Theory of Inhomogeneous Short Range Order and Calphad Modeling.

Part 3. Association Solution Model Reconstructed

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Abstract

Internal problems of Association Solution Model are analyzed, and based on this analysis a few important modifications are introduced in the formalism and in the interpretation of the model.

Reconstructed model is free from the mentioned problems and has significant advantages from the point of view of consistency and applicability.

A set of comparative examples is provided.

Keywords: Phase Diagram calculation; Computational Thermodynamics; Thermodynamic Activity; Thermodynamic Modeling; Quasichemical Model.

1 Introduction

Association Solution Model (ASM) [1–3] is a popular Statistical-Thermodynamic method widely used in Calphad. The model suggests the existence of molecular-like atom groups that define in essence the structure and the thermodynamics of the system.

Association is a common phenomenon for mixtures of organic components, but in this article we are primary interested in the opposite case where the model is applied to those liquid alloys that are known not to be molecular crystals or molecular solids [4] when investigated in solid state.

Many years ago Wagner [5] (see also [6]) expressed the opinion that existence of molecular-like stable atom groups in liquid is improbable since such molecules do not exist in the crystalline state. This point of view should not be neglected [7], [8] however model is systematically applied to the liquids that do not possess any proved molecular substructure.

Model by itself has multiple internal problems [2], [8] where one of the well-known difficulties is high-temperature behavior, which sharply contradicts the intuitive expectations.

As we will show, responsible for these problems are two closely related factors.

The first one is the rude, unjustified form of the combinatorial factor being used. It is critically important since the combinatorial factor is evidently the main functional element of the formalism [6] defining the behavior of the system.

The second one is the traditional form the associates are selected. The choice is justified by referencing the most stable compounds existing in the solid state [9]. Such choice seems quite reasonable but we will see that in reality it creates unsolvable artificial problems when extrapolating theory into the high temperature region.

It is important to note that both problems can be completely resolved if we follow a few simple rules when working with associate-like entities. It immediately brings ASM to a consistent and useful form.

Payment (and reward) for this improvement is the new understanding what "associates" really mean. We will see that in the high temperature region we cannot distinct "associates" from the simple statistical fluctuations, and such new interpretation helps change the theory in the way that significantly increases the applicability region of the theory and its internal consistency.

The Quasichemical Theory (QT) [10–12] is a good example of such interpretation. Specific atom groups – dimers – introduced by QT, serve as the basis of formalism but never are treated as "molecules".

The suggested modifications of ASM bring its basic principles and formalism to a very close similarity with the Theory of Inhomogeneous Short Range Order (TISR) [13]; the few important differences will be discussed.

Using multiple comparative examples we will show that, despite the pronounced distinctions in the basic principles, TISR is capable to reproduce successfully the thermodynamic behavior provided by the existing ASM applications.

2 Association Solution Model Basic Formalism

There are several versions of ASM formalism([2], [3], [11]) but the general idea is the suggestion that the interatomic forces are strong enough to create stable groups of atoms (associates) that coexist inside the binary liquid alloy as additional component (or components).

In the simplest case there is only one associate type (containing, say, i atoms of type a and j atoms of type b) and we need three variables to define the alloy composition – two variables for individual atoms and one for associate. We will use variables with indexes referencing the group structure:

M_{ij} – Number of associates containing every i atoms a and j atoms b ;

M_{10} – Number of atoms of type a ;

M_{01} – Number of atoms of type b .

$$M_{10} + M_{01} + M_{ij} = M \quad (1)$$

These variables are directly related to the integral atom composition of the system:

$$N_a = M_{10} + iM_{ij}; \quad N_b = M_{01} + jM_{ij} \quad (2)$$

The definition of the combinatorial factor is almost always based on the Bragg–Williams approximation [10]:

$$K_0 = \frac{M!}{M_{10}!M_{01}!M_{ij}!} \quad (3)$$

The corresponding expression for the Free Energy of the system [10] with fixed composition (2) can be written as:

$$F = E + \theta (M_{01} \ln p_{01} + M_{10} \ln p_{10} + M_{ij} \ln p_{ij}) + \lambda_a(N_a - M_{10} - iM_{ij}) + \lambda_b(N_b - M_{01} - jM_{ij}) \quad (4)$$

where

λ_a and λ_b are the Lagrange multipliers [10];

$p_\alpha = M_\alpha/M$;

θ is a temperature factor – composition of the absolute temperature and the Boltzmann constant k_B [10];

E is the energy of the system (that may depend on the composition but its precise form is not important in the high temperature limit).

