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Thermodynamic analysis of separation behavior in Ag-Sn, Bi-Sn, Cu-Sn, and Sb-Sn alloys during vacuum distillation

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Abstract

Vacuum distillation represents an effective technique for the separation and purification of metals based on differences in vapor pressure. In this work, the separation behavior in Ag-Sn, Bi-Sn, Cu-Sn, and Sb-Sn alloy systems was thermodynamically evaluated. Activities of liquid phase components were calculated using the CALPHAD method and COST 531 thermodynamic database for lead-free solders. Based on these data, separation coefficients were determined over a wide temperature and composition range. In addition, vapor-liquid equilibrium calculations were performed using Gibbs energy minimization implemented in HSC Chemistry software in order to estimate equilibrium distributions of components between vapor and liquid phases under reduced pressure. The results reveal pronounced differences in separation behavior among the investigated systems. Bi and Sb exhibit significantly higher volatility than Sn, with separation coefficients reaching values much higher than unity over a wide temperature range, enabling efficient removal from tin melts during vacuum distillation. In contrast, Ag and Cu show much lower relative volatility and separation coefficients close to unity, indicating limited separation efficiency. The calculated molar fluxes further represent the theoretical maximum evaporation rates under the considered conditions. These results provide a thermodynamic basis for assessing vacuum distillation as a refining method for Sn-based alloys.

K e y w o r d s: vapor-liquid equilibrium, tin alloys, vacuum refining, separation coefficient

1. Introduction

The rapid expansion of electronic manufacturing and the global transition toward lead-free technologies have significantly increased the production and consumption of tin-based solder alloys [1–3]. Binary alloy systems such as Ag-Sn, Bi-Sn, Cu-Sn, and Sb-Sn represent the fundamental building blocks of modern lead-free solders used in electronic assemblies [3–6]. At the same time, the growing volume of electronic waste has intensified the need for efficient recycling and refining technologies capable of selectively recovering valuable metallic components from complex secondary resources [7–9].

Vacuum distillation represents a promising pyrometallurgical method for the separation and purification of metals based on differences in vapor pressure [10–12]. Under reduced pressure, the boiling temperature of metals decreases significantly, enabling selective evaporation of the more volatile component from a liquid alloy. Compared to conventional fire refining or hydrometallurgical routes, vacuum processing offers several advantages, including high selectivity, reduced environmental impact, and the possibility of direct recovery of high-purity metals [12–14].

The vapor-liquid equilibria and the process of vacuum distillation of several Sn-based alloy systems has been investigated so far. Yao et al. [15] studied saturation vapor pressure, separation coefficients, T-$x(y)$ phase diagram of the silver-tin alloys, condensation rate, and the feasibility of using vacuum evaporation-multistage condensation as a method for separating Ag-Sn alloys. Nan et al. [16] investigated the vapor-liquid equilibria for Sn-Bi binary alloy at 5 Pa at distillation temperatures in the range of 1150–1550 K. The experimental results indicate that Bi can be sat-

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isfactorily removed from crude Sn. The concentration of tin in liquid phase was more than 99.99 wt.% at a temperature higher than 1300 K. The vapor-liquid equilibria of the Sb-Sn and and Bi-Sb-Sn alloys were studied by Nan et al. [17] in the temperature range from 1000 to 1500 K and at pressure of 5 Pa. The experimental values indicated that Sb and Bi can be removed from crude Sn by vacuum distillation. In the study by Wang et al. [18], vapor-liquid equilibria of the Cu-Sn system have been investigated in the temperature range from 1612 to 1650 K and at pressure of 5 Pa. The azeotropic composition for Cu-Sn binary system at 5 Pa was calculated.

While the vacuum evaporation behavior of certain binary systems has been investigated individually, a systematic comparative analysis of Sn-based solder systems remains limited. In particular, the combined influence of equilibrium vapor pressure and activity-composition relationships on evaporation thermodynamics and kinetics in Ag-Sn, Bi-Sn, Cu-Sn, and Sb-Sn systems has not been systematically evaluated.

The aim of the present study is to perform a comparative thermodynamic analysis of component evaporation from liquid Sn-based binary alloys under controlled vacuum conditions. By applying an identical theoretical framework to all investigated systems, it is possible to establish a hierarchy of volatility and to quantify the role of thermodynamic activity in governing selective evaporation. The results provide both fundamental insight into evaporation mechanisms in liquid metallic solutions and practical guidance for the development of vacuum-based recycling and refining processes for Sn-based solder materials.

2. Theoretical basis

The volatility of a metal during evaporation processes is primarily governed by its saturated vapor pressure. The saturated vapor pressure of a metal component i represents the pressure of its vapor in thermodynamic equilibrium with the corresponding pure condensed phase (solid or liquid) at a given temperature. This relationship can be expressed by Eq. (1):

$$\log p_i^{\circ} = AT^{-1} + B\log T + CT + D, \tag{1}$$

where A, B, C, and D are empirical evaporation constants reported in the literature [19], and T denotes the absolute temperature.

When the metal is present in an alloy rather than in its pure state, its partial vapor pressure above the solution (p_i) differs from that of the pure component (p_i°). The relationship between these quantities is described by Eq. (2):

$$p_i = a_i p_i^{\circ} = \gamma_i x_i p_i^{\circ}, \tag{2}$$

where a_i is the activity of the metal in the alloy, γ_i is its activity coefficient, and x_i is its mole fraction. Based on Eq. (2), it is evident that the vapor pressure of a metal above the solution depends on both concentration and its thermodynamic activity in the solution [20].

