Calculation of vapor-liquid equilibrium of binary precious metal alloys using modified molecular interaction volume model

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Abstract

In this work, the activities and activity coefficients of binary precious metal alloys (Ag-Pb, Ag-Sb, Ag-Bi, Au-Pb, Pd-Pb, Pt-Pb and Cu-Pb) were predicted using molecular interaction volume model (MIVM), modified MIVM (M-MIVM), Wilson equation and nonrandom two-liquid (NRTL) model. The average standard deviation and average relative deviations of these models were also calculated. The results show that the prediction deviations of the M-MIVM were smallest among the four thermodynamic models, indicating that the M-MIVM is reliable. On this premise, the separation coefficients were much larger than one, indicating that these alloys can be easily separated by vacuum distillation. There is good agreement between the predicted and experiment VLE data, indicating that M-MIVM is reliable for the VLE calculation in vacuum distillation. The VLE phase diagrams procured in this work can afford theoretical guidance for experimental design and industrial production in vacuum distillation.

1. Introduction

Precious metals (PMs) are widely used in electronics and catalysts industry because of their excellent physical and chemical properties (e.g., high catalytic activity and conductivity, strong corrosion resistance, etc.) [1]. PMs, especially silver, gold and palladium, are mainly used to prepare contacts, bonding wires and switches and computer hard disk drives in electron industry [2]. PGMs (platinum group metals), called ‘vitamin of modern industry’, are usually applied as the active components in automobile emission purification, petrochemical engineering and pharmaceutical industry [3, 4]. With the rapid development of global information industries, the demand for PMs continues to increase [5].

At present, a large part of PMs was recovered from precious metal alloys (e.g., Ag-Pb, Ag-Sb, Ag-Bi, Au-Pb, Pd-Pb, Pt-Pb and Cu-Pb), which were usually produced from the lead smelting process [6, 7]. In addition, huge quantities of precious metal alloys were also produced during the recovery process of secondary resources such as electronic waste, end-of-life electronics and spent automobile exhaust purification catalysts [8, 9]. The conventional treatment method of precious metal alloys was oxidation blowing, in which lead, bismuth, antimony and copper were preferentially oxidized into dust or slag and PMs were concentrated [7, 9]. The drawbacks of the method were low resource utilization rate, high energy consumption, long production period and serious environmental pollution. Vacuum distillation has such advantages as short flow, simple equipment, high metal recovery rate, environmentally friendly [10]. Over the past decades, it has been researched and applied to separate and purify various non-ferrous metals and alloys by Dai, Yang and co-workers [10, 11]. Recently, based on advantages of vacuum distillation and the fact that the difference of vapor pressure between
lead, bismuth, antimony and PMs, the National Engineering Laboratory of Vacuum Metallurgy, China proposed a method of separating precious metal alloys and recovering PMs by vacuum distillation.

Vapor–liquid equilibrium (VLE) phase diagrams are usually used for quantitative analysis of the distribution of alloy components in liquid and vapor phase. Therefore, credible VLE data is significant for experiment design and industrial production in vacuum distillation. However, experimental determination of VLE data is difficult because of high temperature, low pressure, large manpower and material consumption. Thermodynamic model prediction as an efficient and convenient method is frequently used to calculate VLE data of alloy systems. In our previous work, thermodynamic properties of many alloy systems have been calculated based on MIVM and Wilson equation by Yang and Kong [12–15]. The results show that MIVM and Wilson equation has weaknesses in handling asymmetric system while most precious metal alloys belong to asymmetric system. In contrast, M-MIVM shows unique superiority and reliability in calculating the thermodynamic properties of asymmetric systems [16, 17]. However, researches on modeling of VLE of binary precious metal alloys using M-MIVM in vacuum distillation have not been reported until now.

In this work, the activities and activity coefficients of Ag–Pb, Ag–Sb, Ag–Bi, Au–Pb, Pd–Pb, Pt–Pb and Cu–Pb were calculated using MIVM, M-MIVM, Wilson equation and NRTL model. The prediction deviations of separation coefficients and VLE data of these alloys were calculated based on M-MIVM. The VLE phase diagrams obtained in this study can provide theoretical guidance for the efficient separation of binary precious metal alloys by vacuum distillation.

2. Method

2.1. Molecular interaction volume model (MIVM)

MIVM was obtained from statistical thermodynamics and the basic characteristics of the nonrandom transfer of liquid molecules [18]. The expression of mole excess Gibbs free energy $G_{mi}^{E}$ of MIVM is:

$$\frac{G_{mi}^{E}}{RT} = \sum_{i=1}^{C} x_i \ln \frac{V_{mi}}{\sum_{j=1}^{C} x_j V_{mj} B_{ji}} - \frac{1}{2} \sum_{i=1}^{C} \sum_{j=1}^{C} Z_{ij} x_i B_{ji} \ln B_{ji} \left( \frac{\sum_{j=1}^{C} x_j B_{ji}}{\sum_{j=1}^{C} x_j B_{ij}} \right)$$

(1)

