# APPLICABILITY OF QUASICHEMICAL MODEL FOR SOME LIQUID ALLOYS WITH STRONG-INTERACTED COMPONENTS①

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**ABSTRACT** A system of semi-empirical equations has been tested by data fitting using a new computation technique- genetic algorithms. These equations have been developed for the analysis of the thermodynamic properties of some liquid alloys with strong-interacted components such as Na-Tl and Na-Sn. The equations, which are based on the quasichemical model, take into account the dependence of the interaction energy on the microscopic environments. The enthalpy of mixing-composition curves can be rather accurately described by this modified Guggenheim's formula, but the experimental data of the entropy of mixing are in discrepancy with the calculated configurational entropy of mixing. This discrepancy can be explained by nonconfigurational entropy change due to stronger chemical bond formation.

**Key words** genetic algorithms thermodynamic properties quasichemical model Na-Tl alloys Na-Sn alloys

## 1 INTRODUCTION

Regular solution model is a very commonly used statistical model for the description of the composition-property relationships of liquid alloys. The zeroth order approximation of regular solution model, assuming the excess entropy of mixing equal to zero, can be used to describe the thermodynamic properties of the liquid alloys with weak interaction between their components. For the liquid alloys with strong interaction, zeroth order approximation is no more suitable. It is usually to propose the first order approximation, or quasichemical model[1] to describe such kind of alloys. So it is meaningful to investigate the degree or limit of applicability of quasichemical model for such kind of liquid alloys.

As well known, quasichemical approximation is widely used for the study of the thermodynamic properties of the metallurgical melts with strong interaction between their components. In its original form, this model leads to completely symmetrical functions respective to the composition of the mixtures. For many liquid alloys, however, these functions are unsymmetrical. Taking Na-Tl alloys as an example, the $\Delta U$, $\Delta H$ and $\Delta F$ of mixing do not exhibit extreme values at $x_{Na} = x_{Tl} = 0.5$, but at $x_{Tl} \approx 0.55$[2]. The heat of mixing between Na and Tl in dilute solutions of both sides are also not equal, implying that the interaction energy $W$ which has differences between Na-Na pairs, Tl-Tl pairs and Na-Tl pairs are dependent on their microscopic environments, namely

$$W = W_0 + W_1 x + W_2 x^2 + \cdots \quad (1)$$

So a modified quasichemical model is needed for the description of the thermodynamic properties of such liquid alloys systems. In this model, together with the interaction and structural parameters- $W_0$(first term of the interaction energy of atomic pairs) and $z$ (apparent number of

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nearest neighbors), we have to determine the higher order terms $W_1$, $W_2$, etc.. To solve this problem we must use nonlinear technique. Since classical data fitting techniques are poor for the data fitting for a definite mathematical model especially nonlinear ones and genetic algorithms are powerful tools for this target, in this work we use one of them to test the applicability of a modified quasichemical model for Na-Tl and Na-Sn liquid alloys as the examples. Then we discuss the physical significance of the calculation results.

## 2 METHODS OF COMPUTATION

### 2.1 Genetic algorithms

Genetic algorithms (GAs)[3, 4] are computation methods for heuristic searching, based on the simulation of natural selection. Since GAs are more powerful than some traditional searching methods for nonlinear problems, especially when the data space is large, discontinuous, complex, with noisy environments and poorly understood, it has been widely used in many scientific research fields in recent years[5, 6].

A conventional GA can be described by the following steps:

1) Initialization: Generate a random initial population of chromosomes. The chromosomes manipulated in GAs are usually coded parameters of the search space as binary strings. The chromosomes encoded in this way, know nothing about the type of the problem being solved.

2) Evaluation: Evaluate the goodness of each individual in the population. Here, our evaluation criterion is

$$s = \Sigma(\text{experimental values} - \text{calculated values})^2 \quad (2)$$

3) Selection: The chromosomes are selected to be reproduced at rates according to their goodness, until a new population thus formed reaches the size of the current population. The idea behind this is Darwin's "survival of the fittest": the new population is, on average, expected to perform better due to the selection "pressure" exerted.

4) Exploration: To reach potentially better estimates, the chromosomes in the new population are modified to some controlled extent by operators reminiscent of crossover and mutation as applied to biological chromosomes to create new chromosomes.