The equations of equilibrium immediately follow:

$$\begin{aligned} \frac{\partial F}{\partial M_{10}} &= \frac{\partial E}{\partial M_{10}} + \theta \ln p_{10} - \lambda_a = 0 \\ \frac{\partial F}{\partial M_{01}} &= \frac{\partial E}{\partial M_{01}} + \theta \ln p_{01} - \lambda_b = 0 \\ \frac{\partial F}{\partial M_{ij}} &= \frac{\partial E}{\partial M_{ij}} + \theta \ln p_{ij} - i\lambda_a - j\lambda_b = 0 \end{aligned} \quad (5)$$

It brings us to the equilibrium equation

$$\frac{p_{ij}}{p_{10}^i p_{01}^j} = \exp\left(-\frac{\Delta E}{\theta}\right) \quad (6)$$

where

$$\Delta E = \frac{\partial E}{\partial M_{ij}} - i \frac{\partial E}{\partial M_{10}} - j \frac{\partial E}{\partial M_{01}} \quad (7)$$

The only thing we should know about ΔE is the fact that when temperature increases this value should remain finite.

3 Analyzing Combinatorial Factor

The only justification for introduction an associate is the hypothesis that this effect is result of intensive intermolecular forces. Increasing temperature should eventually destroy these formations. Nobody anticipates to find molecular-like associates in the high temperature region. It is why we expect that with the increasing temperature the associate concentration should go to zero and (according to the equation (4)) the alloy approaches the ideal behavior.

More formally, we anticipate that p_{ij}^0 that ensures minimal value of Free Energy (4) (as solution of the equation (6)), will approach zero when temperature increases.

Problem is that analysis of equation (6) shows immediately that it is not the case (unless the concentration of any of the components is zero).

Indeed, when the temperature increases then the right side of the equation (6) approaches finite non zero value; therefore all variables on the left side also must approach some finite non zero values.

Since p_{ij}^0 is the point of minimum of Free Energy (4)), we can right:

$$F(p_{ij}^0) \leq F(p_{ij})$$

where p_{ij} is arbitrary legal value.

Selecting $p_{ij} = 0$ on the right site of the inequality we can see that Free Energy (4) at $p_{ij} = p_{ij}^0$ is less then Free Energy of ideal mixture.

Taking in the account that we consider extremely high temperatures when energy E can be neglected, we come to conclusion that the provided by the expression (3) configurational entropy of system at $p_{ij} = p_{ij}^0$ *exceeds* the ideal entropy of system of $N_a + N_b$ particles – result that looks totally impossible.

It is popular to name this observation a "paradox" [14] but in reality we have here nothing but manifestation of uncontrolled (and in most cases unrecognized) errors in the based on definition (3) expression for the configurational entropy of system.

We would like to point now to several anomalies that may influence calculation, and finally bring the result to the evident error.

The simplest observation is the note [8] that the associate formation decreases the number of objects available for rearrangement *decreasing* therefore the configurational entropy.

To go beyond this evident remark we should provide more careful consideration.

Let us consider some example. In the picture below (simple two dimensional square lattice) we can see one associate $a - b$ (approximately in the middle) and multiple individual atoms around. It is important to realize that somewhere in the alloy can exist an associate $b - a$ (that has opposite orientation) and swapping of two could create a new macroconfiguration. By neglecting this possibility the expression (3) effectively underestimates the configurational entropy.

In addition to two named we have also two other inaccuracies in the expression (3) that outweigh the named ones and bring the final balance to the excess value.

Two atoms a and b in the fig.1 located in the right lower corner (and joined for the clarity by the dotted line) can be swapped with the associate (that, as mentioned, is

Figure 1: Single Atoms Around an Associate

located near the center of the figure). This rearrangement is included into the expression (3) by definition but in high temperature limit the involved macro configurations cannot be distinct. We have here an artificial form of Gibbs paradox [15] that makes it crystal clear that the expression (3) includes physically incorrect contributions.