Although saturated vapor pressure provides a preliminary indication of the potential volatility differences between impurity elements and the base metal, it alone is insufficient for evaluating separation efficiency in vacuum distillation. A more representative parameter is the separation coefficient (β_i), which quantitatively describes the relative tendency of a component to transfer into the vapor phase compared to the reference metal under defined thermodynamic conditions [8, 20]. For binary i-j alloy system, the separation coefficient of component i relative to component j can be expressed as:

$$\beta_i = \frac{\gamma_i p_i^{\circ}}{\gamma_j p_j^{\circ}}, \tag{3}$$

where γ_i and γ_j represent the activity coefficients of components i and j, and p_i° and p_j° represent the saturated vapor pressures of components i and j.

The value of the separation coefficient reflects the relative effective volatility of the two components. If β_i is much greater than or much smaller than unity ($\beta_i \gg 1$ or $\beta_i \ll 1$), a favorable separation tendency exists between the components at the considered temperature. In the case where $\beta_i \gg 1$, component i preferentially evaporates and enters the vapor phase, whereas $\beta_i \ll 1$ indicates that component i remains predominantly in the liquid phase. Conversely, when β_i is close to unity ($\beta_i \approx 1$), efficient separation of the components by vacuum distillation becomes difficult.

Reliable determination of separation coefficients requires accurate knowledge of the thermodynamic activities of the alloy components. Since β_i depends directly on the ratio of activity coefficients and saturated vapor pressures, the evaluation of activity coefficients plays a crucial role in the quantitative analysis of distillation behavior. In many studies dealing with vacuum distillation, activity coefficients are estimated using semi-empirical models such as the Molecular Interaction Volume Model (MIVM) [21–23]. In the present work, however, thermodynamic activities were obtained using the CALPHAD (CALculation of PHAse Diagrams) approach [24]. This method relies on the thermodynamic description of phases through Gibbs energy functions optimized on the basis of available experimental and theoretical data. By minimizing the total Gibbs energy of the system, CALPHAD enables consistent prediction of thermodynamic properties and phase equilibria as functions of temperature

and composition. The calculations were carried out using the COST 531 thermodynamic database for lead-free solder systems [25] together with the *PANDAT software package* [26].

Vapor-liquid equilibrium relationships in the investigated Sn-based systems were further analyzed using the *Equilibrium Compositions* module of HSC Chemistry 10 (Metso), a widely used thermodynamic software package for chemical and metallurgical process simulations [27]. The calculations were performed using the GIBBS equilibrium solver, which determines the equilibrium phase distributions by minimizing the total Gibbs free energy of the system under the specified temperature, pressure, and overall composition. The gaseous phase was assumed to behave as an ideal gas mixture, while the activities of the liquid-phase components were introduced from CALPHAD calculations. The obtained results were used to construct pressure-composition diagrams and to assess the thermodynamic limits of element removal under reduced-pressure conditions. Unlike conventional vapor-liquid equilibrium (VLE) diagrams commonly reported in the literature, which describe phase compositions at fixed pressure [28], the present work adopts a pressure-dependent equilibrium approach. While classical VLE diagrams provide quantitative information on phase partitioning under predefined conditions, they do not allow continuous monitoring of phase redistribution as temperature and total system pressure change during the vacuum distillation process.

The evaporation of atoms from a liquid surface under vacuum conditions can be described using the Hertz-Knudsen equation [29], which originates from the kinetic theory of gases. According to this model, the rate of evaporation is proportional to the equilibrium vapor pressure of the evaporating species and inversely proportional to the square root of temperature and molecular mass. The molar evaporation flux of component i can be expressed as

$$J_i = \alpha \frac{p_i}{\sqrt{2\pi M_i RT}}, \tag{4}$$

where J_i is the molar evaporation flux, p_i is the partial vapor pressure of the evaporating species, M_i is the molar mass, R is the universal gas constant, T is the absolute temperature, and α is the evaporation coefficient.

For multicomponent liquid alloys, the partial pressure of a component above the melt is determined by its thermodynamic activity in the liquid phase according to the relation $p_i = a_i p_i^{\circ}$, where a_i is the activity of component i and p_i° is the vapor pressure of the pure element. Consequently, the evaporation flux depends not only on the vapor pressure of the pure metal but also on the thermodynamic interactions within the liquid alloy. The Hertz-Knudsen equation is therefore widely used for the analysis of evaporation kinetics in vacuum metallurgy and high-temperature materials processing.

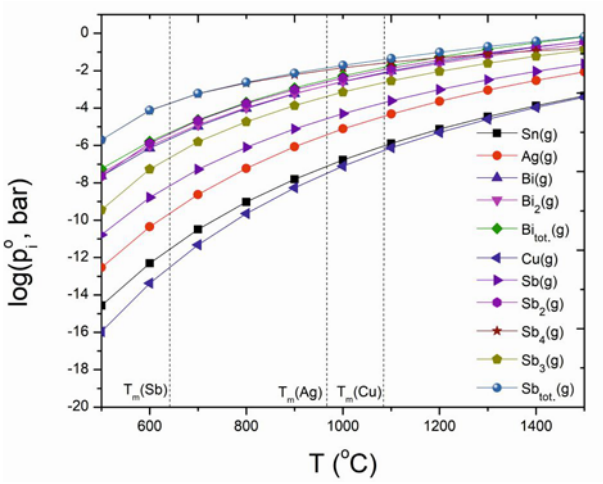

Fig. 1. Calculated equilibrium vapor pressures of gaseous species in the investigated Sn-based systems in the temperature range 500–1500 °C. The total vapor pressures of Bi and Sb were obtained as the sum of all stable gaseous species. Vertical dashed lines indicate the melting temperatures of Sb, Ag, and Cu.