For a binary system $i$-$j$, equation (1) can be rewritten as:

$$\frac{G_{mi}^{E}}{RT} = x_i \ln \frac{V_{mi}}{x_i V_{mi} + x_j V_{mj} B_{ji}} + x_j \ln \frac{V_{mj}}{x_j V_{mj} + x_i V_{mi} B_{ij}}$$

$$- \frac{x_i x_j}{2} \left( \frac{Z_{ii} B_{ji} \ln B_{ji}}{(x_i + x_j B_{ji})^2} + \frac{Z_{jj} B_{ij} \ln B_{ij}}{(x_j + x_i B_{ij})^2} \right)$$

(2)

According to equation (2) and $(\partial G_{mi}^{E}/\partial x_j)_{T, P, x_{mi}} = RT \ln \gamma_j$, the activity coefficients of $i$ and $j$ are:

$$\ln \gamma_i = 1 + \ln \frac{x_i V_{mi}}{x_i V_{mi} + x_j V_{mj} B_{ji}} - \frac{x_i x_j}{2} \left( \frac{Z_{ii} B_{ji} \ln B_{ji}}{(x_i + x_j B_{ji})^2} + \frac{Z_{jj} B_{ij} \ln B_{ij}}{(x_j + x_i B_{ij})^2} \right)$$

(3)

$$\ln \gamma_j = 1 + \ln \frac{x_j V_{mj}}{x_j V_{mj} + x_i V_{mi} B_{ij}} - \frac{x_i x_j}{2} \left( \frac{Z_{ij} B_{ji} \ln B_{ji}}{(x_i + x_j B_{ji})^2} + \frac{Z_{ji} B_{ij} \ln B_{ij}}{(x_j + x_i B_{ij})^2} \right)$$

(4)

where $x_i$ and $x_j$ are the molar fractions; $V_{mi}$ and $V_{mj}$ are the molar volumes; $Z_{ii}$ and $Z_{jj}$ are the first coordination numbers; $B_{ij}$ and $B_{ji}$ are the pair-potential energy interaction parameter which are defined as equation (5). $Z_{ij}$ can be calculated from equation (6).

$$B_{ij} = \exp \left( \frac{\varepsilon_{ij} - \varepsilon_{ji}}{kT} \right)$$

$$B_{ji} = \exp \left( \frac{\varepsilon_{ji} - \varepsilon_{ij}}{kT} \right)$$

(5)
Where $\varepsilon_{ii}$ and $\varepsilon_{ij}$ ($\varepsilon_{ij} = \varepsilon_{ji}$) are the pair-potential energy of $i-i$ and $i-j$, respectively.

\[
Z_i = 4\sqrt{2}\pi \left( \frac{r_{mi}^3 - r_{mj}^3}{r_{mi} - r_{mj}} \right)^2 \rho_i \cdot r_{mi} \cdot \exp \left[ \frac{\Delta H_{mi}(T_{mi} - T)}{Z_c \cdot R T_{mi}} \right]
\]

(6)

where $r_{mi}$ is equal to the atomic diameter, $r_{mj} = \sigma \cdot r_{mi}$ ($\sigma = 0.918d_{cov}$) is proportional to the atomic covalent diameter $d_{cov}$, $\rho_i$ is the molecular number density, $\Delta H_{mi}$ and $T_{mi}$ are the melting enthalpy and melting temperature, respectively; $Z_c$ ($Z_c = 12$) is a close-packed coordination.

### 2.2. Modified molecular interaction volume model (M-MIVM)

M-MIVM and MIVM are deduced from the same partition function [16]. However, M-MIVM is obtained from different hypothesis and theories. In the derivation of M-MIVM, the Scatchard-Hildebrand theory [19, 20] and radial distribution function [19] are further introduced on the base of cell theory [18, 21] which are employed by MIVM. The mole excess Gibbs free energy $G_{E,m}$ of M-MIVM is:

\[
\frac{G_{E,m}}{RT} = -\sum_{i=1}^{C} x_i \ln \left( \frac{\sum_{j=1}^{C} x_j V_{mj} B_{ij}}{V_{mi}} \right) + \sum_{j>i} x_i x_j \frac{A_{ij}}{x_i + x_j \frac{V_{mi}}{V_{mj}} B_{ij}} + \frac{A_{ji}}{x_i + x_j \frac{V_{mi}}{V_{mj}} B_{ij}}
\]

(7)

For $i$-$j$ binary system, equation (7) are rewritten as:

\[
\frac{G_{E,m}}{RT} = -x_i \ln \left( x_i + x_j \frac{V_{mi}}{V_{mj}} B_{ij} \right) - x_j \ln \left( x_j + x_i \frac{V_{mj}}{V_{mi}} B_{ij} \right) + x_i x_j \frac{A_{ij}}{x_i + x_j \frac{V_{mi}}{V_{mj}} B_{ij}} + \frac{A_{ji}}{x_i + x_j \frac{V_{mj}}{V_{mi}} B_{ij}}
\]