5) Repeat step 2 to 4. It will be stopped if the halt condition is achieved. Some important parameters for GA are listed bellow:

| population size | crossover rate | mutation rate | cycle time |
|---|---|---|---|
| 10 | 0.6 | 0.01 | 400 |

### 2.2 Modified quasichemical model

Quasichemical approximation defines the following formula for the energy of mixing:

$$\Delta_m U = \frac{2}{\beta + 1} x(1 - x) W_N \quad (3)$$

Since the volume change in the mixing process is negligible, we have the enthalpy of mixing

$$\Delta_m H = \frac{2}{\beta + 1} x(1 - x) W_N \quad (4)$$

And the free energy of mixing is

$$\Delta_m F = RT\left[(1 - x)\ln(1 - x) + x\ln x + \frac{1}{2} z\left\{(1 - x)\ln\frac{\beta + 1 - 2x}{(1 - x)(\beta + 1)} + x\ln\frac{\beta - 1 + 2x}{x(\beta + 1)}\right\}\right] \quad (5)$$

where

$$\beta = \{1 + 4x(1 - x)(\eta^2 - 1)\}^{\frac{1}{2}} \quad (6)$$

$$\eta = e^{W_N/zkT} \quad (7)$$

In the modified quasichemical model, $W_N$ is defined as a polynomial expansion which introduces asymmetrical property

$$W_N = W_0 + W_1 x + W_2 x^2 + \cdots + W_m x^m \quad (8)$$

Here $x$ is the mole fraction of one component, $T$ is the temperature and $k$ is the Boltzmann constant.

## 3 RESULTS AND DISCUSSION

As we make correlation for the experimental data, it has been found the choice of the value of z exhibits only very small influence on the accuracy of correlation. Although Pelton and Blander[7] have argued that $z = 2$ is suitable for liquid silicate melts which may have necklace struc-

ture, it seems more reasonable to use $z = 6 \sim 8$ for liquid alloys like Na-Tl and Na-Sn systems. We use $z = 6$ for the correlation, $W_N = -13\,316.72 + 21\,372.43x - 25\,452.59x^2$ J·mol$^{-1}$ (here, $x = x_{Tl}$) for Na-Tl alloys and $W_N = -21\,434.02 + 26\,969.70x - 19\,304.01x^2$ J·mol$^{-1}$ (here, $x = x_{Sn}$) for Na-Sn alloys according to the experimental data of enthalpy. So the enthalpy of mixing and the entropy of mixing and others can be calculated for comparison. The results of computation compared with the experimental data are illustrated in Fig. 1 to 4 respectively.

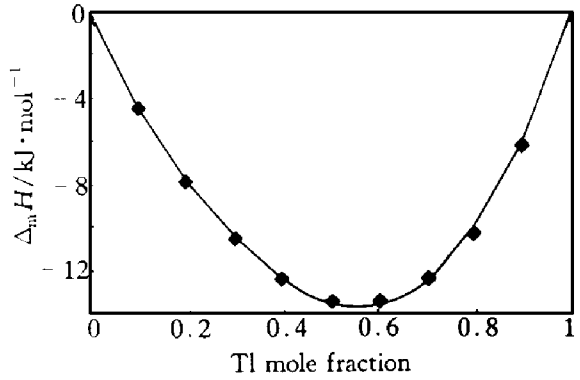


**Fig. 1 Enthalpy of mixing of liquid Na-Tl alloys at 648 K**

◆—Experimental values; ——Calculated values

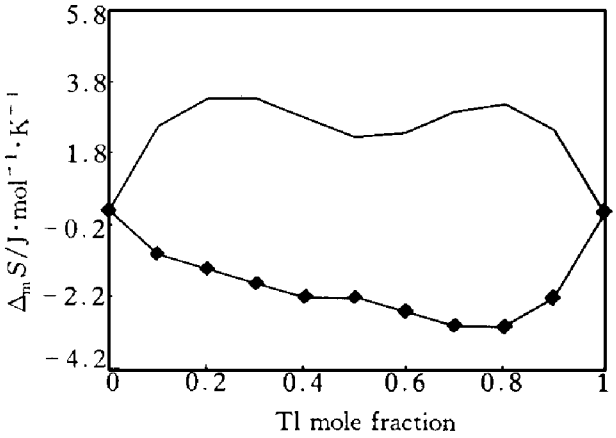


**Fig. 2 Entropy of mixing of liquid Na-Tl alloys at 648 K**

◆—Experimental values; ——Calculated values

From Fig. 1 and Fig. 3, we can know that the modified quasichemical model can give good correlation between the experimental data and calculated data of enthalpy of mixing. That is to say, the dependence of the interaction energy