Other issue, the expression (3) is constructed as if an associate could be swapped with a separate atom as easy as an atom with other atom, but it is evident that in the lattice-like approximation it is almost never possible without shifting *other* atoms around. Correct expression for the configurational entropy should take in account that in general case an associate can be swapped only with an atom group of equal size and form; this nuance is certainly outside the naive formula (3).

4 Fixing Associate Solution Model

Multiple problems discussed in the previous section show clearly one of the main problems of combinatorial factor (3). Contemporary mathematics cannot provide a reliable expression for the entropy of mixing if the mixed objects have distinct sizes. It is why the idea to use only groups of atoms of the same size (as it is done with the groups-dimers in the Quasichemical Theory [1, 10]) can bring significant advantages in the calculations and help to resolve the discussed inconsistencies.

Other issue is the way associates (usually a small set) are selected to be included in the model. At the low temperatures it is usually assumed that associates should inherit the composition of the most stable solid compound (or compounds) found in the system, though at high temperatures this justification looks less convincing.

But no matter how the selection was made, we have to trace it in the domain of high temperatures.

We had seen that when an associate is postulated at low temperatures it continues to exist at all temperatures, including the high temperatures.

What happen when two associates are postulated? Both continue to exist at high temperatures.

What about others compositions?

And here we come to the main paradox of the Association Solution Model. We postulated the existence of associate as the manifestation of especially strong forces at some composition but what we really achieved, we simultaneously *excluded* all other compositions from playing there role at high temperatures.

As result, the high temperature picture looks malformed. All groups at high temperature are equally justified. If some groups assumed to exist at high temperatures other groups also should have a chance.

The only way to achieve such "democratic" behavior is to allow concurrent groups to exist at all temperatures, even at very low ones. Some groups may be quantitatively suppressed but at high temperatures every atom group will start to play its role.

This section includes two main ideas:

- Consider only atom groups of the same size.
- Consider ALL atom groups that can play role at high temperatures.

Combination of these two ideas provides the final prescription:

- Consider all atom groups of some specific size and all possible internal configurations of such groups.

In the next section we will try to apply this prescription to fix the ASM formalism.

5 Adjusted Formalism

The requirements collected in the last section are the result of our attempt to present the configurational entropy in a computable form and removing the most evident logical inconsistencies.

In this section we should like to develop the formalism that follows these recommendations and investigate its high temperature behavior.

We had seen that the existence of intermediate phases and compounds is the main motivation to select a very small set of associates as basis of ASM.

In contrast, we cannot find any criteria that would justify the exclusion any of the atom groups at high temperatures. The only restriction is required mathematically – we selecting groups of only one size to be sure our calculations will be traceable.

In particular, we do not care if most of the introduced "associates" are suppressed at lower temperatures when only a few define the low temperature thermodynamics. By keeping the concentration of these extra elements small but distinct from zero we can investigate there role at high temperatures.

It is necessary now to introduce generalizations of notations used before. $M_{ij\alpha}$ means now the same as the previous symbol M_{ij} but contains an additional index α that distinguishes and numbers all possible for the atom group of specified content micro-configurations:

$$\alpha = 1, 2, \dots \binom{i+j}{i}$$

The combinatorial factor (3) takes the form:

$$K_1 = \frac{M!}{\prod_{ij\alpha} (M_{ij\alpha})!} \quad (8)$$

where (and in all following formulas) $i + j = k$ and k is the fixed size of the atom groups taken for consideration.

The corresponding expression for the Free Energy is now:

$$F = E + \theta \sum_{ij\alpha} M_{ij\alpha} \ln(M_{ij\alpha}/M) + \lambda_1 \left(N_1 - \sum_{ij\alpha} i M_{ij\alpha} \right) + \lambda_2 \left(N_2 - \sum_{ij\alpha} j M_{ij\alpha} \right) \quad (9)$$

Minimizing (9) by $M_{ij\alpha}$ we will get the equilibrium equations:

$$\frac{\partial F}{\partial M_{ij\alpha}} = \frac{\partial E}{\partial M_{ij\alpha}} + \theta \ln p_{ij\alpha} - i\lambda_1 - j\lambda_2 = 0 \quad (10)$$

where $p_{ij\alpha} = M_{ij\alpha}/M$.