For elements forming several gaseous species, such as bismuth and antimony, the evaporation flux was evaluated by considering each gaseous species separately. The partial pressure of each species was calculated from its equilibrium vapor pressure above the pure liquid metal and the corresponding thermodynamic activity of the component in the liquid alloy, taking into account the stoichiometry of the evaporation reaction. The total molar evaporation flux was subsequently obtained as the sum of the individual Hertz-Knudsen fluxes of all thermodynamically stable gaseous species.

3. Results and discussion

3.1. Vapor pressure of constituent metals

The saturated vapor pressures were determined using the Reaction Equations module in HSC Chemistry by evaluating the equilibrium of the corresponding evaporation Metal = Metal(g) reactions. The equilibrium constants of these reactions were used to calculate the corresponding metal vapor pressures as a function of temperature. The calculated temperature dependence of equilibrium vapor pressures for the constituent metals is presented in Fig. 1. For antimony and bismuth, the gas phase was treated as a multicomponent system consisting of several molecular species (Sb(g), Sb_2(g), Sb_3(g), Sb_4(g), and Bi(g), Bi_2(g)), and

the total vapor pressure ($Bi_{tot.}(g)$, $Sb_{tot.}(g)$) was determined as the sum of the partial pressures of all thermodynamically stable gaseous forms. The gas phases of antimony and bismuth are characterized by the coexistence of several gaseous species whose relative abundances depend strongly on temperature. Previous experimental studies based on transpiration and vapor-pressure measurements have shown that the vapor phase of antimony is dominated by Sb_2 and Sb_4 over a wide temperature range, whereas the contribution of monatomic Sb(g) increases with increasing temperature [30]. In contrast, bismuth vapor consists predominantly of Bi(g) and $Bi_2(g)$, with the relative abundance of Bi_2 decreasing as temperature increases [31]. Therefore, reliable evaluation of the volatility of antimony and bismuth requires consideration of all thermodynamically stable gaseous species rather than only the monatomic vapors. The obtained results were compared with the literature data [19] and excellent agreement was found.

The results reveal a pronounced hierarchy in volatility over the entire investigated temperature interval. Among the analyzed elements, antimony exhibits the highest equilibrium vapor pressure, followed by bismuth. Silver shows significantly lower vapor pressures compared to Bi and Sb, while tin occupies an intermediate position. Copper demonstrates the lowest volatility throughout the entire temperature range.

A particularly important observation is the substantial difference in vapor pressure between Sb and Sn, as well as Bi and Sn which reaches several orders of magnitude at intermediate temperatures (800–1100 ℃). This large thermodynamic driving force suggests a strong potential for selective evaporation in Bi-Sn and Sb-Sn systems under vacuum conditions. In contrast, the smaller difference between Sn and Ag, and especially between Sn and Cu, indicates that separation in Ag-Sn and Cu-Sn systems will be considerably more thermodynamically and kinetically constrained.

The inclusion of polyatomic gaseous species for antimony significantly affects its apparent volatility. The presence of Sb_2, Sb_3, and Sb_4 in the gas phase increases the total vapor pressure of antimony relative to a monatomic approximation. This highlights the necessity of considering gas-phase speciation when evaluating evaporation thermodynamics of multivalent elements. A similar, although less pronounced, effect is observed for bismuth due to the formation of Bi_2 molecules.

Another notable feature is the gradual convergence of vapor pressure curves with increasing temperature. As temperature rises, the relative differences between components decrease, which implies that thermodynamic selectivity may diminish at very high temperatures. Consequently, optimal separation conditions should balance sufficient evaporation rates with preservation of volatility contrast between alloy components.

These results define the thermodynamic upper limit of separation efficiency and provide the fundamental basis for interpreting the experimentally observed evaporation kinetics in the investigated Sn-based alloy systems.

3.2. Separation coefficients of Sn-based alloy systems

Reliable calculation of separation coefficients requires prior knowledge of thermodynamic activities of alloy components at the investigated compositions and temperatures (Eq. (3)). In the present study, the activities of components in the investigated binary systems were calculated using the CALPHAD method and thermodynamic descriptions of investigated binary systems included in the COST 531 lead-free solders database. This approach determines thermodynamic properties based on optimized thermodynamic parameters describing the Gibbs energy of individual phases. These parameters are critically assessed using available experimental data and thermodynamic constraints, which ensures internal consistency of the database and high reliability of the calculated thermodynamic quantities.

The calculated activities of the components in the liquid phase of the Ag-Sn, Bi-Sn, Cu-Sn, and Sb-Sn systems at selected temperatures are presented in Fig. 2. The selected temperatures are representative of the experimental vacuum distillation conditions reported for each alloy system in the literature and ensure that the alloys remain completely in the liquid state during the thermodynamic calculations. The results reveal noticeable differences in thermodynamic behavior among the investigated systems. In the Bi-Sn system, the activities show only a slight positive deviation from ideal solution behavior (Fig. 2b). In contrast, the Sb-Sn system exhibits a moderate negative deviation from ideality (Fig. 2d). More pronounced negative deviations are observed in the Ag-Sn and Cu-Sn systems, indicating stronger interactions between the alloy components in these liquid solutions (Figs. 2a,c).

These differences in thermodynamic behavior significantly influence the effective vapor pressures of the alloy components and consequently affect the calculated separation coefficients and the feasibility of separation by vacuum distillation.

