Liquid-vapor equilibrium and evaporation rate of Cd-Zn liquid alloy

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Abstract
In this study, LVE (liquid-vapor equilibrium) data of cadmium-zinc system were determined at pressure of 7.5 Pa. We compare the use of the Redlich-Kister polynomials with the Wilson equation in fitting activities. The LVE for Cd-Zn system in vacuum distillation was modeled using the two models. The results of the two models are reliable, the Redlich-Kister polynomials is better than the Wilson equation. The LVE phase diagram is reliable for predicting the process of vacuum distillation for Cd-Zn system. Evaporation rates of elements in Cd-Zn alloy were experimental measured and calculated by the Langmuir equation. Experimental data on the evaporation of pure metals Cd and Zn are included. The evaporation coefficients of zinc and cadmium under vacuum conditions were calculated. The deviations were discussed. Comparing calculations with experimental results, it can be found that the trend is consistent. The activation energies of Cd and Zn in the Cd-Zn alloy under experimental conditions were also calculated.

Keywords: Cd-Zn alloy; Thermodynamic modeling; Kinetics; Evaporation rate; Vacuum distillation

1. Introduction
As the fourth common metal, zinc plays an irreplaceable role in modern industry. Metal zinc is widely used in galvanized steel sheet, zinc-manganese batteries and so on. The zinc content of crude zinc in fire smelting is about 98.6%, and the rest are impurity elements Pb, Cd, Fe, Sn, etc. [1]. On the basis of previous research, vacuum distillation technology was introduced into the separation and purification process of crude zinc. Vacuum distillation can not only reduce energy consumption, improve efficiency, but also reduce environmental pollution, which is incomparable to traditional smelting process. Xia et al. measured the evaporation rate of pure metal zinc at 80-280 Pa and compared it with the calculated values [2]. Song et al. carried out vacuum distillation experiments on Pb-10% Sb alloy at 10 Pa and plotted the curve of the evaporation rate of the alloys as a function of distillation temperature and
time [3]. Yoshihito et al. established a temperature distribution model and analyzed the heating conditions in different regions of the alloy melt. Combined with the activities of Ni-Ti alloy obtained by a regular solution model, the evaporation rates of Ni and Ti elements in the system were calculated [4]. Li et al. studied the nebulization process of the impurity elements Zn and Pb in the iron solution [5]. Yang et al. measured niobium evaporation in Nb-based alloys by a "smelting ingot" [6]. In our previous work, we measured and modeled the liquid-vapor equilibria for binary and ternary systems in vacuum distillation. Good results have been obtained in predicting the separation conditions under vacuum conditions by LVE diagram [7-9]. The purpose of this study is to investigate the thermodynamics and kinetics of Cd-Zn binary alloy in vacuum distillation. Experiments on both thermodynamics and kinetics were performed. LVE data of Cd-Zn system under vacuum were measured. T-x diagrams for Cd-Zn system were modeled by the Redlich-Kister polynomials and the Wilson equation. The Langmuir equation was applied to calculate the evaporation rate of metal elements.

2. Method

2.1 LVE

According to Raoult’s law, the relationship of liquid-vapor equilibria for a mixture system can be expressed as [10]:

$$x_i \gamma_i (x_i, T) P_i^* (T) = y_i P$$  \hspace{1cm} (1)

where $x_i$ and $y_i$ are the mole fraction of species $i$ in the liquid phase and vapor phase, respectively; $P$ is the total pressure of system, $P_i^*$ is equilibrium vapor pressure above pure component $i$; $\gamma_i$ is activity coefficient of $i$ in the liquid alloy.

For elements Zn and Cd, $P_i^*$ can be calculated by following formula [10, 11]:

$$\lg P_{Zn}^* = -6620 / T - 1.255 \lg T + 12.34$$  \hspace{1cm} (2)

$$\lg P_{Cd}^* = -5819 / T - 1.257 \lg T + 12.287$$  \hspace{1cm} (3)

For a binary alloy system $i-j$

$$x_i + x_j = 1 \quad ; \quad y_i + y_j = 1$$  \hspace{1cm} (4)

$$P = P_i^* \gamma_i x_i + P_j^* \gamma_j x_j$$  \hspace{1cm} (5)