These equations can be rewritten in the "quasichemical" form:

$$\frac{p_{ij\alpha}^k}{p_{k01}^i p_{0k1}^j} = \exp \left(-\frac{\Delta E}{\theta} \right) \quad (11)$$

where

$$\Delta E = k \frac{\partial E}{\partial M_{ij\alpha}} - i \frac{\partial E}{\partial M_{k01}} - j \frac{\partial E}{\partial M_{0k1}} \quad (12)$$

and M_{k01} is the number of the groups consisting from k atoms a only; M_{0k1} is the number of the groups consisting from k atoms b only; in both cases the last index $\alpha = 1$ indicates the only configuration such group can take.

The equations (11) can be explicitly resolved when the temperature is so high that the right side of equation approaches 1:

$$p_{ij\alpha} = x_1^i x_2^j \quad (13)$$

This expression doesn't depend on the sub-index α so we can calculate the proportion of groups having specific composition (independent of the distribution of internal atoms):

$$p_{ij} = \sum_{\alpha} p_{ij\alpha} = \binom{k}{i} x_1^i x_2^j \quad (14)$$

Using this expression we can immediately check that expression (8) reduces directly to the Bragg-Williams limit [10] resolving without difficulties the main ASM problem:

$$\begin{aligned}
1 &= \sum_{ij\alpha} p_{ij\alpha} = \sum_{ij} p_{ij} = \sum_{ij} \binom{k}{i} x_1^i x_2^j \\
&= (x_1 + x_2)^k \\
\ln K_1 &= - \sum_{ij\alpha} M_{ij\alpha} \ln(M_{ij\alpha}/M) = - \sum_{ij\alpha} M_{ij\alpha} \ln(p_{ij\alpha}) \\
&= - \sum_{ij\alpha} i M_{ij\alpha} \ln x_1 - \sum_{ij\alpha} j M_{ij\alpha} \ln x_2 \\
&= -N_1 \ln x_1 - N_2 \ln x_2
\end{aligned} \tag{15}$$

It is evident that this result cannot be kept in place if we artificially exclude any of $p_{ij\alpha}$ or p_{ij} components: every one is a vital part of the binomial theorem [16].

6 Theory of Inhomogeneous Short Range Order

The success of formalism presented in the previous section is based exclusively on the proper selection of atom groups [17]. Similar result was received several years ago in [18] but it is difficult to say if such choice of "associates" was ever used for thermodynamic modeling.

Indeed, direct usage of the developed formalism meets some considerable technical difficulties.

First, formalism requires a very significant increase in the number of associates. For example, if we consider a tetrahedron as a basic element then the model will include 16 types of associates (for binary system!).

Secondly, if we continue with the tetrahedron case, formalism will require solving 14 nonlinear equations, which certainly isn't trivial, unless we consider the *Ideal* ASM – the case where associates are considered not interacting – a popular assumption that is difficult to justify if we consider associates as real quasi-molecules.

Thirdly, the combinatorial factor (8) resolves the main problems of ASM but still has very low precision.

Solution to these problems comes from the Theory of Inhomogeneous Short Range Order (TISR) ([13, 17, 19]).

TISR is based on the same structural elements – atom groups of specific size – but uses more general expression for combinatorial factor:

$$K = \frac{N!}{N_a!N_b!} * \left(\frac{K_1}{K_1^\infty} \right)^\gamma \tag{16}$$

where K_1^∞ is the high temperature limit of K_1 (that occurs to be equal to $N!/(N_a!N_b!)$);

γ is a constant of geometrical nature, that depends on the lattice being considered and on the size of the groups selected for consideration [13]. For example, for the Quasi-chemical Theory (that is partial case of TISR [19]) γ coincides with the coordination

number z of the lattice. In the forth part of this publication [20] we consider an alternative choice of structural element γ which results in significant improvements of quality of approximation.

If we select $\gamma = 1$, the combinatorial factor (16) will reduce to (3). In [20] it is shown that the resulting theory loses the ability to describe immiscibility effects – confirming the low quality assessment of combinatorial factor (3) made above.

Returning to the main case it is necessary to point out right away that, despite of some similarities, TISR should not be considered as "generalization" of ASM. TISR is developed as a form of description the Short Range Order phenomenon, using for this end groups of atoms – cells – conditionally selected inside of alloy. It just happen that the equations of TISR are formally equivalent to some effective Ideal ASM while the interpretation of these equations is fundamentally distinct.