The calculated separation coefficients for the investigated Sn-based binary systems are presented in Fig. 3. The selected temperature ranges for the calculation of separation coefficients were chosen to correspond to the conditions most commonly investigated experimentally for each Sn-based alloy system and to ensure that the alloys remain completely in the liquid

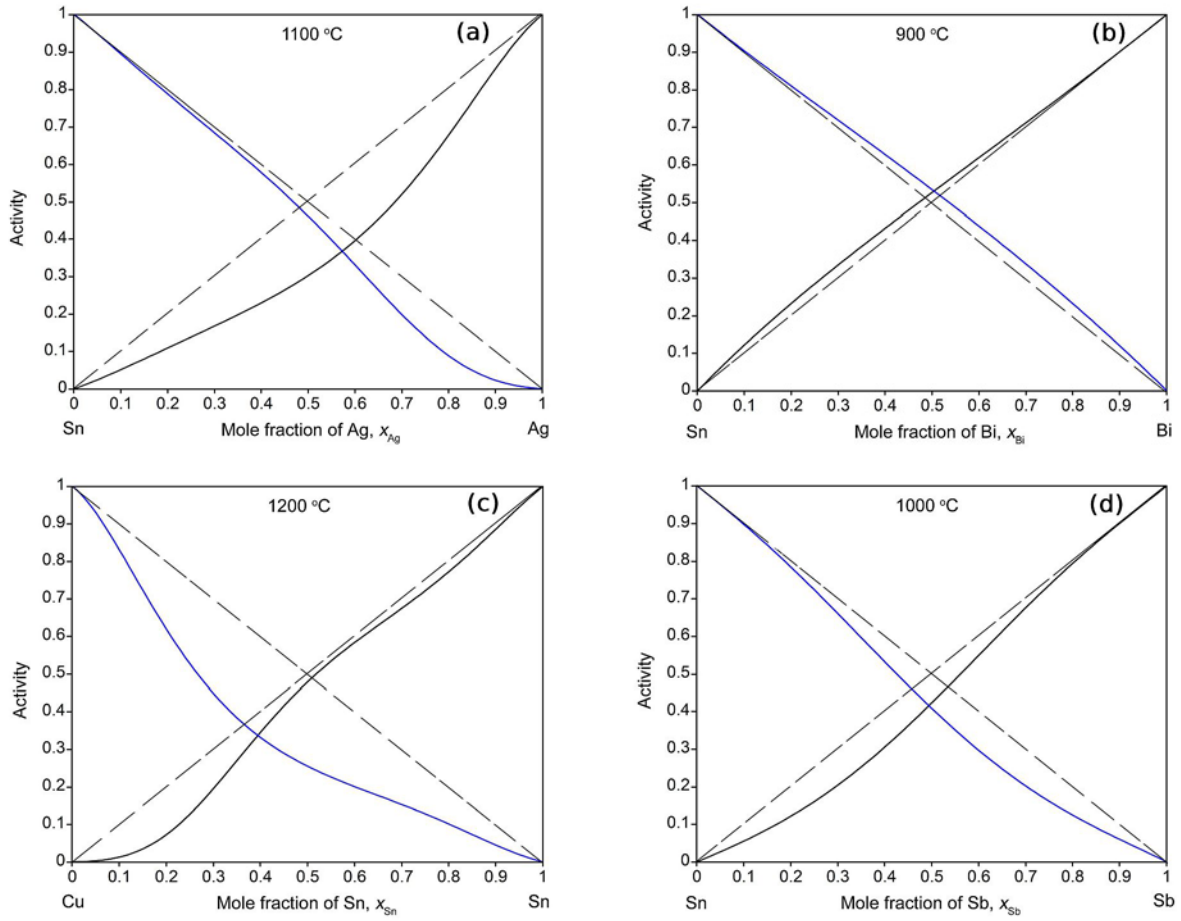

Fig. 2. Calculated activities of components: (a) Ag-Sn system at 1100 °C, (b) Bi-Sn system at 900 °C, (c) Cu-Sn system at 1200 °C, and (d) Sb-Sn system at 1000 °C. (Reference state: pure liquid metals).

state throughout the calculations.

The results show significant differences in the separation behavior of the analyzed systems. The highest separation coefficients were obtained for the Sb-Sn and Bi-Sn alloys, where $\log \beta$ values range approximately between 4.3–5.9 for Sb and 4.4–5.4 for Bi depending on temperature and alloy composition (Figs 3b,d). These values correspond to separation coefficients in the order of 10^4–10^6, indicating extremely favorable thermodynamic conditions for selective evaporation of Sb and Bi from liquid Sn. The high volatility of antimony and bismuth relative to tin originates primarily from their substantially higher equilibrium vapor pressures.

The calculated separation coefficients show different trends with respect to alloy composition for the Bi--Sn and Sb-Sn systems. In the Bi-Sn system, the separation coefficient of bismuth decreases with increasing Bi concentration (Fig. 3b). This behavior can be attributed to the near-ideal thermodynamic behavior of the liquid Bi-Sn solution. At low Bi concentrations, bismuth atoms are predominantly surrounded by tin atoms, which leads to slightly elevated activity coefficients and consequently higher effective volatility. As the Bi content increases, the solution approaches more ideal behavior and the activity coefficient of Bi tends toward unity, resulting in a decrease of the separation coefficient. In contrast, the Sb-Sn system exhibits the opposite trend. The separation coefficient of antimony increases with increasing Sb content (Fig. 3d). This behavior is related to stronger chemical interactions in the Sb-Sn liquid phase and the deviation from ideal solution behavior. At low Sb concentrations, antimony atoms are stabilized within the tin matrix, resulting in lower thermodynamic activity. As the Sb concentration increases, the activity coefficient of Sb rises, which leads to higher effective vapor pressure and consequently larger separation coefficients.

These results indicate that the separation efficiency of Bi from tin is highest at low impurity concentrations, whereas the volatility of Sb becomes more prominent at higher Sb contents. Such composition-dependent behavior should be considered when designing vacuum distillation processes for the refining of tin-based alloys.