Then $x_i$ and $y_i$ are solving by Eqs. (4) and (5):

$$x_i = \frac{P - P_j^* \gamma_j}{P_i^* \gamma_i - P_j^* \gamma_j}$$  \hspace{1cm} (6)

$$y_i = \frac{P_i^* \gamma_i x_i}{P}$$  \hspace{1cm} (7)

2.2 Wilson equation

The Wilson equation [12] was used to calculate activity coefficient $\gamma_i$ of binary
components \( i-j \):

\[
\frac{G^E}{RT} = -x_i \ln(x_i + A_{ij}x_j) - x_j \ln(x_j + A_{ji}x_i)
\]  

(8)

The activity coefficients of components \( i-j \) are:

\[
\ln \gamma_i = -\ln \left(\frac{x_i + x_j A_{ij}}{x_j + x_i A_{ji}}\right) + \frac{x_i}{x_j} \left(\frac{A_{ij}}{x_i A_{ji}} - \frac{A_{ji}}{x_j A_{ij}}\right)
\]  

(9)

\[
\ln \gamma_j = -\ln \left(\frac{x_j + x_i A_{ji}}{x_i + x_j A_{ij}}\right) - \frac{x_j}{x_i} \left(\frac{A_{ji}}{x_i A_{ij}} - \frac{A_{ij}}{x_j A_{ji}}\right)
\]  

(10)

The parameters \( A_{ij} \) and \( A_{ji} \) are expressed by:

\[
A_{ij} = \frac{v_i}{v_j} \exp\left[-\left(\lambda_{\lambda_{ij}} - \lambda_{\lambda_{ji}}\right) / RT\right]
\]  

(11)

\[
A_{ji} = \frac{v_j}{v_i} \exp\left[-\left(\lambda_{\lambda_{ij}} - \lambda_{\lambda_{ji}}\right) / RT\right]
\]  

(12)

where \( v_i \) and \( v_j \) are the molar volumes of components \( i \) and \( j \) which are written as a functions of temperature, the related parameters of Cd and Zn for calculation are given in Table 1. \( \lambda_{\lambda_{ii}}, \lambda_{\lambda_{ij}} \) and \( \lambda_{\lambda_{ij}} (\lambda_{ij}=\lambda_{ji}) \), which are the interaction energies \( i-i, j-j \), and \( i-j \) pairs, respectively. We assume that \( (\lambda_{\lambda_{ji}} - \lambda_{\lambda_{ii}}) \) and \( (\lambda_{\lambda_{ij}} - \lambda_{\lambda_{ji}}) \) in Eqs. (11) and (12) are independent of temperature \( T \) [13]. The interaction energies between Cd and Zn were given in Table 2. The values of \( A_{ij} \) and \( A_{ji} \) at other temperature \( T' \) should be calculated as follows:

\[
A_{ij}' = \frac{v_j}{v_i} \left(\frac{A_{ji}}{v_j / v_i}\right)^{\frac{T'}{T}}
\]  

(13)

\[
A_{ji}' = \frac{v_i}{v_j} \left(\frac{A_{ij}}{v_i / v_j}\right)^{\frac{T'}{T}}
\]  

(14)

Table 1. Molar volume formulas for related metallic elements [11].

| Metal | \( v(\text{cm}^3/\text{mol}) \) | \( T/\text{K} \) |
|-------|----------------|--------|
| Cd    | \( 14.0[1+1.50\times10^{-4}(T-594)] \) | 594~1040 |
| Zn    | \( 9.94[1+1.50\times10^{-4}(T-693)] \) | 693~1181 |

Table 2. The interaction energies between Cd and Zn.

| \( T/\text{K} \) | \( i-j \) | \( \lambda_{\lambda_{ij}} - \lambda_{\lambda_{ii}} \) (J) | \( \lambda_{\lambda_{ij}} - \lambda_{\lambda_{ji}} \) (J) |
|----------------|--------|----------------|----------------|
| 700            | Interaction energies | 7500.98         | 2173.26        |

2.3 Redlich-Kister polynomials
The Redlich-Kister polynomials is usually employed to describe the dependence of excess Gibbs energy on the temperature and composition of binary systems[14]. It can be expressed as follows:

\[
\Delta G = x_i x_j \left( L_{i,j} + L_{i,j} x_i - x_j \right) + L_{i,j}^2 \left( x_i - x_j \right)^2
\]  

(15)

The coefficients \( L_{i,j} \), \( L_{i,j} \), and \( L_{i,j}^2 \) can be found by a least squares method.

