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Comment on “Thermodynamic description of the Hg–Te system” [Journal of Alloys and Compounds 494 (1–2) (2010) 102–108]

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ABSTRACT

Recently Gierlotka [Journal of Alloys and Compounds 494 (1–2) (2010) 102–108] reported on thermodynamic assessments of the Hg–Te binary system using (1) two-sublattice ionic model, (2) associate model, and (3) random mixing model for the liquid phase. And a conclusion was made such that the two-sublattice ionic model and the associate model are superior to the random mixing model in describing thermodynamic properties and phase diagram of the Hg–Te system, and the two-sublattice ionic model seems to be more suitable for describing Hg–Te binary system due to ionic behavior of the Hg–Te liquid. Purpose of the present letter is to point out that (1) the two-sublattice ionic model and the associate model can be made mathematically the same in a binary system as in the Hg–Te system, therefore two different assessments using either the two-sublattice ionic model or the associate model by Gierlotka are essentially very similar as long as the parameters used in both models are similar, and (2) the two models can also be made mathematically equivalent even in higher order system under certain conditions.

1. Discussion on the comparison between two-sublattice ionic model and associate model in the modeling of Hg–Te binary liquid

In a binary A–B system, if species A and B exhibit a strong attraction, then there is a short-range ordering (SRO) in liquid phase, and a stable solid compound is often observed at the composition of maximum SRO. Such SRO has been thermodynamically modeled by associate model [1], two-sublattice ionic model [2], cell model [3] or the modified quasichemical model [4]. Recently, Pelton and Kang [5] discussed how to treat such SRO in solutions.

Gierlotka [6] have thermodynamically assessed a binary Hg–Te system where the liquid phase was modeled using three different approaches: (1) two-sublattice ionic model, (2) associate model, and (3) random mixing model (referred to as subregular model in Ref. [6]). Model parameters for each model were obtained after optimization process by reproducing all available experimental data within experimental error limit. And conclusions were made such that (1) the two-sublattice ionic model and the associate model are superior to the random mixing model in describing thermodynamic properties and phase diagram of the system, (2) and the two-sublattice ionic model seems to be more suitable for describing Hg–Te binary liquid phase than the associate model due to ionic behavior of the Hg–Te liquid phase. The present author agrees to the first conclusion, but not to the second conclusion. In a binary system, the two-sublattice ionic model and the associate model are mathematically the same under certain condition. It has been already discussed by Hillert et al. [2], and will be shown in the case of Hg–Te in this communication.

In the Hg–Te binary liquid, a strong SRO is observed at $X_{\mathrm{Te}} = 0.5$, therefore the binary liquid phase was modeled either by the two-sublattice ionic model with the following formula [6]:

$$(\mathrm{Hg}^{2+})_P(\mathrm{Te}^{2-}, \mathrm{Te}^{\circ}, \mathrm{Va}^{2-})_Q \tag{1}$$

or by the associate model assuming random distribution of “HgTe” associate along with unassociated Hg and Te on a quasilattice [6]:

$$(\mathrm{Hg}, \mathrm{HgTe}, \mathrm{Te}) \tag{2}$$

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When the two-sublattice ionic model is used, the Gibbs energy of mixing per mole of atom is given as:

$$\Delta G^{\text{ionic}} = \frac{[y_{\text{Te}^{2-}}\Delta G_{\text{Hg}_2\text{Te}_2} + QRT(y_{\text{Te}^{2-}}\ \ln y_{\text{Te}^{2-}} + y_{\text{Te}^{\circ}}\ \ln y_{\text{Te}^{\circ}} + y_{\text{Va}^{2-}}\ \ln y_{\text{Va}^{2-}}) + y_{\text{Te}^{2-}}y_{\text{Te}^{\circ}}L^{\text{ionic}}_{\text{Hg}^{2+}:\text{Te}^{2-},\text{Te}^{\circ}} + y_{\text{Te}^{2-}}y_{\text{Va}^{2-}}L^{\text{ionic}}_{\text{Hg}^{2+}:\text{Te}^{2-},\text{Va}^{2-}}]}{[P + Q(y_{\text{Te}^{2-}} + y_{\text{Te}^{\circ}})]} \quad (3)$$

where y_i is site fraction of species i (thus, $y_{\text{Hg}^{2+}} = 1$), $\Delta G_{\text{Hg}_2\text{Te}_2}$ is the Gibbs energy of formation of $(\text{Hg}^{2+})_2(\text{Te}^{2-})_2$.