The results of experimental investigations of the Sb-Sn system reported by Nan et al. [17] further con-

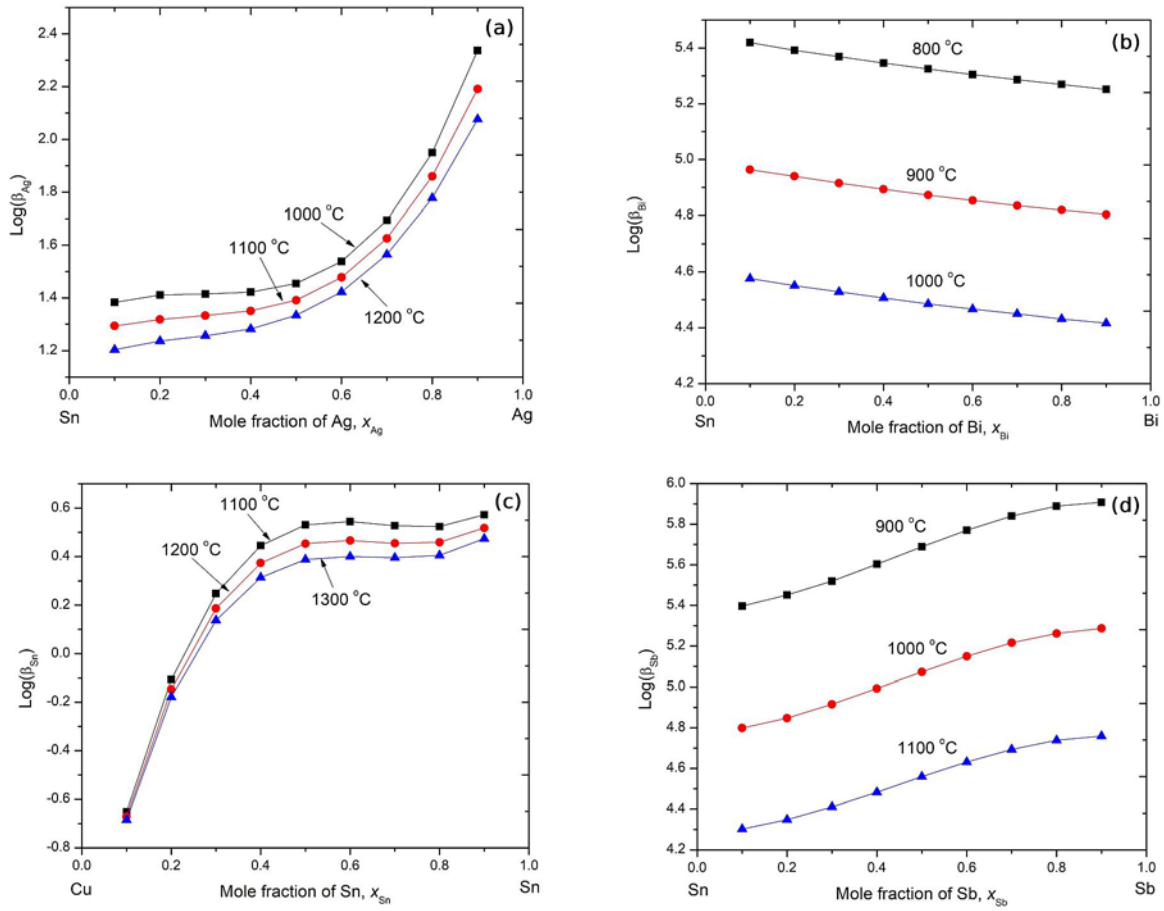

Fig. 3. Calculated temperature and composition dependences of the logarithm of the separation coefficient: (a) Ag in the Ag-Sn system, (b) Bi in the Bi-Sn system, (c) Sn in the Cu-Sn system, and (d) Sb in the Sb-Sn system.

firm the high efficiency of vacuum distillation for removing antimony from tin. Their measurements at a total pressure of 5 Pa showed that the mole fraction of tin in the liquid phase reached 0.99281 at temperatures above 1500 K, indicating effective removal of antimony from crude tin. This behavior is consistent with the thermodynamic calculations performed in the present work, which predict high separation coefficients for antimony relative to tin. The large values of the separation coefficient imply that Sb preferentially evaporates into the vapor phase, while Sn remains predominantly in the liquid phase.

The high separation efficiency of bismuth from tin reported by Nan et al. [16] confirms the large separation coefficients obtained in the present thermodynamic analysis of the Bi-Sn system. Their experimental results show that the Bi content in crude tin decreases from 0.2 to 1.7 × 10^{-5} mol fraction during a single-stage vacuum distillation at 1550 K and 5 Pa, resulting in tin purity higher than 99.99 wt.%. Such a drastic reduction of Bi concentration clearly indicates a very high relative volatility of bismuth with respect to tin, which is fully consistent with the high separation coefficients predicted in this work.

In contrast, the Ag-Sn system exhibits significantly lower separation coefficients (Fig. 3a). The calculated $\log \beta$ values vary approximately between 1.2 and 2.3, corresponding to β values in the range of about 15–210. Although selective evaporation of silver is still thermodynamically possible, the lower driving force suggests that the overall separation efficiency will be strongly influenced by kinetic limitations. Yao et al. [15] reported to some extent lower β values (2.8–8.3) in the temperature range of 1000–1600 ℃ using the MIVM model to calculate the activity coefficients of the Ag-Sn alloys. The value of the silver separation coefficient increases with increasing silver content and decreasing temperature, which is in agreement with the results of Yao et al. [15].

The lowest separation coefficients were obtained for the Cu-Sn system, where $\log \beta$ values remain in the range from –0.7 to 0.6 over the investigated temperature and composition intervals (Fig. 3c). Such values correspond to separation coefficients close to unity, indicating very limited thermodynamic selectivity. Under these conditions, the vacuum distillation process would not effectively remove copper from molten tin.

