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# Prediction on thermodynamic properties of ternary molten mattes from Wilson equation

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## Abstract

An attempt was made to use the Wilson equation to predict the thermodynamic properties of ternary molten mattes. The activities of components of ternary molten mattes were found to be conveniently predicted from their binary parameters. The predicted values were in good agreement with the ternary experimental data. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Activities; Ternary molten mattes, prediction; Wilson equation

## 1. Introduction

To make up for a shortcoming of classical thermodynamics, many empirical or semiempirical models based on the theory of regular solutions have been developed for predicting the thermodynamic properties of ternary and even multicomponent systems. A common characteristic among them is to be more empirical, namely, if only binary data are used to predict the thermodynamic properties of a ternary system, the deviations of predicted values will be larger; and if it is desirable for the values to match the required accuracy, a portion of experimental data of a ternary system has to be employed in the fitting computation. For this reason, more characteristic parameters have been introduced into the models, which reduces their predicting ability [1]. It can be seen that searching for a model that can be conveniently and reliably used to predict the thermodynamic properties of a ternary system from its binary data is of much significance for both scientific research and engineering designs.

A significant feature of the Wilson equation [2] is that the equation for a multicomponent solution requires only constants that can be obtained from binary mixture data, which provides an important economic advantage, since the amount of experimental and computing work required to characterize a multicomponent solution is thereby very much reduced. The purpose of this work, therefore, is to show the advantage of the Wilson equation for ternary molten mattes and to make a comparison of its predicted values with a ternary data.

## 2. Determination of Wilson parameters

The Wilson equation does not introduce any specific ternary constants in its multicomponent form.

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The activity coefficient is given by [2,3]

$$\ln\gamma_i = 1 - \ln\left(\sum_{j=1}^{n} A_{ji}x_j\right) - \sum_{j=1}^{n}\left(\frac{A_{ij}x_j}{\sum_{k=1}^{n} A_{kj}x_k}\right) \qquad (1)$$

where $\gamma_i$ is the activity coefficient of component $i$, $x_{j,\text{ or }k}$ the molar fraction of component $j$ or $k$, and $A_{ji}$ or $A_{ij}$ the binary constant or the Wilson parameter. To examine the suitability and reliability of Eq. (1) for ternary molten mattes, the experimental data of activity of the component SnS in the SnS–FeS–$Cu_2S$ [4] melts and the component PbS in the PbS–FeS–$Cu_2S$ [5] melts at 1473 K are employed. Let components SnS or PbS=1, FeS=2, and $Cu_2S$=3; thus the activity coefficient of component 1 in a ternary system 1-2-3 can be written from Eq. (1):

$$\begin{aligned}\ln\gamma_1 = {} & 1 - \ln(x_1 + A_{21}x_2 + A_{31}x_3) \\ & - \frac{x_1}{x_1 + A_{21}x_2 + A_{31}x_3} \\ & - \frac{A_{12}x_2}{A_{12}x_1 + x_2 + A_{32}x_3} \\ & - \frac{A_{13}x_3}{A_{13}x_1 + A_{23}x_2 + x_3}\end{aligned} \qquad (2)$$

The 10 binary constants of the two ternary melts can be obtained from the activities of the five binary melts: SnS–FeS [6], SnS–$Cu_2S$, FeS–$Cu_2S$ [4], PbS–FeS and PbS–$Cu_2S$ [5]. The calculation steps are as follows:

For a binary system *i-j*, the activity coefficients of components *i* and *j* can be also written from Eq. (1) as

$$\begin{aligned}\ln\gamma_i = {} & 1 - \ln(x_i + A_{ji}x_j) - \frac{x_i}{x_i + A_{ji}x_j} \\ & - \frac{A_{ij}x_j}{x_j + A_{ij}x_i}\end{aligned} \qquad (3)$$

$$\begin{aligned}\ln\gamma_j = {} & 1 - \ln(x_j + A_{ij}x_i) - \frac{A_{ji}x_i}{x_i + A_{ji}x_j} \\ & - \frac{x_j}{x_j + A_{ij}x_i}\end{aligned} \qquad (4)$$