2.2 Theory of evaporation kinetics

The rate of evaporation \( W_i \) is quantitatively calculated by the Langmuir equation [15] which derived from the kinetic theory of ideal gas. Through the equation, we obtain:

\[
W_i = 4.376 \times 10^{-4} \cdot \alpha_i x_i \gamma_i P_i^* \sqrt{\frac{M_i}{T}}
\]  

(16)

where \( \alpha_i \) is evaporation coefficient (usually \( \alpha_i \approx 1 \) for pure metals); \( x_i \) is molar mass of \( i \); \( P_i^* \) is saturated vapor pressure; \( T \) is the system temperature; \( M_i \) is molar mass; \( \gamma_i \) is the activity coefficient of \( i \).

The evaporation rate constant \( K_i \) can be expressed as:

\[
K_i = \frac{4.376 \times 10^{-4} \gamma_i P_i^*}{\rho} \sqrt{\frac{M_i^2}{MT}}
\]  

(17)

where:

\[
\rho = \frac{1}{\frac{w_i}{\rho_i} + \frac{w_j}{\rho_j}}
\]  

(18)

\[
M = x_i M_i + x_j M_j
\]  

(19)

where \( M_i \) and \( M_j \) are molar mass of components \( i \) and \( j \), respectively. \( w_i \) and \( w_j \) are mass fraction, \( \rho_i \) and \( \rho_j \) are density of components \( i \) and \( j \) respectively; \( M \) is average molar mass of molten alloy [6]; \( \rho \) is density of alloy.

The evaporation rate constant of alloy in vacuum distillation is usually composed of three parts: (1) The mass transfer of metal atoms in the liquid phase, \( K_m \); (2) Metal atoms transfer mass at the interface, \( K_i \); (3) The diffusion of metal atoms in the gas phase, \( K_r \). If the pressure of the system is less than the vapor pressure of the evaporating element, it can be considered that the gas phase does not affect evaporation. In this work, the evaporation rate constant \( K_i = \frac{1}{(1/K_m + 1/K_i + 1/K_r)} \) was calculated [16, 17]. Experimental evaporation rate of components in alloy can be expressed [2]:

\[
W_i = \frac{m_{i0} - m_i}{S \cdot t}
\]  

(20)

Where \( m_{i0} \) and \( m_i \) are the mass of component \( i \) before and after experiment, respectively; \( S \) is the surface area of the interface between molten liquid and argon, that is the cross-sectional area of the crucible \( (S = 7.07 \ cm^2, \ Radius = 1.5 \ cm) \). \( t \) is the
distillation time, min. In the process of alloy evaporation, the mass fraction of component \( i \) which evaporate out of the alloy per unit mass in a unit time is \( \frac{W_i}{m} \cdot S \), according to Eq. (16), we have:

\[
\frac{W_i}{m} \cdot S = 4.376 \times 10^{-4} \cdot \frac{S}{m} \alpha_i \gamma_i P_i \sqrt{\frac{M_i}{T}} \quad (21)
\]

The concentration change of volatile components in \( dt \) time is given by:

\[
\frac{W_i}{m} \cdot S = \frac{dx_i}{dt} \quad (22)
\]

Combining Eqs. (17) and (22), substitute \( m=\rho v \) into Eq. (21), we have:

\[
\frac{dx_i(t)}{dt} = -\frac{S}{V} K_i x_i(t)^n \quad (23)
\]

Integration of Eq. (23) is expressed as:

\[
\ln w_i = -\frac{S}{V} K_i t \quad (24)
\]

Where \( m \) is total mass of the alloy; \( c_i \) is melt concentration. Vacuum distillation of alloy can be considered follow first order reaction (\( n=1 \)).

According to the Arrhenius equation [10], the activation energy of the evaporation process can be obtained if the \( K_i \) value is determined:

\[
\ln K_i = -\frac{E}{RT} + \ln A \quad (25)
\]

Where \( A \) is pre-exponential factor, which is independent of temperature.