L parameters are given in Table 2 in Ref. [6].

$$L^{\text{ionic}}_{\text{Hg}^{2+}:\text{Te}^{2-},\text{Va}^{2-}} = {}^0L^{\text{ionic}}_{\text{Hg}^{2+}:\text{Te}^{2-},\text{Va}^{2-}} + {}^1L^{\text{ionic}}_{\text{Hg}^{2+}:\text{Te}^{2-},\text{Va}^{2-}}(y_{\text{Te}^{2-}} - y_{\text{Va}^{2-}}) \quad (4)$$

$$L^{\text{ionic}}_{\text{Hg}^{2+}:\text{Te}^{2-},\text{Te}^{\circ}} = {}^0L^{\text{ionic}}_{\text{Hg}^{2+}:\text{Te}^{2-},\text{Te}^{\circ}} \quad (5)$$

In Eq. (3), Q is calculated as

$$\sum_{i=\text{cation}} \nu_i y_i = \nu_{\text{Hg}^{2+}} y_{\text{Hg}^{2+}} = 2 \quad (6)$$

where ν_i is electrical charge of species i. The denominator $[P + Q(y_{\text{Te}^{2-}} + y_{\text{Te}^{\circ}})]$, which represents total number of moles of atoms in the formula unit $(\text{Hg}^{2+})_P(\text{Te}^{2-}, \text{Te}^{\circ}, \text{Va}^{2-})_Q$, is calculated to be $[2y_{\text{Te}^{2-}} + 2]$. Therefore, the Gibbs energy of mixing per mole of atom given in Eq. (3) is finally:

$$\Delta G^{\text{ionic}} = \frac{[y_{\text{Te}^{2-}}\Delta G_{\text{HgTe}} + RT(y_{\text{Te}^{2-}}\ \ln y_{\text{Te}^{2-}} + y_{\text{Te}^{\circ}}\ \ln y_{\text{Te}^{\circ}} + y_{\text{Va}^{2-}}\ \ln y_{\text{Va}^{2-}}) + y_{\text{Te}^{2-}}y_{\text{Te}^{\circ}}((1/2)L^{\text{ionic}}_{\text{Hg}^{2+}:\text{Te}^{2-},\text{Te}^{\circ}}) + y_{\text{Te}^{2-}}y_{\text{Va}^{2-}}((1/2)L^{\text{ionic}}_{\text{Hg}^{2+}:\text{Te}^{2-},\text{Va}^{2-}})]}{[y_{\text{Te}^{2-}} + 1]} \quad (7)$$

where ΔG_{HgTe} is the Gibbs energy change of the following reaction:

$$\text{Hg}(l) + \text{Te}(l) = \text{HgTe}(l); \quad \Delta G_{\text{HgTe}} \quad (8)$$

On the other hand, the binary Hg–Te liquid is modeled using the associate model assuming "HgTe" associate, then the Gibbs energy of mixing per mole of atom is given by:

$$\Delta G^{\text{associate}} = \frac{[X_{\text{HgTe}}\Delta G_{\text{HgTe}} + RT(X_{\text{HgTe}}\ \ln X_{\text{HgTe}} + X_{\text{Te}}\ \ln X_{\text{Te}} + X_{\text{Hg}}\ \ln X_{\text{Hg}}) + X_{\text{Hg}}X_{\text{HgTe}}L^{\text{associate}}_{\text{Hg,HgTe}} + X_{\text{Te}}X_{\text{HgTe}}L^{\text{associate}}_{\text{HgTe,Te}}]}{[1 + X_{\text{HgTe}}]} \quad (9)$$

where X_i is mole fraction of species i.[1]

The L parameters are given in Table 2 in Ref. [6].

$$L^{\text{associate}}_{\text{Hg,HgTe}} = {}^0L^{\text{associate}}_{\text{Hg,HgTe}} + {}^1L^{\text{associate}}_{\text{Hg,HgTe}}(X_{\text{Hg}} - X_{\text{HgTe}}) \quad (10)$$

$$L^{\text{associate}}_{\text{HgTe,Te}} = {}^0L^{\text{associate}}_{\text{HgTe,Te}} \quad (11)$$