(8)

where $V_{mi}$ and $V_{mj}$ are liquid molar volumes of $i$ and $j$, respectively; the volume parameters ($B_{ij}$ and $B_{ji}$) and the energy parameters ($A_{ij}$ and $A_{ji}$) are defended as equation (9) and equation (10) as follows, respectively.

\[
A_{ij} = -\frac{3K}{k_B} C_i^0 (\varepsilon_{ij} - \varepsilon_{ji}) A_{ji} = -\frac{3K}{k_B} C_j^0 (\varepsilon_{ji} - \varepsilon_{ij})
\]

(9)

\[
B_{ij} = p_j / p_i \quad B_{ji} = p_i / p_j
\]

(10)

where $K$ is a constant; $k_B$ is the Boltzmann constant; $C_i^0$ and $C_j^0$ are temperature independent proportional constants; $\varepsilon_{ij}$($\varepsilon_{ji} = \varepsilon_{ij}$), $\varepsilon_{ii}$ and $\varepsilon_{ij}$ are pair potential energy of $i-j$, $i-i$ and $j-j$, respectively; $p_{ij}$ is the probabilities that the molecule $i$ arise in the first coordination layer of the centrical molecule $j$. $A_{ij}$ and $A_{ji}$ are temperature independent in the system of weak intermolecular interaction such as alloys separation during vacuum distillation. However, $B_{ij}$ and $B_{ji}$ are temperature dependent and the $B_{ij}(T_1)$ and $B_{ji}(T_1)$ at other temperature $T_1$ are obtained from equation (11).

\[
B_{ij}(T) = \exp \left( \frac{T}{T_1} \ln B_{ij} \right) \quad B_{ji}(T) = \exp \left( \frac{T}{T_1} \ln B_{ji} \right)
\]

(11)

According to the relationship ($\partial G_{E,m}/\partial x_i$)$_{T,p,x_j=0} = RT \ln \gamma_i$ the activity coefficients of $i$ and $j$ are:

\[
\ln \gamma_i = -\ln D_{ij} = -x_i x_j \frac{C_i^0}{D_i^0} + x_i^2 \left( \frac{A_{ij} + C_{ij}}{D_{ij}} \right) + A_{ji} x_j \left( \frac{A_{ij} \cdot C_{ji}}{D_{ij}} + \frac{A_{ij} \cdot C_{ij}}{D_{ij}} \right)
\]

(12)

\[
\ln \gamma_j = -\ln D_{ij} = -x_i x_j \frac{C_j^0}{D_j^0} + x_j^2 \left( \frac{A_{ij} + C_{ij}}{D_{ij}} \right) + A_{ji} x_i \left( \frac{A_{ij} \cdot C_{ji}}{D_{ij}} + \frac{A_{ij} \cdot C_{ij}}{D_{ij}} \right)
\]

(13)

where the parameters $C_{ij}$, $C_{ji}$ and $D_{ij}, D_{ji}$ are defended as equations (14) and (15).

\[
C_{ij} = 1 - \frac{V_{mi}}{V_{mj}} B_{ij} \quad C_{ji} = 1 - \frac{V_{mj}}{V_{mi}} B_{ji}
\]

(14)
\[ D_\eta = x_i + x_i \frac{V_{mi} B_{\eta}}{V_{mj} B_{\eta}} \quad D_\eta = x_i + x_i \frac{V_{mi} B_{\eta}}{V_{mj} B_{\eta}} \]

(15)

2.3. Separation coefficient

Separation coefficient \( \beta \) is used for the judgement of separation feasibility of alloys in vacuum distillation [10]. For \( i-j \)-binary system,

\[ \beta_i = \frac{\gamma_i}{\gamma_j} \cdot \frac{P_i^*}{P_j^*} \]

(16)

where \( \gamma_i \) and \( \gamma_j \) are the activity coefficients of \( i \) and \( j \), respectively; \( P_i^* \) is the saturated vapor pressure of component \( i \) which can be obtained from Van Laar equation [10]:

\[ \lg P_i^* = AT^{-1} + B \lg T + CT + D \]

(17)

where \( A, B, C \) and \( D \) are evaporation constants; \( T \) is the absolute temperature in Kelvin.

2.4. Vapor-liquid equilibrium (VLE)

The thermodynamic condition of VLE of \( i-j \)-binary system is the fugacity of component \( i \) in liquid phase \( f_i^L \) equal to that of \( i \) in vapor phase \( f_i^V \):

\[ f_i^L(x_i, T, P) = f_i^V(y_i, T, P) \]

(18)

If pressure effect can be neglected, in other words, the vapor phase is an ideal gas, \( f_i^V \) can be expressed as equation (19). In this case, the liquid phase cannot be considered ideal. The deviations from ideality are investigated by introducing a correction factor \( \gamma_i \) into Raoult’s law and \( f_i^L \) can be expressed as equation (20).

\[ f_i^L(y_i, T, P) = f_i^V \cdot y_i = f_i^V \cdot y_i \]

(19)

\[ f_i^L(x_i, T, P) = f_i^* \cdot x_i \cdot P \]

(20)

where \( f_i^V \) is vapor phase fugacity coefficient of \( i \); \( f_i^* \) is saturated fugacity coefficient of pure \( i \) in liquid phase; \( V_i^L \) is liquid molar volume of component \( i \).

