or artificial sublattices. That method will be discussed in a later section.

Recommendations

An analytical description of a method of predicting the properties of a higher system from the properties of the lower, component systems has two advantages. It can yield analytical expressions of derivatives and thus allow the direct calculation of chemical potentials and it may be useful for the representation of experimental data. The numerical methods of predicting the properties of a higher system from the properties of the lower, component systems have the advantage of yielding a formulation which is simple even in complicated cases. Both types of methods should thus be used and it is advantageous to select one method of each type which are equivalent to each other.

It seems very attractive to choose Muggianu's numerical method in combination with the analytical methods based upon the v parameters or the special combination x_1-x_2. One could then choose anyone of eqs. 10a, 10b, 11c and 11d and easily transform from one to another by the use of Tables I and II.

If an asymmetric description is required, it is recommended to use a new asymmetric method eq. 35. Analytical equivalences can be calculated for various descriptions of the binary properties. In particular, eq. 30 is recommended when the binary properties can be represented by the subregular solution model.

Ordering systems

The discussion in the present paper has only concerned the excess term of the Gibbs energy It should be emphasized that it is also essential to use a realistic expression for the positional entropy. For example, the ideal entropy of mixing is different for a substitutional solution where all the atoms occupy the same type of lattice sites, and for an interstitial solution, where the interstitial atoms occupy a separate sublattice. In fact, each type of ordering leads to its own expression for the ideal of mixing.

When formulating the ideal entropy of mixing for an ordered phase one makes use of a special type of mole fraction, y, based upon the occupancy of each sublattice. At the same time one should use y instead of x in the representation of the excess Gibbs energy. Each sublattice will thus be treated separately and the resulting expression will mainly account for the interactions within each sublattice. For a simple reciprocal system where A and B occupy one sublattice and C and D another one obtains the following expression,

$$^{E}G = y_A {}^{E}G_{AD,AC}(y_C) + y_B {}^{E}G_{BD,BC}(y_C) + y_D {}^{E}G_{AD,BD}(y_B) + y_C {}^{E}G_{AC,BC}(y_B) \qquad (36)$$

The question of how to represent the interaction between atoms in different sublattices is related to the fact that the pure elements can no longer be used as reference states because they do not exist within the y_B, y_D coordinate system. Instead, a non-planar surface of reference should be chosen based upon the compounds AC, AD, BC and BD [14]. The interactions between atoms in different sublattices is thus entered into the total expression for the Gibbs energy. The same method can also be used for ternary solution phases where two elements substitute for each other on one sublattice and the third element goes into a sublattice of interstitial sites. An interesting possibility is also to use the method in ternary cases where there is a physical reason why one should treat the system in an asymmetric fashion. This may often occur in the liquid phase if one component is a metal and two are non-metals or if two are metals and one is a non-metal. One would thus obtain an expression which is symmetric with respect to four real or hypothetical compounds. This possibility was recently tried for the Fe-Mn-S system [15] and it is illustrated in Figure 4. The property of a ternary phase is thus predicted to be a weighted average of the four binary alloys represented by circles in the diagram.

In order to represent experimental information from the interior of the system, which may differ from this prediction, one may add a term $y_A y_B y_C y_D P_{ABCD}$ where P_{ABCD} is a constant or a power series expansion. In order to allow an extension to higher-order systems, similar consi-

derations to those discussed for P_{12} in the first paragraph should be applied.

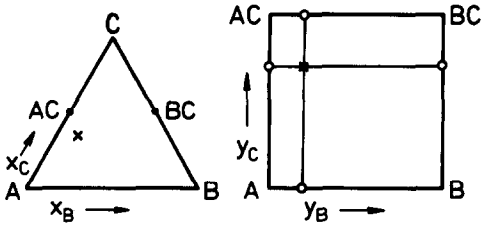

FIG. 4

Transformation of a highly asymmetric ternary system into a reciprocal system where the ternary properties are given as an average of those of four binary or quasi-binary systems.

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