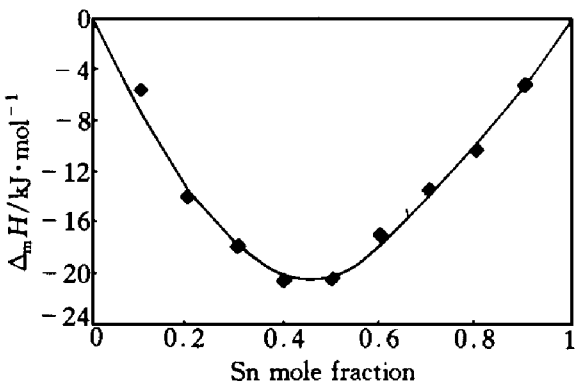


**Fig. 3 Enthalpy of mixing of liquid Na-Sn alloys at 773 K**

◆—Experimental values; ——Calculated values

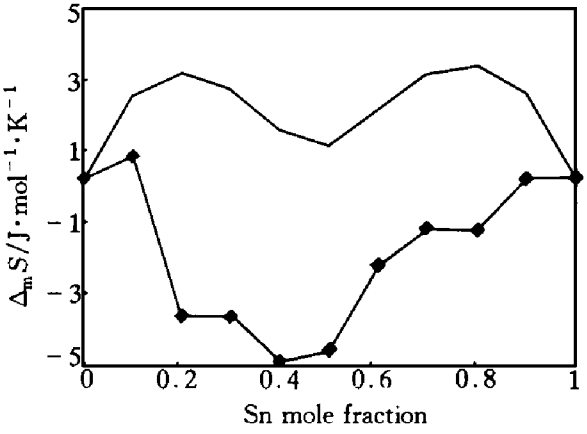


**Fig. 4 Entropy of mixing of liquid Na-Sn alloys at 773 K**

◆—Experimental values; ——Calculated values

between atoms on their microscopic environments is indeed a reasonable explanation of the asymmetry of enthalpy-composition curves. But also we can find that the calculated entropy of the mixing process does not correlated with the experimental data. Those two calculated entropy curves are all in "m" shape. Those calculated data conform to the quasichemical model. The "theoretical" curve of the entropy of mixing in the quasichemical model is "m" type. It is understandable that the configurational entropy of mixing is always positive. While the experimental values of entropy are negative and not agree with the values calculated by quasichemical model. This discrepancy can be explained by the fact that the quasichemical model and the modified quasichemical model do not consider the noncon-

figurational entropy (or thermal entropy) change during mixing.

In our previous work[8], it has been found that negative entropy of mixing is a common phenomenon for liquid alloys whose $\Delta\varphi^*$ and $\Delta n_{WS}^{1/3}$ are both large ($\Delta\varphi^*$ and $\Delta n_{WS}^{1/3}$ are parameters proposed by Miedema). This can be explained by the change of nonconfigurational entropy of mixing. According to Miedema's cellular model[9] of alloy phases, large $\Delta\varphi^*$ induces charge transfer which makes the alloy phase more stable while large $\Delta n_{WS}^{1/3}$ resists the formation of neighboring pairs of different kinds of atoms. When both $\Delta\varphi^*$ and $\Delta n_{WS}^{1/3}$ are large, the best arrangement of atoms should be in such a manner that the atoms of higher $\Delta n_{WS}^{1/3}$ form atomic clusters surrounded by atoms of lower $\Delta n_{WS}^{1/3}$. This kind of structure can lead smaller interfaces between atoms of different kinds (thus to reduce the resistance induced by large $\Delta n_{WS}^{1/3}$) and can keep enough charge transfer due to large $\Delta\varphi^*$ at the same time. Na-Tl and Na-Sn systems indeed exhibit large $\Delta\varphi^*$ and $\Delta n_{WS}^{1/3}$, so it is reasonable to imagine that thallium or tin atoms tend to form clusters in liquid alloys. The clustering of atoms will obviously reduce the non-configurational entropy which is induced by the translation motion etc..

So we can see the applicability and the limit of the quasichemical model and the modified quasichemical model applied for the description of the thermodynamic properties of some liquid alloys with strongly interacted components. For the systems whose $\Delta\varphi^*$ and $\Delta n_{WS}^{1/3}$ are large, the influence of non-configurational entropy change due to atomic cluster formation have to be considered. So, for these systems, although the enthalpy-composition relationship can be apparently described by the formula derived from modified quasichemical model, it should be very cautious to use the $W_N$ values obtained from the data processing of one kind of thermodynamic functions to describe others without considering the influence of non-configurational entropy.

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