The vapor phase is regarded as an ideal gas in vacuum distillation, thus \( f_i^V \) and \( f_i^* \) are equal to one and \( \exp [V_i^L(P - P_i^*)/RT] \) equals approximately one at low pressure. Simultaneous equations (18)–(20), the equation of modified Raoult’s law can be written as:

\[ y_i \cdot P = \gamma_i \cdot x_i \cdot P_i^* \]

(21)

For \( i-j \)-binary alloy system:

\[ x_i + x_j = 1 \]

(22)

\[ P = P_i^* \gamma_i x_i + P_j^* \gamma_j x_j \]

(23)

Combining equations (21)–(23), \( x_i \) and \( y_i \) are:

\[ x_i = \frac{P - P_j^* \gamma_j}{P_i^* \gamma_i - P_j^* \gamma_j} = \frac{P_i^* \gamma_i x_i}{P} \]

(24)

3. Results and discussion

3.1. Thermodynamic model calculation and comparison

Substituting the corresponding parameters of pure metals (table 1) [22, 23] into equation (6), the coordination numbers \( Z_i \) and \( Z_j \) of MIVM were obtained. Substituting \( Z_i \), \( Z_j \), the experimental data of activity coefficients (\( \gamma_i, \exp. \) and \( \gamma_j, \exp. \)) [24, 25] and the relevant parameters into equations (3) and (4), the pair-potential energy interaction parameters (\( B_{ij} \) and \( B_{ji} \)) of MIVM were obtained by fitting at least squares principle.

Similarly, the volume parameters (\( B_{ij} \) and \( B_{ji} \)) and the energy parameters (\( A_{ij} \) and \( A_{ji} \)) of M-MIVM can be obtained from equations (12) to (15). The calculated model parameters of MIVM and M-MIVM are shown in table 2.

Substituting \( B_{ij}, B_{ji}, Z_i, Z_j \) and corresponding parameters of MIVM into equation (3) and equation (4), the activities and activity coefficients of components of Ag-Pb, Ag-Sb, Ag-Bi, Au-Pb, Pd-Pb, Pt-Pb and Cu-Pb alloys
can be predicted. Similarly, substituting $A_{ij}$, $A_{ij}$, $B_{ij}$, $B_{ij}$ and relevant parameters of M-MIVM into equations (12) to (15), the activities of above binary precious alloys can be calculated.

For the purpose of confirming the dependability of M-MIVM, two other successful classical thermodynamic model Wilson equation and NRTL model were employed to calculate the activities of these binary precious metal alloys. Wilson equation is a two-parameter model and the adjustable parameters $A_{ij}$ and $A_{ij}$ can be obtained by utilizing the Newton-Raphson methodology on the condition that the experimental values of activities are known [26]. NRTL model is deduced from the two-liquid solution theory of Scott [27] and local composition concepts of Wilson. It is also regarded as a reliable model to predict the activities of liquid alloys. NRTL model is a three-parameter model and the non-randomness factors $\alpha_{ij}(\alpha_{ij} = \alpha_{ij})$ and the energy parameters $\tau_{ij}$ and $\tau_{ij}(\tau_{ij} = \tau_{ij})$ are calculated by the Newton-Raphson methodology under the condition of the experimental values of activity coefficients are known. All of the obtained model parameters of Wilson equation and NRTL model were listed in table 2.

The activities and activity coefficients of these precious metal alloys calculated from MIVM, M-MIVM, Wilson equation and NRTL model are shown in figure 1 (a) to (g).

Figures 1(a) and (b) show that all models display great data fitting capability in Au-Pb and Pd-Pb alloys. The reason is that MIVM, Wilson equation and NRTL model are good at handling symmetric systems. The characteristic of the symmetric system is that the experimental activity curves of the two components intersect near $x = 0.5$ in the coordinate axis, and are symmetrical about $x = 0.5$ or near.). M-MIVM inherits this good capacity from MIVM and plays it better. For Ag–Pb, Ag–Bi, Ag–Sb, Pt–Pb and Cu–Pb alloys, figures 1 (c) to (g) show that the predicted values of MIVM, Wilson equation and NRTL model are obviously disagreement with the experimental data. However, M-MIVM shows great data fitting capability in these asymmetric systems. The characteristic of the asymmetric system is that the two experimental activity curves are generally not mirror-symmetrical, and the abscissa of the focus of the measurement curve has different degrees of deviation relative to $x = 0.5$), especially for the alloy system with complex trend of activity coefficients such as Ag–Pb, Ag–Bi and Ag–Sb alloys. In fact, the complicated change trend is the characteristics of the alloy system and these characteristics will directly affect the VLE calculation.

