



Calculation of phase equilibrium in vacuum distillation by molecular interaction volume model

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ABSTRACT

Phase equilibrium of Pb–Au and Pb–Sn systems in vacuum distillation have been predicted based on molecular interaction volume model (MIVM). A significant advantage of the model lies in its ability to predict the thermodynamic properties of liquid alloys using only binary infinite activity coefficients. The calculated activity coefficients are compared with experimental data showing good agreement with each other. This shows that the prediction effect of the proposed method is of better stability and reliability because the MIVM has a good physical basis.

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1. Introduction

Refining and separation of various impurities from nonferrous crude metals by vacuum distillation have many the advantage of high metal recovery, impurities recovered in metallic state, flow sheet simplified, good environmental protection, low operation costs and in complex equipment. So vacuum distillation has been studied and used in separation of various elements from nonferrous alloys and the area of its application is being extended rapidly [1–7].

The knowledge of the thermodynamic properties of alloys is important for providing important thermodynamic information in metallurgical process. But the experimental thermodynamic study is very time consuming since a great number of measurements are necessary. Therefore, theoretical predicting is a significant and effective approach to obtain thermodynamic properties of alloys, especially for multicomponent ones.

The purpose of this work is to calculate phase equilibrium of Pb–Au and Pb–Sn systems in vacuum distillation based on the MIVM. The predicted results are important to estimate the separation degree and the products' composition quantitatively.

2. Method

2.1. Separation coefficient and phase equilibrium of vacuum distillation

The reason of refining of crude metals or separation of alloys by vacuum distillation is the composition difference between distilled gas product and liquid phase. A concept β , i.e. separation coefficient was introduced from theoretical derivation for i – j binary alloy, that is

$$\beta = \frac{\gamma_i p_i^*}{\gamma_j p_j^*} \quad (1)$$

where γ_i and γ_j are activities coefficient of i and j components, respectively; p_i^* and p_j^* are saturated vapor pressure of i and j components, respectively.

When $\beta > 1$ or $\beta < 1$, the separation of alloys could happen, but when $\beta = 1$ it could not. Therefore, the separation coefficient β can be used to estimate whether the components may be separated via vacuum distillation for all alloys.

And we use equilibrium components diagram between gas phase and liquid phase to precisely calculate the elements distribution of metals in vacuum refining process. When the two phases are equilibrium, the quantity fraction $w_{i,g}$ in gas phase is related the vapor densities of these two components as:

$$w_{i,g} = \frac{\rho_i}{\rho_i + \rho_j} = \frac{1}{1 + (\rho_j / \rho_i)} \quad (2)$$

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Table 1
Vapor pressure of the components at the different temperature [14].

	T (K)					
	1073	1173	1273	1373	1473	1573
p_{Au}^* (Pa)	2.99×10^{-7}	9.29×10^{-6}	1.67×10^{-4}	1.97×10^{-3}	1.65×10^{-2}	1.05×10^{-1}
p_{Pb}^* (Pa)	7.24	42.25	185.82	655.13	1936.82	4968.10
p_{Sn}^* (Pa)	8.11×10^{-5}	1.38×10^{-3}	1.51×10^{-2}	1.16×10^{-1}	6.79×10^{-1}	3.17

Table 2
The related parameters of the components [14,15].

<i>i</i>	V_{mi} (cm ³ /mol)	ΔH_{mi} (kJ/mol)	σ_i ($\times 10^{-8}$ cm)	r_{0i} ($\times 10^{-8}$ cm)
Au	$11.3[1 + 0.69 \times 10^{-4}(T - 1336)]$	11.09	2.88	2.46
Pb	$19.4[1 + 1.24 \times 10^{-4}(T - 600)]$	4.81	3.50	2.70
Sn	$17.0[1 + 0.87 \times 10^{-4}(T - 505)]$	7.20	3.26	2.59

where ρ_i and ρ_j are the vapor densities for vapor component *i* and *j* respectively, and $\rho_i/\rho_j = \beta w_{i,l}/w_{j,l}$. Then the mass fraction of component *i* in vapor,

$$w_{i,g} = \left[\frac{1 + w_{j,l}}{\beta w_{i,l}} \right]^{-1} = \left[1 + \left(\frac{w_{j,l}}{w_{i,l}} \right) \cdot \left(\frac{\gamma_j}{\gamma_i} \right) \cdot \left(\frac{p_j^*}{p_i^*} \right) \right]^{-1} \quad (3)$$

The relationship diagram of $w_{i,g}$ – $w_{i,l}$ can be calculated by γ , p^* and a series of $w_{j,l}/w_{i,l}$ at specific temperatures, that is the vapor–liquid equilibrium composition for *i*–*j* system. The vapor pressures of pure Pb, Au and Sn at the different temperature are shown in Table 1.