The following relations between the site fraction in Eq. (7) and the mole fraction in Eq. (9) hold:

$$y_{\text{Te}^{2-}} = X_{\text{HgTe}}, \quad y_{\text{Te}^{\circ}} = X_{\text{Te}}, \quad y_{\text{Va}^{2-}} = X_{\text{Hg}} \quad (12)$$

Therefore, from Eqs. (7) and (9), it is evident that two models becomes mathematically identical if the following conditions are fulfilled:

$$\begin{aligned} L^{\text{associate}}_{\text{Hg,HgTe}} &= \frac{1}{2}L^{\text{ionic}}_{\text{Hg}^{2+}:\text{Te}^{2-},\text{Va}^{2-}} \\ L^{\text{associate}}_{\text{HgTe,Te}} &= \frac{1}{2}L^{\text{ionic}}_{\text{Hg}^{2+}:\text{Te}^{2-},\text{Te}^{\circ}} \end{aligned} \quad (13)$$

Indeed, the model parameters for the two-sublattice ionic model and the associate model in Table 2 in Ref. [6] seems to satisfy the above relations (Eq. (13)). That is why the model calculations using two models look very similar as shown in Ref. [6]. Therefore, it is not reasonable to conclude that one model (either the two-sublattice ionic model or the associate model) is better than the other model (either the associate model or the two-sublattice ionic model), at least in a binary system, in describing thermodynamic properties of a phase. They are mathematically identical as long as the model parameters in both models satisfy the above relations (Eq. (13)), or they are very similar as long as the model parameters in both models are very similar. In any case, mathematical forms of both models are the same. In the work of Gierlotka [6], therefore, he actually described thermodynamic properties of the Hg–Te binary liquid using *almost* same models, and concluded that the two-sublattice ionic model is better than the associate model for the modeling of Hg–Te liquid solution. This conclusion cannot be justified just doing modeling in a binary solution. In order to conclude such that a model is better than the other, one should look at ternary or higher order system.

2. Comparison between two-sublattice ionic model and associate model in the modeling of ternary or higher-order solution

The equivalence between the two-sublattice ionic model and associate model in a binary system was already mentioned in the original work of Hillert et al. [2], and it was shown in the case of Hg–Te binary liquid in the previous section. For ternary and higher-order systems, according to Hillert et al. [2], "the two models cannot be made identical". This is generally true, however depending on how the models are constructed, the equivalence between the two models can be kept.

Consider a ternary solution with components A, B and C in which the binary solution A–B exhibits a strong tendency to SRO at the $A_{-\nu_B/n}B\nu_A$ composition, while the B–C and C–A binary solutions are less strongly ordered. According to the associate model, one may consider $A_{-\nu_B/n}B_{\nu_A/n}$ associate along with unassociated A, B, and C (n is arbitrary number which may be set conviniently). Then the ternary solution is described as a substitutional solution composed of A, B, C and $A_{-\nu_B/n}B_{\nu_A/n}$. Similarly, if the two-sublattice ionic model is described with the following model structure, $(A^{\nu_A})_P(B^{-\nu_B}, B^{\circ}, \text{Va}^{-\nu_{Va}}, C^{\circ})_Q$, then the model would describe the solution so as to mix A_PB_Q, B_Q, A_P and C_Q. Since $Q = \nu_A$ and $P = -\nu_B y_B + \nu_A y_{Va}$, the components of the model would then be $A_{-\nu_B}B_{\nu_A}$, B_{ν_A}, A_{ν_A}, and C_{ν_A}. Therefore, if the components of the two-sublattice ionic model are normalized by the factor ν_A, and the arbitrary number n in the associate model is set to ν_A, then both models are reduced to a substitutional solution model composed of A, B, C and $A_{-\nu_B/\nu_A}B$. This equivalence has been demonstrated for the case of Mg–Al–Sn ternary liquid solution by Pelton et al. [7].

This equivalence between the two models holds as long as new component in the system does not exhibits strong interaction with other already existing components (no more associate formation in the associate model, or entering in the anionic sublattice as neutral species in the two-sublattice ionic model). Therefore, in such case, it is still not true to conclude that one model (either the two-sublattice ionic model or the associate model) is better than the other model (either the associate model or the two-sublattice ionic model) in describing thermodynamic properties of a phase. Obviously, if the new component exhibits a strong interaction with other already existing components, then the two models will be different.

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[1] The very last term $(1 + 2X_{\text{HgTe}})$ in Eq. (8) given in Ref. [6] must be corrected as $(1 + X_{\text{HgTe}})$.

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