In order to accurately characterize the deviation extent between experimental values and calculated data and the reliability of M-MIVM, the average standard deviation $S_{ae}$, and the average relative deviations $S_{i}$ of each model are also calculated from equation (29), as shown in figure 2 and table 3.

$$S_{i} = \pm \left[ \frac{1}{n} \sum_{i=1}^{n} \left( \frac{a_{i,pre} - a_{i,exp}}{a_{i,exp}} \right)^2 \right]^{1/2}$$

$$S_{i} = \pm \frac{100}{n} \sum_{i=1}^{n} \frac{a_{i,pre} - a_{i,exp}}{a_{i,exp}}$$

(29)

Figure 2 shows that the values of $S_{ae}$ and $S_{i}$ of M-MIVM were smallest among the four models, indicating that the M-MIVM has higher reliability and universality.

Table 3 shows that in symmetric system (Au-Pb and Pd-Pb), the average relative deviations of each model are low enough, less than 3% in Au-Pb alloy and less than 10% in Pd-Pb alloy, respectively. The differences of the average standard deviations of each model are not very significant. However, the values of $S_{ae}$, and $S_{i}$ of M-MIVM are lower than that of other three models. In asymmetric system (Ag-Pb, Ag-Bi, Ag-Sb, Pt-Pb and Cu-Pb alloys), the values of $S_{ae}$, and $S_{i}$ of MIVM, Wilson equation and NRTL model are several times larger than that of M-MIVM. Particularly, for Ag-Sb alloy, the values of $S_{i}$ of Wilson equation and NRTL model are over 10% and MIVM over 20%, while M-MIVM less than 4%; for Pt-Pb alloy, it is hard to estimate whether it is symmetric or asymmetric system because of the absence of partial experimental data, the values of $S_{i}$ of MIVM and NRTL model are around 14% and Wilson equation are close to 20%, while M-MIVM is 6.02% and the $S_{ae}$ values of M-MIVM are decreased about three times than that of other three models. The Cu-Pb alloy usually produced
Table 2. The calculated parameters of MIVM, M-MIVM, Wilson and NRTL.

| Systems  | Parameters of MIVM | Parameters of M-MIVM | Parameters of Wilson | Parameters of NRTL |
|----------|--------------------|----------------------|----------------------|--------------------|
|          | T/K    | \( B_\text{ij} \) | \( B_{ji} \) | \( Z_i \) | \( Z_j \) | \( B_\text{ij} \) | \( B_{ji} \) | \( A_\text{ij} \) | \( A_{ji} \) | \( A_{ij} \) | \( A_{ji} \) | \( \tau_{ij} \) | \( \tau_{ji} \) | \( \alpha_{ij} \) |
| Ag-Pb    | 1273   | 1.3968              | 0.5960              | 10.68              | 9.29            | 0.5358              | 0.3429              | -0.4931            | 0.0000             | 0.2866           | 1.5091          | -1.3873             | 2.5055           | 0.1700               |
| Ag-Sb    | 1250   | 0.7950              | 1.3132              | 10.72              | 6.96            | 1.9215              | 7.0125              | 1.5936             | 6.6747             | 6.1161           | 0.1636          | 1.2028             | -1.7164          | 0.4496               |
| Ag-Bi    | 1000   | 1.7191              | 0.4386              | 11.24              | 7.84            | 2.7088              | 1.8016              | 2.8230             | -0.0062            | 0.1240           | 1.8216          | -1.9819             | 4.0415           | 0.1700               |
| Au-Pb    | 1200   | 1.0195              | 1.1245              | 11.15              | 9.39            | 1.1943              | 0.2301              | -1.2561            | -0.4813            | 2.0547           | 1.3164          | -0.2441             | -0.7562          | 0.4499               |
| Pd-Pb    | 1873   | 0.6641              | 1.6102              | 10.55              | 8.59            | 3.0941              | 2.5130              | 0.2692             | -0.1100            | 5.1943           | 1.2958          | -0.0652             | -1.7507          | 0.4500               |
| Pt-Pb    | 1273   | 1.5224              | 1.0434              | 13.05              | 9.29            | 1.4543              | 2.2197              | -3.9129            | 10.0991            | 2.9020           | 3.9017          | -1.9793             | -0.9579          | 0.1700               |
| Cu-Pb    | 1473   | 0.8097              | 0.8351              | 10.46              | 9.03            | 0.4958              | 0.3932              | -0.1887            | 1.0352             | 0.3810           | 0.3331          | 1.0737             | 0.7085           | 0.1700               |

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Figure 1. Predicted values (line) and experimental data (points) of activities and activity coefficients of binary precious metal alloys: (a) Au–Pb; (b) Pd–Pb; (c) Ag–Pb; (d) Ag–Bi; (e) Ag–Sb; (f) Pt–Pb; (g) Cu–Pb.
with the precious alloys during the recovery process of electronic waste and it is necessary to be studied. It is an asymmetric system, and the values of $S_i^*$ and $S_i$ of M-MIVM are 0.0058 and 0.62%, respectively, which are quite small than that of other three models. The average relative deviations of M-MIVM in all binary precious metal alloys are less than 7%, which indicates that M-MIVM is reliable and stable. The prediction capacity and effect of M-MIVM are better than other models in symmetric or asymmetric alloy system. M-MIVM with excellent data fitting capability can describe the characteristics of these binary precious metal alloys more accurately which will in turn improve the calculation accuracy of the separation coefficients and VLE data in vacuum distillation. In addition, this excellent capability undoubtedly makes up for the drawback of other classic models in asymmetric systems and will greatly expend the application range of M-MIVM.