2.2. Molecular interaction volume model

The MIVM was obtained from the physical prospect of liquid molecular movements in that liquid molecules are not like gas molecules, which are in continuous irregular motion, and not like solid ones, which are vibrating continuously at one site but are migrating no randomly from one cell to another. This means that the basic feature of moving of liquid molecules is nonrandom migrating, more details in literature [8]. It is a two-parameter model and is able to predict the thermodynamic properties in a multicomponent solution system using only the ordinary physical quantities of pure liquid metals and the related binary infinite dilute activity coefficients. The prediction effect of MIVM is of better stability and safety through our previous work [9–13]. According to MIVM, the molar excess Gibbs energy G_m^E of the multicomponent can be expressed as:

$$\frac{G_m^E}{RT} = \sum_{i=1}^n x_i \ln \frac{V_{mi}}{\sum_{j=1}^n x_j V_{mj} B_{ji}} - \frac{1}{2} \sum_{i=1}^n Z_i x_i \left(\frac{\sum_{j=1}^n x_j B_{ji} \ln B_{ji}}{\sum_{k=1}^n x_k B_{ki}} \right) = -\frac{S_m^E}{R} + \frac{H_m^E}{RT} \quad (4)$$

where Z_i is the nearest molecule or first coordination number. x_i , x_j and x_k the molar fractions; and the pair-potential energy interaction parameters B_{ij} and B_{ji} are defined as, respectively,

$$B_{ij} = \exp \left[- \left(\frac{\varepsilon_{ij} - \varepsilon_{jj}}{kT} \right) \right] \quad B_{ji} = \exp \left[- \left(\frac{\varepsilon_{ji} - \varepsilon_{ii}}{kT} \right) \right] \quad (5)$$

where ε_{ii} , ε_{jj} and ε_{ij} are the *i*–*i*, *j*–*j*, and *i*–*j* pair-potential energies, $\varepsilon_{ij} = \varepsilon_{ji}$, k the Boltzmann constant, and T the absolute temperature. For a binary mixture *i*–*j*, the activity coefficients of component *i* and

j are, respectively

$$\ln \gamma_i = \ln \left(\frac{V_{mi}}{x_i V_{mi} + x_j V_{mj} B_{ji}} \right) + x_j \left(\frac{V_{mj} B_{ji}}{x_i V_{mi} + x_j V_{mj} B_{ji}} - \frac{V_{mi} B_{ji}}{x_j V_{mj} + x_i V_{mi} B_{ij}} \right) - \frac{x_j^2}{2} \left(\frac{Z_i B_{ji}^2 \ln B_{ji}}{(x_i + x_j B_{ji})^2} + \frac{Z_j B_{ij} \ln B_{ij}}{(x_j + x_i B_{ij})^2} \right) \quad (6)$$

$$\ln \gamma_j = \ln \left(\frac{V_{mj}}{x_j V_{mj} + x_i V_{mi} B_{ij}} \right) + x_i \left(\frac{V_{mj} B_{ji}}{x_i V_{mi} + x_j V_{mj} B_{ji}} - \frac{V_{mi} B_{ji}}{x_j V_{mj} + x_i V_{mi} B_{ij}} \right) - \frac{x_i^2}{2} \left(\frac{Z_j B_{ij}^2 \ln B_{ij}}{(x_j + x_i B_{ij})^2} + \frac{Z_i B_{ji} \ln B_{ji}}{(x_i + x_j B_{ji})^2} \right) \quad (7)$$

when x_i or x_j approaches zero, the infinite dilution activity coefficients γ_i^∞ and γ_j^∞ , respectively, are derived from Eqs. (4) and (5):

$$\ln \gamma_i^\infty = 1 - \ln \left(\frac{V_{mj} B_{ji}}{V_{mi}} \right) - \frac{V_{mi} B_{ji}}{V_{mj}} - \frac{1}{2} (Z_i \ln B_{ji} + Z_j B_{ij} \ln B_{ij}) \quad (8)$$

$$\ln \gamma_j^\infty = 1 - \ln \left(\frac{V_{mi} B_{ij}}{V_{mj}} \right) - \frac{V_{mj} B_{ji}}{V_{mi}} - \frac{1}{2} (Z_i \ln B_{ij} + Z_i B_{ji} \ln B_{ji}) \quad (9)$$

In order to determine the required binary parameters B_{ij} and B_{ji} , the infinite dilution activity coefficients of the binary liquid alloys and the related parameters of their components must be obtained. The related parameters of pure metals [14,15] are shown in Table 2. The coordination number Z_i of liquid metals can be predicted from their atomic parameters, molar volumes, melting points and melting enthalpies [16]. The infinite dilution activity coefficients of binary liquid alloys [17] and the required binary parameters B_{ij} and B_{ji} are shown in Table 3, respectively.

Table 3
The values of γ_i^∞ , γ_j^∞ , B_{ij} and B_{ji} of the binary alloys *i*–*j* at the required temperatures [17].

<i>i</i> – <i>j</i>	T (K)	γ_i^∞	γ_j^∞	B_{ij}	B_{ji}	Z_i	Z_j
Pb–Au	1400	1.101	1.530	1.5808	0.4558	8.99	10.90
Pb–Sn	1050	2.057	1.710	1.1131	0.8052	9.60	8.81

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