The calculated separation coefficients for the Cu-

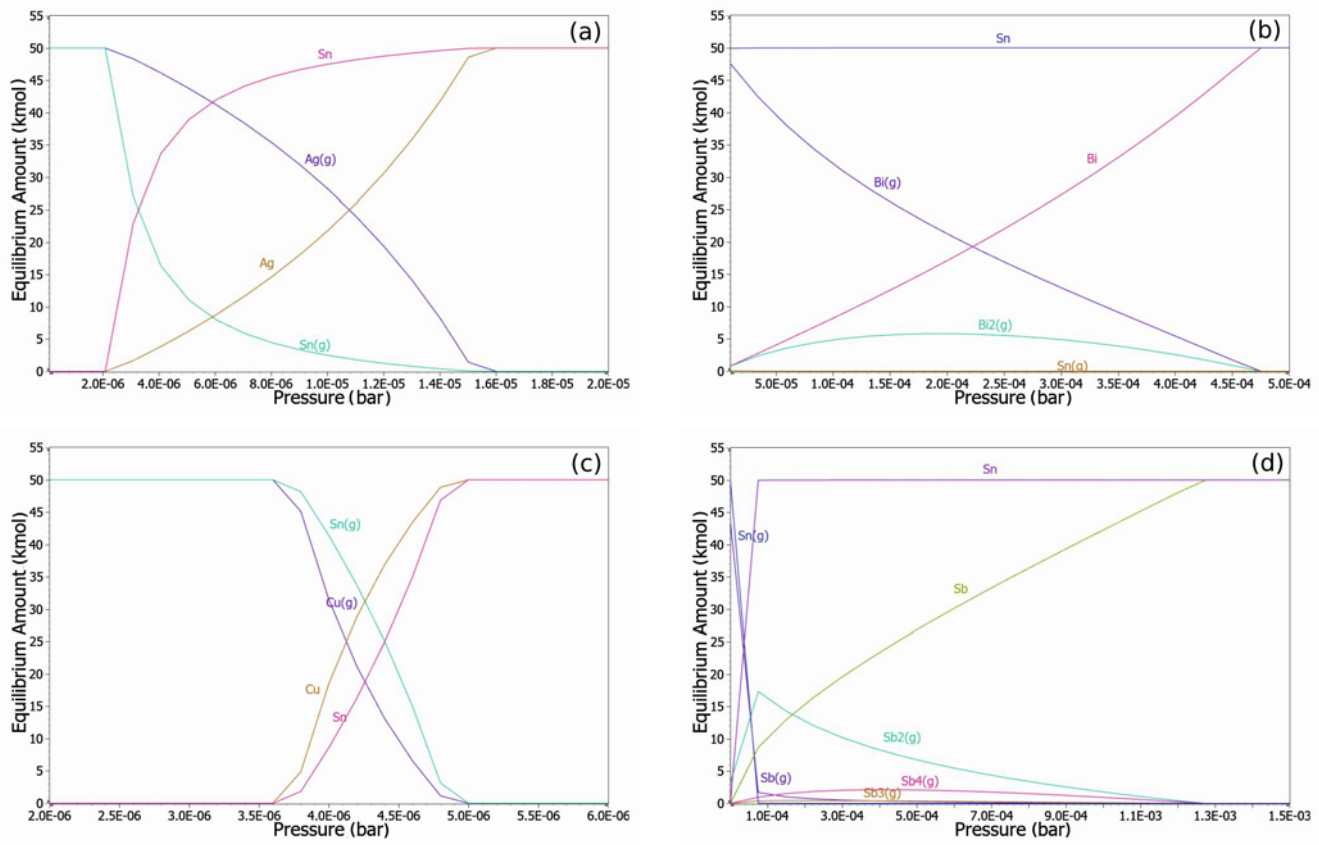

Fig. 4. The equilibrium distribution of components between the liquid and gas phases for equiatomic alloy in: (a) Ag-Sn system at 1100 °C, (b) Bi-Sn system at 900 °C, (c) Cu-Sn system at 1200 °C, and (d) Sb-Sn system at 1000 °C.

-Sn system indicate the existence of an azeotropic composition (vapor phase has the same composition as the liquid phase) where the separation coefficient becomes equal to unity ($\log \beta = 0$) (Fig 3c). Based on interpolation of the calculated data, the azeotropic compositions were determined to be approximately $x_{\mathrm{Sn}} = 0.230$, 0.244 and 0.257 at 1100, 1200, and 1300 °C, respectively. These values correspond to $x_{\mathrm{Cu}} \approx 0.77$–0.74, indicating that the azeotropic point slightly shifts toward higher tin concentrations with increasing temperature. Since the separation coefficient depends on both the activity coefficients and the saturated vapor pressures of the pure components, which are temperature dependent, the composition satisfying the condition $\beta = 1$ changes slightly with temperature. The obtained results are in reasonable agreement with literature data. Wang et al. [18] reported that the Cu-Sn system forms an azeotrope at $x_{\mathrm{Cu}} = 0.71$ ($x_{\mathrm{Sn}} = 0.29$) at 1649 K under vacuum conditions (5 Pa).

Although the exact compositions differ slightly, the predicted azeotropic region lies within a similar composition range. The present results confirm the existence of an azeotropic region in the Cu-Sn system and demonstrate a consistency with previously reported thermodynamic analysis.

Another important observation is the slight decrease of separation coefficients with increasing temperature for most alloy compositions. This trend reflects the gradual convergence of vapor pressures of the alloy components at elevated temperatures, which reduces the thermodynamic driving force for selective evaporation.

The calculated separation coefficients clearly indicate that vacuum distillation is highly suitable for the purification of Sn-based alloys containing bismuth and antimony, moderately effective for systems containing silver, and thermodynamically unfavorable for the removal of copper from molten tin.