### 3.2. Separation coefficient

The separation coefficient plays a relatively important role on researching these binary precious metal alloys in vacuum distillation. The yields of silver, gold, palladium and platinum are far higher than that of other PMs, and the Ag-Pb, Au-Pb, Pd-Pb and Pt-Pb are the commonest alloys in PMs production and recycling. Therefore, the separation coefficients of Ag-Pb, Au-Pb, Pd-Pb and Pt-Pb alloys were calculated from equation (16) based on M-MIVM, as shown in figures 3(a) to (d). The saturated vapor pressure $P_{i}^*$ of each component was calculated form equation (17) and the relevant parameters for $P_{i}^*$ calculation of pure metals are presented in table 4.

The separation coefficients of Ag-Pb, Au-Pb, Pd-Pb and Pt-Pb alloys are much larger than one, indicating that they can be easily separated by vacuum distillation. In addition, the results show that the separation coefficients are decreased with the temperature increasing, indicating that the tendency of liquid phase volatilization is more obvious with the temperature increasing, and that it is not favorable for separation when the temperature too high.

![Figure 2](image)

**Figure 2.** The mean value of deviations of each model in different alloy systems: (a) the average standard deviations $S^*$; (b) the average relative deviations $S$.  

### Table 3. The average standard deviations $S^*$ and average relative deviations $S$ of MIVM, M-MIVM, Wilson equation and NRTL model.

| System | $T$/K | MIVM $S_i^*$ | M-MIVM $S_i^*$ | Wilson $S_i^*$ | NRTL $S_i^*$ |
|--------|-------|--------------|----------------|----------------|--------------|
| Au-Pb  | 1200  | 0.0083       | 2.25           | 0.0050         | 1.66         | 0.0079       | 2.18         | 0.0084       | 2.26         |
| Pd-Pb  | 1873  | 0.0270       | 9.54           | 0.0182         | 6.09         | 0.0181       | 6.53         | 0.0242       | 8.09         |
| Ag-Pb  | 1273  | 0.0169       | 3.61           | 0.0061         | 1.26         | 0.0168       | 3.56         | 0.0153       | 3.30         |
| Ag-Bi  | 1000  | 0.0477       | 7.22           | 0.0124         | 2.42         | 0.0534       | 8.66         | 0.0405       | 5.94         |
| Ag-Sb  | 1250  | 0.0761       | 23.16          | 0.0156         | 3.71         | 0.0419       | 12.04        | 0.0515       | 14.42        |
| Pt-Pb  | 1273  | 0.0392       | 14.28          | 0.0129         | 6.02         | 0.0425       | 18.58        | 0.0368       | 13.65        |
| Cu-Pb  | 1473  | 0.0264       | 2.97           | 0.0058         | 0.62         | 0.0392       | 4.65         | 0.0198       | 2.19         |
| Over mean | 0.0345 | 9.00         | 0.0109         | 3.11           | 0.0314       | 8.03         | 0.0281       | 7.12         |
3.3. VLE calculation

Separation coefficient can judge the feasibility of separation of precious metal alloys by vacuum distillation, but cannot predict the separation degree. Therefore, the VLE phase diagram is needed to be calculated to quantitatively and accurately analysis of the distribution of alloy components in liquid and vapor phase in vacuum distillation.

Substituting corresponding parameters $\gamma_i$, $\gamma_j$, $P^*_i$, and $S^*_i$ under different temperatures into equations (22) to (24), the VLE data can be obtained, and then $T$-$x$-$y$ and $P$-$x$-$y$ phase diagram can be drawn. The saturated vapor pressure $P^*_i$ is calculated from equation (17) and the needed constants are shown in table 4. The flowchart of $T$-$x$-$y$ and $P$-$x$-$y$ phase diagram calculation is displayed in figures 4(a) and (b), respectively. $T$-$x$-$y$ phase diagram calculation is an iterative procedure in which a reasonable and estimated temperature $T$ is needed first, and then the partial pressure $P_i$ can be calculated from $P_i = P^*_i \gamma_i X_i$ at the temperature $T$. When