3. Experimental

Samples of Cd-Zn alloy with 60 g each for the experiment were prepared by zinc and cadmium, with a purity higher than 99.99\% which obtained from Hebei RunDe Company. Two kinds of pure metals were put into the alloy melting device which drained into dry argon to clean the air inside. Turned on the heater, and waited for the temperature to reach 723 K and hold the temperature for 1 hour. For better homogenisation the samples were turned over and repeated two or three times. Finally, a homogeneous alloy was obtained by quenching. The weight loss of the sample is less than 2\%. Different compositions of Cd-Zn alloys were used for LVE investigation and Cd_{40}Zn_{60} was chose for kinetics experiment of alloy evaporation. Table 3 shows the information of experimental samples for Cd-Zn alloy. The schematic diagram of the equipment and the internal structure of vertical vacuum furnace are shown in Figs.1 and 2, respectively.

| \( x_{Zn} \) | \( m_{Zn}(g) \) | \( m_{Cd}(g) \) | Total(g) |
|---|---|---|---|
| 0.1 | 3.65 | 56.35 | 60 |
| 0.2 | 7.62 | 52.38 | 60 |
0.3 11.97 48.03 60
0.4 16.77 43.23 60
0.5 22.07 37.93 60
0.6 27.96 32.04 60
0.7 34.55 25.45 60
0.8 41.97 18.03 60
0.9 50.39 9.61 60

Standard uncertainties: $u(m) = \pm 0.01\,\text{g}$

**Fig. 1.** Schematic of apparatus used for vacuum distillation equilibrium experiments: 1. cooling water; 2. control system; 3. vacuum pump; 4. vacuum furnace; 5. argon gas; 6. McLeod vacuum gauge.
The chamber was evacuated to 1 Pa under Pure argon (99.9 mass %) atmosphere. This procedure was repeated three times to ensure that oxygen and nitrogen molecules were kept as low as possible. In the course of experiment, ventilation with pure argon gas to keep the pressure stable. For LVE experiment of Cd-Zn alloy, pressure was controlled at 7.5 Pa with an accuracy of 1 Pa and temperatures were separately at 588, 609, 616, 623 and 630 K (+1K). For better measurement compositions of residues (liquid phase) and volatiles (vapor phase), we determined a suitable temperature according to different compositions. 60 minutes was chose as distillation time in this work which allows the system approach to the phase equilibrium sufficiently.

For kinetic experiment of Cd-Zn alloy evaporation, we measured one temperature point every 10 K between 590 and 630 K at 7.5 Pa. To improve accuracy of the experiment, more than twice distillation tests will be performed at each temperature. For comparison between evaporation of components in alloy and pure metal, vacuum distillation experiments of pure metals Cd and Zn were also performed.

4. Results and discussion

Using experimental data of Cd-Zn system [18], the Wilson equation parameters $A_{ji}=0.4816$ and $A_{ij}=0.3939$ for the Cd-Zn system at 700 K were obtained by the least squares method. Table 4 gives the thermodynamic parameters required in Redlich-Kister polynomials. The calculated activity coefficients of components for Cd-Zn system were calculated using Eqs. (9) and (10) which shown in Table 5 and Fig.3. It can be seen that the calculated results are in good agreement with experimental values, the Redlich-Kister polynomials is better than the Wilson equation. Experimental LVE data for Cd-Zn system are shown in Table 6. Substituting
the calculated activity coefficients using the two models into Eqs. (6) and (7), the contents of Zn and Cd in the vapor and liquid phases can be obtained. $T - x$ phase diagram for Cd-Zn system at 7.5 Pa can be draw which shown in Fig. 4. The agreement of the LVE phase diagram with the experimental data of Cd-Zn system indicates that the calculation method of LVE is reliable for the process of vacuum distillation. There is slight deviation between experimental values and calculations. It may be arising from: (1) the boiling points of zinc and cadmium are different under experimental conditions. Then, temperature fluctuation in the furnace has a great influence on the experimental data; (2) Zinc volatilizes slowly if the temperature is low, then the experiment time needs to be extended to make it volatilize more fully; (3) Although the deviation caused by operation is minimized during experiment, sampling imbalance may still occur in the sampling test.