When $x_i$ or $x_j$ approaches zero, the infinite dilution activity coefficients $\gamma_i^\infty$ and $\gamma_j^\infty$ are derived from Eqs. (3) and (4), respectively

$$\ln\gamma_i^\infty = 1 - A_{ij} - \ln A_{ji} \qquad (5)$$

Table 1
Binary constants $A_{ji}$ and $A_{ij}$ and the average fitting deviations $S_i$ and $S_j$ in binary molten mattes at 1473 K

| $i$–$j$ | $A_{ji}$ | $A_{ij}$ | $\pm S_i$ | $\pm S_j$ |
|---|---|---|---|---|
| SnS–FeS | 0.27 | 1.24 | 0.0041 | 0.0042 |
| SnS–$Cu_2S$ | 1.65 | 1.53 | 0.0030 | 0.0043 |
| FeS–$Cu_2S$ | 1.44 | 1.97 | 0.0105 | 0.0124 |
| PbS–FeS[a] | 1 | 1 | – | – |
| PbS–$Cu_2S$ | 3.62 | 2.78 | 0.0162 | 0.0351 |

[a] PbS–FeS melts are ideal solutions within limits of experimental error [5].

$$\ln\gamma_j^\infty = 1 - A_{ji} - \ln A_{ij} \qquad (6)$$

From Eq. (6), $A_{ij}$ is given by

$$A_{ij} = \exp(1 - A_{ji} - \ln\gamma_j^\infty) \qquad (7)$$

Let a function and its derivative be respectively

$$\begin{aligned}f(A_{ji}) = {} & \ln A_{ji} + \exp(1 - A_{ji} - \ln\gamma_j^\infty) \\ & + \ln\gamma_i^\infty - 1\end{aligned} \qquad (8)$$

$$f'(A_{ji}) = \frac{1}{A_{ji}} - \exp(1 - A_{ji} - \ln\gamma_j^\infty) \qquad (9)$$

According to the Newton formulas,

$$A_{ji(n+1)} = A_{ji(n)} - \frac{f[A_{ji(n)}]}{f'[A_{ji(n)}]} \qquad (10)$$

The initial values of $A_{ji}$ and $A_{ij}$ can be obtained from the given data of $\gamma_i^\infty$ and $\gamma_j^\infty$ through computing repeatedly ($n$+1) times until $|A_{ji(n)} - A_{ji(n+1)}| \le 10^{-8}$. Then substituting the values into Eq. (3)and (4), the final values of $A_{ji}$ and $A_{ij}$ are determined by making the average fitting deviation $S_{i,\text{or}j} = \pm\left\{\sum_{i,\text{or}j=1}^{n}\frac{[a_{i,\text{or}j(\text{exp})} - a_{i,\text{or}j(\text{cal})}]^2}{n}\right\}^{1/2}$ be less than that (±0.01–0.02) of experimental data as far as possible through adjusting $A_{ji}$ and $A_{ij}$, as shown in Table 1.

## 3. Results and discussion

Tables 2 and 3 shows that the Wilson equation has been able to predict thermodynamic properties of ternary molten mattes and the predicted values are in good agreement with experimental data.

Table 2
A comparison of experimental data with predicted values of activities of SnS in the SnS–FeS–$Cu_2S$ melts at 1473 K