Basic principles of TISR are inconsistent with any attempt to treat cells as molecular-like entities; it is evident from the explicit requirement that the interactions inside cells cannot be differentiated from the interactions between cells. As result, the energy of cell's formation and the energy of cell's interaction can be summed up in a single expression:

$$E = \beta \sum_{ij\alpha} U_{ij\alpha} M_{ij\alpha} \quad (17)$$

If we neglect the multiplicative factor β , the sum on the right site of (17) is just the formation energy of the collection of cells. Factor $\beta > 1$ is responsible for inclusion into the total energy E the part that is equal to the energy of cell's interaction.

Detailed description of this subject can be found in [13].

Formally, expression (17) looks just as if the entire energy of system comes from the formation energy of cells. As result, equations of TISR are *always* formally equivalent to equations of *Ideal* ASM.

Opposite to this case, energy expression in general ASM consists from two distinct parts: one – for formation energy of associates, and other – for the energy of associate interaction.

The described peculiarity of energy expression in TISR dramatically simplifies the formalism of theory.

The formalism of TISR starts by considering all possible cells of given size (16 types for tetrahedron approximation) but if we introduce new notation W_{ij} (as analogs of statistical sums of cells of indicated composition):

$$W_{ij} = \sum_{\alpha} \exp \left(-\frac{\beta U_{ij\alpha}}{\theta\gamma} \right) \quad (18)$$

and corresponding molar fractions

$$p_{ij} = \sum_{\alpha} p_{ij\alpha} \quad (19)$$

then it occurs that all thermodynamic properties and composition of the system can be expressed through the new reduced variables [13].

It means, as example, that tetrahedron approximation uses only *three* not trivial combinations of variables (instead of originally introduced 14). This simplification dramatically improves maintainability and predicative ability of TISR, compared to ASM and other popular methods.

This section includes several examples where ASM based approximations for thermodynamic functions reported by different authors are reinterpreted using TISR. Selection of sources was random without attempt to bring up "good" cases only.

In all figures below the results of ASM approximations are shown as solid lines. TISR results are presented by the dotted lines. The parameters of TISR approximation are available in the table below (where $\theta * \partial W_i / \partial \theta$ is abbreviated as dW_i).

The presented examples show that TISR can successfully compete with the traditional ASM in a large number of cases including the systems with the advanced Short Order, however it requires in many cases to go beyond the tetrahedron approximation that was practically 100% successful ([13], [19]) as the replacement of the Redlich-Kister approximation [21] and Modified Quasichemical Model [22].

As explained above, difficulties increase when the deviations from the ideality achieve extreme values or when the interpolated according ASM charts show pronounced irregularities. In one case (system Hg-Te) the statistical sum W of one of the cells turns negative, taking the results over the borders of physically acceptable values. This result is, probably, a reflection of pronounced irregularities in behavior of four Redlich-Kister coefficients used by ASM approximation [23].

One of these four coefficients has value that exceeds the creation energy of associate, making it questionable if this associate can be treated as real quasi-molecule or is just a by-effect of irregularities introduced by approximation itself.

The presentation in this section is purely formal. We treat all examples based on the simplest substitution model though it is evident that at least in some cases two-lattice approach would be more natural. Such treatment requires some modifications to the basic formalism and will be presented elsewhere.

Table 1: TISR parameters adjusted to the ASM approximation.