3.3. Thermodynamic analysis of phase redistribution during vacuum distillation

In order to further evaluate the thermodynamic feasibility of impurity removal from tin-based alloys, equilibrium phase compositions were calculated using the Gibbs energy minimization approach implemented in HSC Chemistry. The calculations were performed for equiatomic liquid alloys of the investigated binary systems using activity coefficients obtained from CALPHAD thermodynamic descriptions based on the COST 531 database.

The results are presented in the Figs. 4a–d as pressure-composition diagrams showing the equilib-

Table 1. Recommended thermodynamic conditions for vacuum distillation of Sn-based binary alloys

System	Temperature (°C)	Optimal pressure range (Pa)	Dominant gaseous species	Separation efficiency
Sn-Bi	850–950	~ 5	Bi(g), Bi_2(g)	Very high
Sn-Sb	900–1100	10–20	Sb_2(g), Sb(g)	High
Sn-Ag	1000–1150	~ 1	Ag(g)	Moderate
Sn-Cu	1150–1250	< 0.5	Cu(g), Sn(g)	Low

rium distribution of components between the liquid and gas phases at selected temperatures.

The diagrams clearly illustrate the strong dependence of phase partitioning on the total system pressure. As the pressure decreases, the more volatile component preferentially transfers into the gas phase, while the less volatile component remains in the liquid alloy. This behavior represents the thermodynamic basis of the vacuum distillation process.

For the Bi-Sn system (Fig. 4b), bismuth exhibits significantly higher volatility compared to tin. Even at relatively moderate vacuum levels ($\sim 5.0 \times 10^{-5}$ bar), the equilibrium calculations predict almost complete transfer of Bi into the gas phase, while Sn remains predominantly in the liquid phase. This finding is consistent with experimental studies reported in the literature [16], where highly efficient removal of Bi from crude tin has been achieved by vacuum distillation.

A similar trend is observed for the Sb-Sn system (Fig. 4d). Antimony forms stable gaseous species such as Sb_2(g), which dominate the vapor phase under reduced pressure conditions. Consequently, Sb can be efficiently removed from tin melts at elevated temperatures and sufficiently low pressures (1×10^{-4}–2×10^{-4} bar).

The Cu-Sn system exhibits much less favorable separation conditions (Fig. 4c). Due to the relatively small difference in vapor pressures of Cu and Sn, both components appear in the vapor phase within a similar pressure range. This behavior indicates that vacuum distillation is considerably less effective for separating copper from tin, which is consistent with the calculated separation coefficients.

The Ag-Sn system shows intermediate behavior (Fig. 4a). Although silver demonstrates somewhat higher volatility compared to tin, the difference is not sufficiently large to ensure highly selective separation. Therefore, efficient removal of Ag would require deeper vacuum conditions and possibly multistage distillation [15].

Overall, the obtained equilibrium diagrams provide valuable insight into the thermodynamic limits of impurity removal from tin-based alloys and complement the analysis based on separation coefficients.

Based on the obtained results, favorable thermodynamic conditions for vacuum distillation of Sn-based binary alloys can be summarized (Table 1).

3.4. Evaporation kinetics of Sn-based alloy systems

The calculated logarithmic values of molar evaporation fluxes for the investigated alloy components are presented in Fig. 5. The fluxes were determined using the Hertz-Knudsen equation (Eq. (4)) based on the calculated thermodynamic activities and equilibrium vapor pressures of the alloy constituents. For the Bi-Sn and Sb-Sn systems, the calculated molar evaporation fluxes represent the sum of the individual fluxes of all thermodynamically stable gaseous species (Bi(g), Bi_2(g), Sb(g), Sb_2(g), Sb_3(g), and Sb_4(g)). It should be noted that the calculated molar fluxes represent theoretical maximum evaporation rates under the assumed conditions ($\alpha = 1$). The obtained results should therefore be interpreted primarily as a thermodynamic-kinetic potential for evaporation, rather than as exact process rates.

The obtained results reveal substantial differences in the evaporation kinetics of the investigated systems. The highest molar evaporation fluxes were observed for bismuth and antimony, whose values exceed those of tin by several orders of magnitude over the investigated temperature range. Such behavior reflects the significantly higher vapor pressures of these elements compared to tin and confirms the strong thermodynamic driving force for their selective evaporation. For bismuth and antimony, the calculated evaporation fluxes include contributions from all thermodynamically stable gaseous species. Although the polyatomic species possess larger molecular masses and therefore slightly lower individual Hertz-Knudsen fluxes, their contribution to the total evaporation flux remains significant owing to their relatively high equilibrium partial pressures. This treatment provides a more realistic description of the evaporation behavior of these elements under vacuum conditions.

In the Bi-Sn and Sb-Sn systems, the calculated fluxes of the more volatile component are several orders of magnitude greater than those of tin. This indicates that vacuum distillation can provide highly efficient separation in these alloys. The Ag-Sn system exhibits significantly lower evaporation fluxes compared to Bi and Sb. Although silver still evaporates faster than tin, the difference between the fluxes is considerably smaller. Consequently, the separation efficiency