| $x_1$ | $x_2$ | $x_3$ | $a_{1(\mathrm{pred.})}$ | $a_{1(\mathrm{exp.})}$[4] |
|---|---|---|---|---|
| 0.10 | 0.72 | 0.18 | 0.1506 | 0.171 |
| 0.20 | 0.64 | 0.16 | 0.2694 | 0.300 |
| 0.30 | 0.56 | 0.14 | 0.3705 | 0.381 |
| 0.40 | 0.48 | 0.12 | 0.4621 | 0.458 |
| 0.50 | 0.40 | 0.10 | 0.5491 | 0.542 |
| 0.60 | 0.32 | 0.08 | 0.6347 | 0.618 |
| 0.70 | 0.24 | 0.06 | 0.7212 | 0.708 |
| 0.80 | 0.16 | 0.04 | 0.8101 | 0.804 |
| 0.90 | 0.08 | 0.02 | 0.9027 | 0.901 |
| 0.10 | 0.54 | 0.36 | 0.1176 | 0.130 |
| 0.20 | 0.48 | 0.32 | 0.2263 | 0.244 |
| 0.30 | 0.42 | 0.28 | 0.3288 | 0.342 |
| 0.40 | 0.36 | 0.24 | 0.4270 | 0.427 |
| 0.50 | 0.30 | 0.20 | 0.5225 | 0.510 |
| 0.60 | 0.24 | 0.16 | 0.6167 | 0.607 |
| 0.70 | 0.18 | 0.12 | 0.7106 | 0.704 |
| 0.80 | 0.12 | 0.08 | 0.8052 | 0.802 |
| 0.90 | 0.06 | 0.04 | 0.9014 | 0.900 |
| 0.10 | 0.36 | 0.54 | 0.0901 | 0.071 |
| 0.20 | 0.32 | 0.48 | 0.1844 | 0.162 |
| 0.30 | 0.28 | 0.42 | 0.2821 | 0.262 |
| 0.40 | 0.24 | 0.36 | 0.3826 | 0.365 |
| 0.50 | 0.20 | 0.30 | 0.4850 | 0.473 |
| 0.60 | 0.16 | 0.24 | 0.5886 | 0.581 |
| 0.70 | 0.12 | 0.18 | 0.6926 | 0.689 |
| 0.80 | 0.08 | 0.12 | 0.7963 | 0.795 |
| 0.90 | 0.04 | 0.06 | 0.8990 | 0.899 |
| 0.10 | 0.18 | 0.72 | 0.0652 | 0.058 |
| 0.20 | 0.16 | 0.64 | 0.1430 | 0.133 |
| 0.30 | 0.14 | 0.56 | 0.2325 | 0.230 |
| 0.40 | 0.12 | 0.48 | 0.3320 | 0.332 |
| 0.50 | 0.10 | 0.40 | 0.4395 | 0.442 |
| 0.60 | 0.08 | 0.32 | 0.5526 | 0.557 |
| 0.70 | 0.06 | 0.24 | 0.6683 | 0.674 |
| 0.80 | 0.04 | 0.16 | 0.7837 | 0.788 |
| 0.90 | 0.02 | 0.08 | 0.8954 | 0.897 |
| $S_1=\pm0.0089$ | | | | |

Table 3
A comparison of experimental data with predicted values of activities of PbS in the PbS–FeS–$Cu_2S$ melts at 1473 K