System	System Parameters		
Ag-In fig.2	$W_0 = 1.0$ $W_3 = 5.478$ $dW_0 = 0.0$ $dW_3 = -49.681$	$W_1 = 4.033$ $W_4 = 1.0$ $dW_1 = -1.898$ $dW_4 = 0.0$	$W_2 = 6.995$ $dW_2 = -30.458$
Al-Ni fig.3	$W_0 = 1.0$ $W_3 = 5.009$ $dW_0 = 0.0$ $dW_3 = -7.805$	$W_1 = 5.009$ $W_4 = 1.0$ $dW_1 = -7.81$ $dW_4 = 0.0$	$W_2 = 8.555$ $dW_2 = -24.125$
Bi-Rb fig.4	$W_0 = 1.0$ $W_3 = 2015.612$ $W_6 = 613.024$ $dW_0 = 0.0$ $dW_3 = -120486.476$ $dW_6 = -29214.15$	$W_1 = 66.605$ $W_4 = 16111.744$ $W_7 = 35.13$ $dW_1 = -1378.246$ $dW_4 = -1282437.877$ $dW_7 = -766.061$	$W_2 = 2954.006$ $W_5 = 2677.368$ $W_8 = 1.0$ $dW_2 = -212295.721$ $dW_5 = -156948.362$ $dW_8 = 0.0$
Ca-Sb fig.5	$W_0 = 1.0$ $W_3 = 3.2773\text{e}+08$ $W_6 = 1.0$ $dW_0 = 0.0$ $dW_3 = -5.9511\text{e}+10$ $dW_6 = 0.0$	$W_1 = 1.3111\text{e}+05$ $W_4 = 1.0939\text{e}+06$ $dW_1 = -1.4803\text{e}+07$ $dW_4 = -9.0692\text{e}+07$	$W_2 = 9.8907\text{e}+09$ $W_5 = 1063.147$ $dW_2 = -1.7007\text{e}+12$ $dW_5 = -7.8388\text{e}+04$
Ca-Sn fig.6	$W_0 = 1.0$ $W_3 = 1.9334\text{e}+09$ $W_6 = 2.1864\text{e}+13$ $W_9 = 1.2666\text{e}+09$ $W_{12} = 1.0$ $dW_0 = 0.0$ $dW_3 = -3.1838\text{e}+11$ $dW_6 = -6.8617\text{e}+15$ $dW_9 = -2.7751\text{e}+11$ $dW_{12} = 0.0$	$W_1 = 4149.078$ $W_4 = 1.5283\text{e}+11$ $W_7 = 1.0495\text{e}+14$ $W_{10} = 1.8288\text{e}+07$ $dW_1 = -2.1680\text{e}+05$ $dW_4 = -3.2320\text{e}+13$ $dW_7 = -5.0235\text{e}+16$ $dW_{10} = -3.5110\text{e}+09$	$W_2 = 5.4210\text{e}+06$ $W_5 = 5.9711\text{e}+12$ $W_8 = 3.9894\text{e}+13$ $W_{11} = 6255.301$ $dW_2 = -8.8741\text{e}+08$ $dW_5 = -2.1849\text{e}+15$ $dW_8 = -2.1034\text{e}+16$ $dW_{11} = -7.3856\text{e}+05$
Cd-Te fig.7	$W_0 = 1.0$ $W_3 = 149368.068$ $W_6 = 1.0$	$W_1 = 90.423$ $W_4 = 801.613$	$W_2 = 6099.441$ $W_5 = 90.226$

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Table 1 – *Continued from previous page*

System	System Parameters		
Cd-Te fig.7	$dW_0 = 0.0$ $dW_3 = -16930032.234$ $dW_6 = 0.0$	$dW_1 = -3191.984$ $dW_4 = 118662.559$	$dW_2 = -418015.295$ $dW_5 = -1653.437$
Cu-Si fig.8	$W_0 = 1.0$ $W_3 = 205.054$ $W_6 = 851.527$ $dW_0 = 0.0$ $dW_3 = -966.178$ $dW_6 = -31846.25$	$W_1 = 10.258$ $W_4 = 1368.61$ $W_7 = 83.094$ $dW_1 = -39.658$ $dW_4 = -24635.186$ $dW_7 = -1852.374$	$W_2 = 147.945$ $W_5 = 839.133$ $W_8 = 1.0$ $dW_2 = -1605.21$ $dW_5 = -9597.291$ $dW_8 = 0.0$
Hg-Te fig.9	$W_0 = 1.0$ $W_3 = 242.239$ $W_6 = 92.123$ $dW_0 = 0.0$ $dW_3 = -10113.631$ $dW_6 = -688.044$	$W_1 = 13.252$ $W_4 = 685.122$ $W_7 = 10.427$ $dW_1 = -97.49$ $dW_4 = -14973.371$ $dW_7 = -51.863$	$W_2 = 56.46$ $W_5 = -48.057$ $W_8 = 1.0$ $dW_2 = -654.64$ $dW_5 = 338.43$ $dW_8 = 0.0$
Mg-Nd fig.10	$W_0 = 1.0$ $W_3 = 28.226$ $W_6 = 1.0$ $dW_0 = 0.0$ $dW_3 = -679.054$ $dW_6 = 0.0$	$W_1 = 6.511$ $W_4 = 36.775$ $dW_1 = -88.02$ $dW_4 = -787.836$	$W_2 = 21.039$ $W_5 = 12.681$ $dW_2 = -331.89$ $dW_5 = -429.367$
Mg-Pb fig.11	$W_0 = 1.0$ $W_3 = 125.376$ $W_6 = 1.0$ $dW_0 = 0.0$ $dW_3 = -1895.932$ $dW_6 = 0.0$	$W_1 = 11.814$ $W_4 = 182.902$ $dW_1 = -66.905$ $dW_4 = -3406.186$	$W_2 = 57.458$ $W_5 = 20.648$ $dW_2 = -596.927$ $dW_5 = -173.394$
Mg-Zn fig.12	$W_0 = 1.0$ $W_3 = 76.002$ $W_6 = 1.0$ $dW_0 = 0.0$ $dW_3 = -615.827$ $dW_6 = 0.0$	$W_1 = 17.919$ $W_4 = 45.246$ $dW_1 = -118.017$ $dW_4 = -339.289$	$W_2 = 107.589$ $W_5 = 10.633$ $dW_2 = -1364.75$ $dW_5 = -46.101$