![Figure 3. The separation coefficient at 1073K to 1573K: (a) Ag-Pb; (b) Au-Pb; (c) Pd-Pb; (d) Pt-Pb.](image)

| Element, $i$ | $A$ | $B$ | $C$ | $D$ | Temperature range, K |
|--------------|-----|-----|-----|-----|-----------------------|
| Ag           | $-14400$ | $-0.85$ | $0$  | $13.82$ | $1234$–$2420$       |
| Bi           | $-10400$ | $-1.26$ | $0$  | $14.47$ | $300$–$1837$        |
| Au           | $-19820$ | $-1.01$ | $0$  | $14.50$ | $1337$–$3130$       |
| Cu           | $-17250$ | $-1.21$ | $0$  | $15.33$ | $1356$–$2843$       |
| Pb           | $-10130$ | $-0.98$ | $0$  | $13.28$ | $601$–$2023$        |
| Pd           | $-17500$ | $1.00$  | $0$  | $2.69$  | $1828$–$3256$       |
| Pt           | $-27890$ | $-1.77$ | $0$  | $17.83$ | $2042$–$4443$       |
| Sb           | $-6500$  | $0.00$  | $0$  | $8.49$  | $904$–$1948$        |
The corresponding $y_i$ and $T$ can be obtained. The calculation process of $P-x-y$ phase diagram resembles that of $T-x-y$ phase diagram.

Following the procedure shown in figure 4, the VLE phase diagrams of Ag-Pb, Au-Pb, Pd-Pb and Pt-Pb alloys were calculated based on M-MIVM, as shown in figures 5 to 8.

It is found that the calculation values are basically consistent with the experimental data in figures 5(a), 6(a) and 8(a). These deviations are inevitable and reasonable because of the complex experimental conditions, high temperature and low pressure in the procedure of intermittent and small-scale vacuum distillation.

Besides, the $T-x-y$ phase diagrams show that the temperature fluctuation extent of vapor and liquid phase lines decrease with pressure of system reduction, indicating that the alloys can be separated more easily at lower pressure with less energy consumption. For example, for Au-Pb alloy, if Au purity is required to be larger than
0.999 (mole fraction), when the system pressure is decreased from 15 Pa to 5 Pa, the minimum design temperature can be decreased from 1907.6 K to 1771.2 K.

The optimal experimental conditions of separation can also be acquired through $T$-$x$-$y$ phase diagrams. For instance, if the precious metal purity is required to be larger than 0.999 (mole fraction), the temperature of separation is needed to be higher than 1369.7 K for Ag-Pb alloy, 1771.2 K for Au-Pb, 2176.9 K for Pd-Pb and 2304.7 K for Pt-Pb at 5 Pa.

Furthermore, the law of leverage can also be utilized into VLE phase diagram analysis to quantitatively forecast the amount of substance of distillate and residue under the condition of the separated temperature and pressure are determined. Take $T$-$x$-$y$ phase diagram of Ag-Pb alloy as an example, suppose $x_E$ is the mole fraction of Pb in Ag-Pb binary system under the condition of the separation pressure and temperature of the system are 5 Pa and 1200 K, respectively. And then make a straight line that intersects the liquidus and gaseous lines at points A and B, respectively, as shown in figure 5(a). The components of A and B are $x_L$ and $y_g$, respectively when the alloy system reaches VLE. According to the law of leverage:

$$\frac{n_l}{n_g} = \frac{y_g - x_E}{x_E - x_l} = \frac{|EB|}{|EA|}$$

where $n_l$ and $n_g$ are the amount of substance of residues and volatiles, respectively. $|EA|$ and $|EB|$ are the length of line of segment $EA$ and $EB$, respectively.

If the total moles of raw materials are $n$ ($n = n_l + n_g$), then the moles of residues and volatiles ($n_l$ and $n_g$) can be calculated from equations (31) and (32), respectively:

$$n_l = \frac{y_g - x_E}{y_g' - x_l} = \frac{|EB|}{|AB|}$$

$$n_g = \frac{x_E - x_l}{y_g' - x_l} = \frac{|EA|}{|AB|}$$
\[ n_g = \frac{x_g - x_i}{y_g - x_i} = \frac{[EA]}{[AB]} \]  

where \(|AB|\) is the length of \(AB\).

The \(P-x-y\) phase diagrams of Ag-Pb, Au-Pb, Pd-Pb and Pt-Pb alloys with a certain temperature range were obtained based on M-MIVM. The \(P-x-y\) phase diagrams can be used to analyze the product component dependence of temperature or pressure in the process of vacuum distillation. In other words, if the temperature and system pressure of operation are selected based on VLE phase diagrams, the metal content in residue and volatile can be predicted.