| $x_1$ | $x_2$ | $x_3$ | $a_{1(\mathrm{pred.})}$ | $a_{1(\mathrm{exp.})}$[5] |
|---|---|---|---|---|
| 0.2000 | 0.2000 | 0.6000 | 0.0575 | 0.058 |
| 0.3000 | 0.1750 | 0.5250 | 0.1185 | 0.109 |
| 0.4000 | 0.1500 | 0.4500 | 0.2030 | 0.143 |
| 0.5000 | 0.1250 | 0.3750 | 0.3104 | 0.251 |
| 0.6000 | 0.1000 | 0.3000 | 0.4382 | 0.406 |
| 0.7000 | 0.0750 | 0.2250 | 0.5817 | 0.535 |
| 0.8000 | 0.0500 | 0.1500 | 0.7329 | 0.740 |
| 0.9000 | 0.0250 | 0.0750 | 0.8788 | 0.885 |
| 0.2500 | 0.3750 | 0.3750 | 0.1298 | 0.134 |
| 0.3500 | 0.3250 | 0.3250 | 0.2145 | 0.210 |
| 0.4500 | 0.2750 | 0.2750 | 0.3162 | 0.314 |
| 0.5500 | 0.2250 | 0.2250 | 0.4324 | 0.436 |
| 0.6500 | 0.1750 | 0.1750 | 0.5596 | 0.555 |
| 0.7500 | 0.1250 | 0.1250 | 0.6927 | 0.714 |
| 0.8500 | 0.0750 | 0.0750 | 0.8248 | 0.847 |
| 0.1500 | 0.6375 | 0.2125 | 0.1010 | 0.099 |
| 0.2500 | 0.5625 | 0.1875 | 0.1846 | 0.203 |
| 0.3500 | 0.4875 | 0.1625 | 0.2790 | 0.305 |
| 0.4500 | 0.4125 | 0.1375 | 0.3825 | 0.411 |
| 0.5500 | 0.3375 | 0.1125 | 0.4930 | 0.515 |
| 0.6500 | 0.2625 | 0.0875 | 0.6079 | 0.619 |
| 0.7500 | 0.1875 | 0.0625 | 0.7244 | 0.740 |
| 0.8500 | 0.1125 | 0.0375 | 0.8392 | 0.847 |
| $S_1=\pm0.0173$ | | | | |

The author think that an original cause of the Wilson equation applied successfully to predicting thermodynamic properties of organic solutions [3,10], liquid alloys [7–9,11], molten salts [12], molten slags [13] and molten mattes lies in its implied assumption that liquid molecules in a solution are somewhat in local orderly condition, which just reflects the nonideality of solutions. In fact, both stronger and weaker interactions exist among liquid molecules, which means that the probability of determining stronger pairs on intermolecular attraction is reasonably larger than that of weaker pairs in random condition. Thus, some differences between the local concentrations of components around a type of molecule and their average concentrations in bulk solutions exist. On the basis of this consideration, Wilson first proposed a concept concerning the local molecular fraction $x_{ji}$, which is defined as a ratio of the number of molecules of $j$ around a center molecule $i$ to the sum of molecules of types $j$ and $i$ around a center molecule $i$ (the number is only confined to the first coordination shell), and derived the well-known Eq. (1), which resulted in the establishment of more local composition equations later [10].

## 4. Conclusion

A significant advantage of the Wilson equation lies in its ability to predict the thermodynamic properties of ternary molten mattes using only the experimental data of binary molten mattes, and the predicted values are in good agreement with the experimental data of ternary molten mattes, which show that the Wilson equation is reliable, convenient and economic.

## References

[1] H.R. Null, Phase Equilibrium in Process Design, Wiley/Interscience, New York, 1970, 37–61.

[2] G.M. Wilson, J. Am. Chem. Soc. 86 (1964) 127.

[3] R.V. Orye, J.M. Prausnitz, Ind. Eng. Chem. 57 (1965) 18.

[4] R.H. Eric, Metall. Trans. B. 24 (1993) 301.

[5] R.H. Eric, M. Timucin, Metall. Trans. B. 12 (1981) 495.

[6] R.H. Eric, A. Ergeneci, Miner. Eng. 43 (1992) 421.

[7] D.P. Tao, Acta Metall. Sinica. 27 (1991) B380 (in Chinese).

[8] D.P. Tao, Acta Metall. Sinica. 5B (1992) 162.

[9] D.P. Tao, Metall. Trans. B. 23B (1992) 526.

[10] J.M. Prausnitz, R.N. Lichtenthaler, E.G.D. Azevedo, Molecular Thermo-dynamics of Fluid-Phase Equilibria, 2nd Edition, Prentice-Hall, Englewood Cliffs, NJ, 1986, 233–65.

[11] D.P. Tao, X.W. Yang, Acta Metall. Sinica. 33(1997) 1079 (in Chinese).

[12] D.P. Tao, X.W. Yang, Acta Metall. Sinica. 11 (1998) 39.

[13] D.P. Tao, X.W. Yang, Metall. Mater. Trans. B. 28B (1997) 725.