**Table 4. The parameters of Redlich-Kister polynomials in the Cd-Zn binary system.**

| $^0L$  | $^1L$ | $^2L$ |
|-------|-------|-------|
| 8142.42 | -193.78 | 913.43 |

**Table 5. Comparison of the predicted activities of the Wilson equation and Redlich-Kister polynomials with experimental data [18] of Cd-Zn alloy at 700 K.**

| $x_{Zn}$ | $a_{Zn,Exp}$ | $a_{Cd,Exp}$ | $a_{Zn,Cal}$ | $a_{Cd,Cal}$ | $a'_{Zn,Cal}$ | $a'_{Cd,Cal}$ |
|---------|---------------|---------------|---------------|---------------|---------------|---------------|
| 0.1     | 0.305         | 0.914         | 0.304         | 0.916         | 0.310         | 0.913         |
| 0.2     | 0.477         | 0.849         | 0.466         | 0.853         | 0.472         | 0.851         |
| 0.3     | 0.585         | 0.794         | 0.564         | 0.801         | 0.576         | 0.799         |
| 0.4     | 0.66          | 0.745         | 0.633         | 0.754         | 0.653         | 0.749         |
| 0.5     | 0.717         | 0.696         | 0.688         | 0.704         | 0.716         | 0.697         |
| 0.6     | 0.765         | 0.643         | 0.737         | 0.646         | 0.768         | 0.638         |
| 0.7     | 0.809         | 0.578         | 0.788         | 0.571         | 0.814         | 0.570         |
| 0.8     | 0.857         | 0.484         | 0.845         | 0.461         | 0.860         | 0.479         |
| 0.9     | 0.917         | 0.323         | 0.913         | 0.290         | 0.916         | 0.327         |
| ±$S$    | 0.020         | 0.015         | 0.005         | 0.005         |
| ±$S$(%) | 2.513         | 2.303         | 0.750         | 0.692         |

-Redlich-Kister polynomials, $±S$ = average relative error, $±S$(%) = average standard error.
Fig. 3. Comparison of the predicted activities with experimental data [18] of Zn-Cd alloy at 700K.

Table 6. Experimental LVE data for the Cd-Zn binary alloy system.

| Experiment condition | Content of Zn (mole fraction) |
|----------------------|------------------------------|
| Temperature (K) | Pressure (Pa) | Time (min) | $x_{\text{Zn}}$ | $y_{\text{Zn}}$ |
| 588 | 7.5 | 90 | 0.3024 | 0.0049 |
| 588 | 7.5 | 90 | 0.2833 | 0.0044 |
| 588 | 7.5 | 90 | 0.3745 | 0.0073 |
| 588 | 7.5 | 90 | 0.4938 | 0.0130 |
| 609 | 7.5 | 90 | 0.9289 | 0.1466 |
| 616 | 7.5 | 90 | 0.9779 | 0.2130 |
| 616 | 7.5 | 90 | 0.9755 | 0.2120 |
| 623 | 7.5 | 90 | 0.9395 | 0.2570 |
| 630 | 7.5 | 90 | 0.9265 | 0.3230 |

Standard uncertainties $u$ are $u(x) = \pm 0.0001$ mol; $u(T) = \pm 1$ K; $u(P) = \pm 1$ Pa.
Substituting calculated $\gamma_i$ by the Redlich-Kister polynomials into Eq. (16) and combing Eq. (20), the maximum evaporation rates of calculation and experiment for Cd and Zn in Cd-Zn alloy were obtained at 7.5 Pa which shown in Table 7. Table 8 presents the results on the evaporation of pure metals Cd and Zn. It can be seen from Fig. 5 although there is a gap between experiment and calculation of evaporation rate, the $W_{Zn}/W_{Cd}$ ratios tend are consistent. The reason is perhaps that the evaporation coefficient $\alpha_i$ of the alloy is not close to 1 when the temperature is low under vacuum condition. For Pure Zn and Cd, it can be seen from Table 8 that the calculated and experimental values of evaporation rate are almost identical. The experimental results should not differ much from the calculations for $Cd_{40}Zn_{60}$ alloy. The evaporation coefficients of Cd and Zn in the alloy were calculated which reported in Table 9. The evaporation coefficient of cadmium is very close to 1/13.6 in the literature[19]. If $\alpha=1$, it means that no preferential separation is possible. Since interaction and different thermodynamic properties of components for alloy, the evaporation coefficients should exhibit large or small values.