7 Conclusions

Detailed analysis of formalism and ideology of ASM revealed multiple problems associated with the way the basic elements of the structure are selected and with the used combinatorial factor that is not capable to ensure acceptable precision in calculation of thermodynamic functions. It was explicitly shown how these basic errors inevitably lead to the well known ASM problems in the high temperature region.

We made attempt to modify the ASM by imposing a few additional requirements necessary to resolve the identified inconsistencies but as result we received a model that is exceptionally close to the Theory of Inhomogeneous Short Range Order that was developed based on absolutely different principles. It happen because the equations of TISR are formally equivalent to some effective Ideal ASM where the role of "associates" play groups of atoms – cells – conditionally selected inside an alloy.

Cells in TISR are introduced as a form of Short Range Order description and cannot be considered as molecular-like aggregates as it is in ASM. This distinction in interpretation is a great advantage of TISR, extending it internal consistency and the area of applicability.

The inherited from TISR version of ASM resolves, as shown in the previous sections, the long standing problems of the ASM [22]:

- Theory has the correct high temperature behavior;
- Precision in the high temperature region is at least as good as in the Quasichemical Theory;
- Theory can describe systems both with negative and *positive* deviations from the ideality;
- The concept of "self-association" introduced inside ASM to describe system with positive deviations from ideality is artificial and meaningless from TISR point of view;
- Theory can be easily extended to arbitrary large cell sizes as it may be necessary when considering systems with the advanced form of the Short Range Order.

It is especially interesting that the correct high temperature behavior is achieved by the mechanism fundamentally distinct from the traditionally expected inside ASM. Instead of anticipated decay of associates we can see that the concentrations of all atom groups approach there statistically determined non zero values and these concentrations sum up to the Bragg–Williams limit thanks to the binomial theorem [16]. It is the breaking point that shows that interpretation of "associates" as the normal statistical fluctuations may have much more reasons than it is usually accepted; at least it is certainly correct in the high temperature region.

A question arises naturally if it is still possible to combine this picture with the idea of molecular-like associates.

From the physical point of view an atom group can be treated as a "molecule" only when the forces inside associates are significantly stronger than the forces between groups. In this case we can expect that the equilibrium in the system is shifted to a complete extinction of one of the components.

Simultaneously it becomes very probably that the role of all other atomic groups can be neglected; but if it is really done and these "low importance" groups are excluded

from the consideration then we come back to the picture that is absolutely impossible to keep intact when considering the high temperature limit.

On the contrary, the version of Ideal ASM derived from TISR and described in the previous sections is expected to work good at high and intermediate temperatures but may have problems at low temperatures when intensive interatomic forces completely destroy quasi-lattice model this version is based on.