4. Conclusions

In this work, the activities and activity coefficients of Ag-Pb, Au-Pb, Cu-Pb, Pd-Pb, Pt-Pb, Ag-Sb and Ag-Bi alloys were predicted using MIVM, M-MIVM, Wilson equation and NRTL model. The average standard deviation and average relative deviation of each model were calculated. The results show that the prediction deviations of M-MIVM are smallest among four thermodynamic models, indicating that M-MIVM is stable and reliable. The separation coefficients and VLE phase diagrams of Ag-Pb, Au-Pb, Pd-Pb and Pt-Pb alloys were calculated based on M-MIVM. The separation coefficients are much larger than one, indicating that they can be separated easily by vacuum distillation. The consistency between the VLE calculation values and the experimental data shows that the VLE phase diagrams calculated from M-MIVM are reliable. Based on the VLE phase diagrams obtained in this paper, the optimized and relatively accurate experimental conditions for separating Ag-Pb, Au-Pb, Pd-Pb and Pt-Pb alloys by vacuum distillation can be determined.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Zientek M L and Loeferski P J 2014 USGS fact sheet 2014–3064: platinum-group elements-so many excellent properties U.S. Geological Survey 2014 2327–6932
[2] Diaz I A et al 2016 Comprehensive process for the recovery of value and critical materials from electronic waste J. Clean. Prod. 125 236–44
[3] Dong H et al 2015 Recovery of platinum group metals from spent catalysts: a review Int. J. Miner. Process. 145 108–13
[4] Cowley A 2020 PGM Report May 2020, Johnson Matthey PLC
[5] USGS. Mineral Commodity Summaries 2020. (https://usgs.gov/centers/amics/mineral-commodity-summaries)
[6] Ding Y et al 2019 Recovery of precious metals from electronic waste and spent catalysts: a review Resour. Conserv. Recycl. 141 284–98
[7] Zhai X 2011 Heavy Metal Metallurgy (Beijing: Metallurgical Industry Press)
[8] Cui J and Zhang L 2008 Metallurgical recovery of metals from electronic waste: a review J. Hazard. Mater. 158 228–56
[9] Wang Y and Liu Z 2007 Recycling of Gold, Silver And Platinum Group Metals (Hunan: Central South University Press)
[10] Dai Y and Yang B 2009 Vacuum Metallurgy of Nonferrous Metals (Beijing: Metallurgical Industry Press)
[11] Yang B 2009 Selected Papers from Institute of Vacuum Metallurgy and Materials, Kunning University of Science and Technology (Beijing: Metallurgical Industry Press)
[12] Yang H et al 2015 Vapor-liquid phase diagrams of Pb-Sn and Pb-Ag alloys in vacuum distillation Vacuum 119 179–84
[13] Kong L et al 2016 Vapor-liquid phase equilibria of binary tin-tin antimony system in vacuum distillation: experimental investigation and calculation Fluid Phase Equilib. 415 176–83
[14] Nan C et al Experimental and modeling vapor-liquid equilibria: separation of Bi from Sn by vacuum distillation Vacuum 135 109–14
[15] Gao J et al 2018 Calculation of vapor-liquid equilibria of binary lead-based alloys in vacuum distillation using simplified molecular interaction volume model Fluid Phase Equilib. 483 154–65
[16] Dai H and Tao P 2018 A statistical thermodynamic model with strong adaptability for liquid mixtures Fluid Phase Equilib. 473 154–65
[17] Dai H and Tao P 2019 Application of the modified molecular interaction volume model (M-MIVM) to vapor-liquid phase equilibria of binary alloys in vacuum distillation Vacuum 163 342–51
[18] Tao D 2000 A new model of thermodynamics of liquid mixtures and its application to liquid alloys Thermochim. Acta 105–13
[19] Hu Y 1982 Molecular Thermodynamics of the Fluid (Beijing: Higher Education Press)
[20] Hildebrand J H and Wood S E 1933 The derivation of equations for regular solutions J. Chem. Phys. 1 817–22
[21] Prausnitz J M, Lichtenthaler R N and Azevedo E G D 1986 Molecular Thermodynamics of Fluid-phase Equilibria (New Jersey: Prentice-Hall)
[22] Ferro R and Saccone A (ed) 1993 Structure of Solids (VCH Verlagsgesellschaft, Weinheim)
[23] Guthrie R I L and Iida T 1988 The Physical Properties of Liquid Metals (Oxford: Oxford University Press)
[24] Hultgren R, Desai P D, Hawkins D T, Geiser M and Kelley K K 1973 Selected Values of the Thermodynamic Properties of Binary Alloys (Metals Park, OH: ASM)
[25] Franke P and Neuschutz D 2006 Binary Systems. Part 4: Binary Systems from Mn-Mo to Y-Zr. (Berlin Heidelberg: Springer)
[26] Wilson G M and New A 1964 Expression for the excess free energy of mixing J. Am. Chem. Soc. 86 127–30
[27] Renon H and Prausnitz J M 1968 Local compositions in thermodynamic excess functions for liquid mixtures AIChE J. 14 135–44
[28] Jiang W et al 2014 Separation of lead–silver alloy deposited in hydrometallurgy of non-ferrous metals by vacuum distillation Chinese Journal of Vacuum Science and Technology 34 533–7
[29] Yang C, Qiu K and Lin D 2010 Vacuum distillation of Pb-Pd alloy The Chinese Journal of Process Engineering 10 80–3
[30] Yang C, Qiu K and Lin D 2009 Vacuum distillation for separation of Pb-Pt alloy The Chinese Journal of Process Engineering 9 887–91 (http://www.en.cnki.com.cn/Article_en/CJFDOTAL-HGYJ200905011.htm)