**Table 7. Experimental data and calculated results of Cd-Zn system at 7.5 Pa.**

| T/K  | S/V | t/min | $W_{Zn}$ Final(%) | $W_{Cd}$ Final(%) | $W_{Zn}$ | $W_{Cd}$ | $W_{Zn}$ | $W_{Cd}$ |
|------|-----|-------|-------------------|-------------------|----------|----------|----------|----------|
| 590  | 22.10 | 20   | 55.9             | 44.1              | 2.19x10^{-3} | 7.23x10^{-2} | 4.97x10^{-2} | 1.13     |
| 600  | 16.76 | 15   | 56.4             | 43.6              | 3.61x10^{-3} | 1.01x10^{-1} | 7.40x10^{-2} | 1.60     |
| 610  | 10.85 | 10   | 54.7             | 45.3              | 4.80x10^{-3} | 1.30x10^{-1} | 1.08x10^{-1} | 2.22     |

*Fig. 4. Comparison of the predicted LVE of calculation (lines) with experimental data (Symbols) of Cd-Zn system at 7.5 Pa.*
Table 8. Experimental data of evaporation rates of pure metals Zn and Cd at 7.5Pa.

| Metal | T/K  | t/min | m_{Initial}/g | m_{Final}/g | W*/cm²·min | W/cm²·min |
|-------|------|-------|---------------|-------------|-------------|------------|
| Cd    | 630  | 10    | 50            | 14.08       | 0.536       | 0.502      |
| Zn    | 630  | 15    | 50            | 47.18       | 0.027       | 0.023      |

W*-experimental value; W-calculated result.

Fig. 5. The curve of the experimental value and the calculated value of evaporation rate.

Table 9. The evaporation coefficients of Cd and Zn in the Cd-Zn system.

| T/K  | γ_{Cd} | γ_{Zn} | P_{Cd}/Pa | P_{Zn}/Pa | α_{Zn}= W^*_Zn/ W_{Zn} | α_{Cd}= W^*_Cd/ W_{Cd} |
|------|--------|--------|-----------|-----------|-------------------------|-------------------------|
| 590  | 1.692  | 1.290  | 11.64     | 0.59      | 0.044                   | 0.064                   |
| 600  | 1.680  | 1.286  | 16.65     | 0.88      | 0.049                   | 0.063                   |
| 610  | 1.669  | 1.283  | 23.51     | 1.31      | 0.044                   | 0.059                   |
| 620  | 1.659  | 1.280  | 32.83     | 1.92      | 0.048                   | 0.058                   |
| 630  | 1.648  | 1.277  | 45.35     | 2.78      | 0.057                   | 0.066                   |

The experimental value of $K^*_i$ can be obtained directly by $S/V \cdot t$ and $\ln w_i$. Meanwhile,
$K_i$ can be calculated by Eq. (17). The values of calculated $K_i$ and experimental $K_i^*$ at different temperatures are shown in Table 10. Figure 6 shows the calculated and experimental results of evaporation rate constant for one element in Cd-Zn alloy, as well as pure metal values $K_i$. It can be seen that there are slight differences and consistent trends between $K_{Cd}$ and $K_{Cd}^*$. The ratios of experimental value and calculated data of Cd are about 1.7 times. The main reason may be that the system pressure is lower than the equilibrium vapor pressure of Cd. Since the ratios of Zn is 22 times, however, the trend of the experimental values is consistent with the calculated values.

**Table 10. Summary of results for the calculated $K_i$ (cm/s) and experimental values $K_i^*$ (cm/s) at different temperatures.**