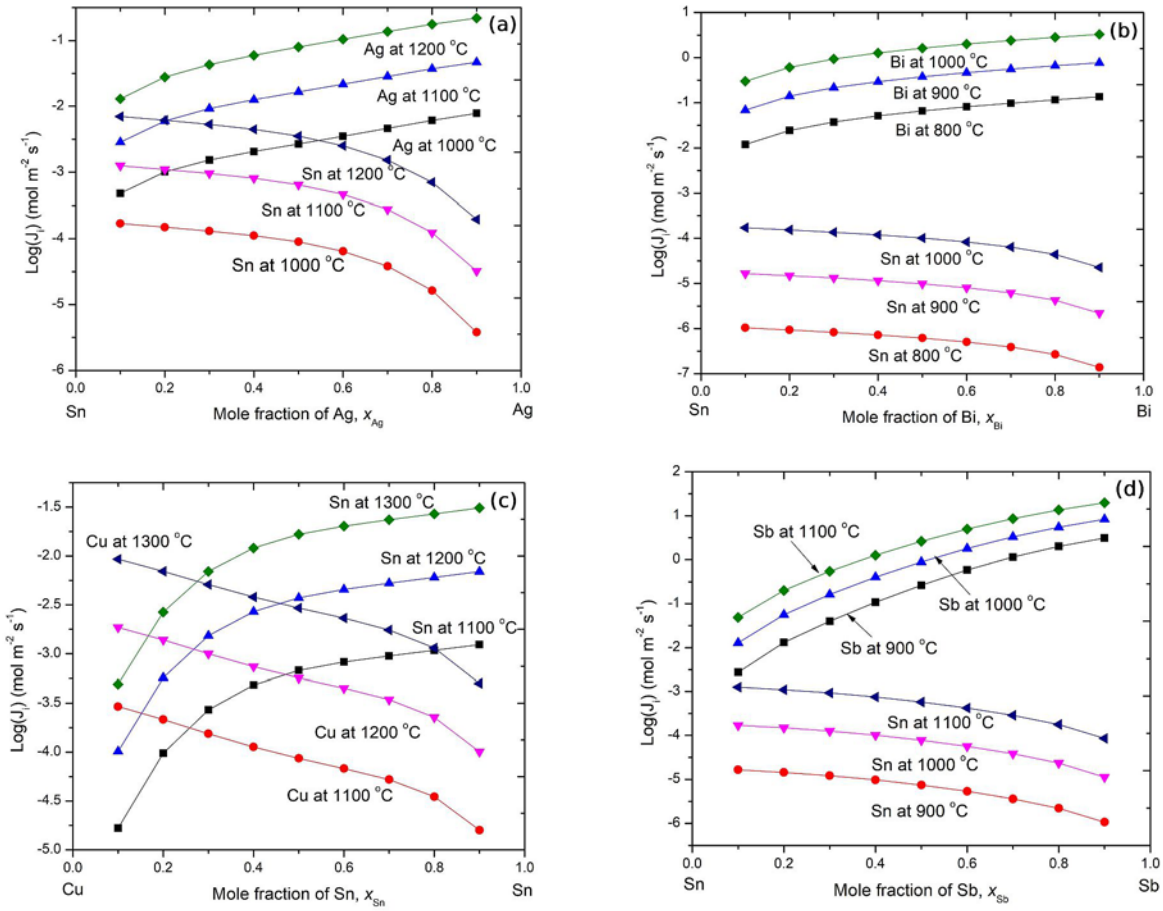

Fig. 5. The calculated logarithmic values of molar evaporation fluxes for the investigated alloy components: (a) Ag-Sn system, (b) Bi-Sn system, (c) Cu-Sn system, and (d) Sb-Sn system.

in this system is expected to be more strongly influenced by kinetic limitations and experimental conditions such as temperature and pressure.

The lowest evaporation fluxes were obtained for copper in the Cu-Sn system, whereas tin exhibits considerably higher evaporation fluxes throughout the investigated temperature range. Consequently, tin preferentially evaporates under vacuum conditions, while the evaporation of copper remains negligible. Therefore, vacuum distillation cannot be used for the selective removal of copper from tin-based alloys. An increase in temperature leads to a systematic increase in evaporation fluxes for all components, as expected from the exponential dependence of vapor pressure on temperature. However, the relative differences between components slightly decrease at higher temperatures, which may reduce the selectivity of the process.

The calculated evaporation fluxes confirm that vacuum distillation is particularly suitable for the purification of tin alloys containing bismuth or antimony, while its applicability is more limited for alloys containing silver and especially copper.

4. Conclusions

The thermodynamic feasibility of separating Ag, Bi, Cu and Sb from liquid tin by vacuum distillation was investigated using CALPHAD-based thermodynamic calculations combined with vapor pressure and evaporation rate analysis.

The results indicate significant differences in the thermodynamic behavior of the investigated binary systems. The calculated activities show strong negative deviations from ideality in the Ag-Sn and Cu-Sn systems, moderate negative deviations in the Sb-Sn system, and slightly positive deviations in the Bi-Sn system.

The calculated saturated vapor pressures reveal large differences in volatility between the components. Among the investigated elements, Sb exhibits the highest vapor pressure relative to Sn, followed by Bi, while Ag and Cu show significantly lower volatility.

The calculated separation coefficients confirm these trends. The highest separation efficiency is obtained for the Sb-Sn and Bi-Sn system, where separation coefficients reach values of $10^{4.3}$–$10^{5.9}$ and $10^{4.4}$–

$10^{5.4}$ in the investigated temperature range, indicating very favorable conditions for antimony and bismuth removal from liquid tin. In the Sb-Sn system the separation coefficient increases with increasing antimony content, while in the Bi-Sn system it decreases with increasing bismuth concentration due to different thermodynamic interactions in the liquid phase.

Equilibrium calculations performed for equiatomic alloys further demonstrate that under typical vacuum distillation conditions the liquid phase becomes strongly enriched in tin, reaching tin mole fractions above 0.95–0.99, depending on the alloy system and temperature.

Kinetic analysis based on the Hertz-Knudsen equation indicates that the evaporation rate is primarily controlled by the vapor pressure of the more volatile component and increases significantly with temperature.

The obtained results confirm that vacuum distillation represents a highly efficient method for the separation of volatile impurities from liquid tin alloys and provide thermodynamic parameters useful for the design and optimization of industrial vacuum refining processes.

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