The multiple examples presented in the previous section show that TISR can successfully compete with the traditional ASM in a large number of cases including the systems with the advanced SRO, however it requires in many cases to go beyond the tetrahedron approximation that was practically 100% successful ([13], [19]) as the replacement of the Redlich-Kister approximation [21] and Modified Quasichemical Model [22].

Interpretation of model theories is always difficult. We noted above that the energy of formation of "real" associate, if any, is expected to exceed significantly the energy of associate interaction and the last can be even neglected in the first approximation. But we have no practical method to distinct such effective Ideal ASM from the Ideal ASM provided by TISR where all "associate interaction energies" are not present in the formalism explicitly, but being included, as not separable part, into the formation energy of associates. Without direct method of measurement of interaction between associates the discussed criteria occurs useless.

As other aspect of the ambiguity in interpretation we should like to point to multiple cases when ASM is mechanically applied to the systems that have probably multi-lattice atom configuration. Typical example is description of system Fe-S using ASM [24] that can be equally good described by multi-lattice model [25], [17]; this description looks physically more founded. Number of such examples may be very significant.

The presentation in this article is based on substitutional model of alloy and in this sense is purely formal since in many cases systems reveal evident two-lattice behavior.

An important aspect of charts collected in this article is the fact that TISR presentation is based on the data already approximated using ASM. It is not clear if the pronounced irregularities found in some of the systems have to be attributed to the physical system itself or are just artifacts of ASM approximation. To answer this question TISR has to be applied directly to the experimental data rather than to charts generated using ASM machinery. Using the two-lattice model, where adequate, we could also significantly improve and simplify the result.

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Figure 2: System Ag-In ($T = 1100$ K): solid lines – [26]; dotted lines - TISR;
TISR parameters: $k = 4$; $\beta = 4$; $\gamma = 4$

Figure 3: System Al-Ni ($T = 1728$ K): solid lines – [27]; dotted lines - TISR;
TISR parameters: $k = 4$; $\beta = 4$; $\gamma = 4$

Figure 4: System Bi-Rb ($T = 1273$ K): solid lines – [28]; dotted lines - TISR;
TISR parameters: $k = 8$; $\beta = 4$; $\gamma = 4$

(a) Component Activities

(b) Enthalpy of Mixing (kJ/mol)

Figure 5: System Ca-Sb ($T = 1073$ K): solid lines – [29]; dotted lines - TISR;
TISR parameters: $k = 6$; $\beta = 2$; $\gamma = 2$

(a) Component Activities

(b) Enthalpy of Mixing (kJ/mol)

Figure 6: System Ca-Sn ($T = 1273$ K): solid lines – [30]; dotted lines - TISR;
TISR parameters: $k = 12$; $\beta = 2$; $\gamma = 2$

(a) Component Activities

(b) Enthalpy of Mixing (kJ/mol)

Figure 7: System Cd-Te ($T = 1273$ K): solid lines – [23]; dotted lines - TISR;
TISR parameters: $k = 8$; $\beta = 8$; $\gamma = 8$

(a) Component Activities

(b) Enthalpy of Mixing (kJ/mol)

Figure 8: System Cu-Si ($T = 1753$ K): solid lines – [31]; dotted lines - TISR;
TISR parameters: $k = 8$; $\beta = 4$; $\gamma = 4$

(a) Component Activities

(b) Enthalpy of Mixing (kJ/mol)

Figure 9: System Hg-Te ($T = 873$ K): solid lines – [23]; dotted lines - TISR;
TISR parameters: $k = 8$; $\beta = 4$; $\gamma = 4$

(a) Component Activities

(b) Enthalpy of Mixing (kJ/mol)

Figure 10: System Mg-Nd ($T = 1073$ K): solid lines – [32]; dotted lines - TISR;
TISR parameters: $k = 6$; $\beta = 4$; $\gamma = 4$

(a) Component Activities

(b) Enthalpy of Mixing (kJ/mol)

Figure 11: System Mg-Pb ($T = 905$ K): solid lines – [33]; dotted lines - TISR;
TISR parameters: $k = 6$; $\beta = 4$; $\gamma = 4$

(a) Component Activities

(b) Enthalpy of Mixing (kJ/mol)

Figure 12: System Mg-Zn ($T = 933$ K): solid lines – [34]; dotted lines - TISR;
TISR parameters: $k = 6$; $\beta = 4$; $\gamma = 4$