| T/K | $K_{Zn}$ | $K_{Cd}$ | $K_{Zn}^*$ | $K_{Cd}^*$ | $K_{Zn}^*/K_{Zn}$ | $K_{Cd}^*/K_{Cd}$ |
|-----|---------|---------|-----------|-----------|------------------|------------------|
| 590 | $1.80 \times 10^{-5}$ | $4.69 \times 10^{-4}$ | $4.39 \times 10^{-4}$ | $6.17 \times 10^{-4}$ | 24.40 | 1.72 |
| 600 | $2.68 \times 10^{-5}$ | $6.61 \times 10^{-4}$ | $5.70 \times 10^{-4}$ | $8.26 \times 10^{-4}$ | 21.28 | 1.64 |
| 610 | $3.93 \times 10^{-5}$ | $9.20 \times 10^{-4}$ | $9.27 \times 10^{-4}$ | $1.22 \times 10^{-3}$ | 23.56 | 1.73 |
| 620 | $5.71 \times 10^{-5}$ | $1.27 \times 10^{-3}$ | $1.11 \times 10^{-3}$ | $1.53 \times 10^{-3}$ | 19.49 | 1.58 |
| 630 | $8.18 \times 10^{-5}$ | $1.72 \times 10^{-3}$ | $1.80 \times 10^{-3}$ | $2.44 \times 10^{-3}$ | 22.05 | 1.85 |

**Fig. 6. The calculated $K_i$ and experimental values $K_i^*$ (symbols) of components in the Cd-Zn system (dash lines), and for pure metal (lines): (a) Cd and (b) Zn.**

Based on the experimental values of $K_i$ at different temperatures, we plotted $\ln K_i$ vs. $1/T$ using Eq. (25) which shown in Fig. 7. The activation energies of calculation and experiment for Zn and Cd in the alloy under vacuum conditions can be obtained which presented in Table 11. It can be observed that the calculated value for zinc is slightly higher and that for cadmium is relatively close. It indicates that the method
has high reliability.

![Graph](image)

**Fig.7.** Plot of $\ln K_f - 1000/T$.

**Table 11.** The activation energies of Zn and Cd in the Cd-Zn system under vacuum conditions.

| Element | $E$(kJ/mol) | Exp. | Cal. |
|---------|-------------|------|------|
| Zn      | 107.72      | 117.04 |
| Cd      | 103.91      | 100.48 |

5. Conclusion

Experimental LVE data for Cd-Zn system in vacuum distillation were well compared with those calculated by using the Redlich-Kister polynomials and the Wilson equation. The evaporation rates of Cd and Zn were measured under vacuum conditions. The experimental data were correlated using the Langmuir equation. Evaporation rates of pure metals exceed the rates from the melt surface. The activation energies of Cd and Zn in the alloy were experimentally determined.

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Fig. 1. Schematic of apparatus used for vacuum distillation equilibrium experiments:
1. cooling water; 2. control system; 3. vacuum pump; 4. vacuum furnace; 5. argon gas;
6. McLeod vacuum gauge.

Fig. 2. Schematic diagram of the vacuum distillation experimental set-up. 1. furnace lid;
2. furnace body; 3. furnace bottom; 4. electrode; 5. cold plate; 6. observation door; 7.
heat holding cover; 8. heating unit; 9. graphite evaporator.

Fig. 3. Comparison of the predicted activities with experimental data [18] of Zn-Cd alloy at 700K.

Fig. 4. Comparison of the predicted LVE of calculation (lines) with experimental data (Symbols) of Cd-Zn system at 7.5 Pa.

Fig. 5. The curve of the experimental value and the calculated value of evaporation rate.

Fig. 6. The calculated $K_i$ and experimental values $K_i^*$ (symbols) of components in the Cd-Zn system (dash lines), and for pure metal (lines): (a) Cd and (b) Zn.

Fig. 7. Plot of $\ln K_i$-1000/$T$. 
Table 1. Molar volume formulas for related metallic elements

Table 2. The interaction energies between Cd and Zn.

Table 3. The weight of pure component used in this work.

Table 4. Comparison of the predicted activities of the Wilson equation with experimental data [17] of Cd-Zn alloy at 700K.

Table 5. The parameters of Redlich-Kister polynomials in the Cd-Zn binary system.

Table 6. Experimental LVE data for Cd-Zn binary alloy system.

Table 7. Experimental and calculated results of Cd-Zn system at 7.5 Pa

Table 8. Experimental data of evaporation rates of pure metals Zn and Cd at 7.5Pa.

Table 9. The evaporation coefficients of Cd and Zn in the Cd-Zn alloy

Table 10. Summary of results for the calculated $K_i$ (cm/s) and experimental values $K^*_{i}$ (cm/s) at different temperatures.

Table 11. The activation energies of Zn and Cd in the Cd-Zn system under vacuum conditions.