

Vacuum distillation refining of crude lithium (II)^①

—Kinetics on vacuum distillation of crude lithium

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[Abstract] Kinetics on vacuum refining process of crude lithium was studied by using maximum evaporation rate, critical pressure and mean free path of elements in the crude lithium at different temperatures. Behaviors of impurities in the vacuum distillation process have been examined in detail. The results show that fractional vacuum distillation should be taken to obtain lithium with high purity; if the mass loss amount of lithium is 3% ~ 5%, metal K, Na, Mg and Ca can be eliminated at lower temperature of 673~ 873 K at pressure of less than 1.30 Pa; the maximum rate of lithium distillation reaches $1.492 \times 10^{-1} \sim 8.244 \times 10^{-1} \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ at higher temperature of 973~ 1073 K at the pressure of 3.0 ~ 3.2 Pa, which ensure complete separation of lithium from Al, Si, Fe and Ni.

[Key words] lithium; refining; vacuum distillation; kinetics

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1 INTRODUCTION

Lithium is widely used in the fields of aerospace, atomic energy, metallurgy, chemical engineering, electronics, glass and ceramics, battery, air-conditioner and refrigerant, lubricant, and medicine, etc.^[1~3]. The crude lithium, generally produced by electrolytic or metallic thermoreduction methods, however, contains some impurities including Na, K, Mg, Ca, Al, Fe, Si, Ni and so on, which affect the physiochemical properties of lithium product. Refining of the crude lithium is beneficial to satisfy with the final purity of the product. It is of great importance to carry on a fundamental study as to provide a theoretical base for pure lithium production. Thermodynamics on separating impurities from the crude lithium by vacuum distillation has been studied in our previous work^[4], which solves some problems, such as the separation possibility of impurities from lithium by vacuum distillation, the separation extent and the purity of distilled lithium. However, the production efficiency, namely the evaporation rate, is more important in practice. Therefore, it is necessary to study the kinetics in the vacuum distillation process of the crude lithium. It has proved that evaporation rate of element is affected mainly by temperature and pressure. This paper is aimed at investigating influences of temperature, pressure and free mean path on evaporation rate of the element in the crude lithium,

which provide a basis for selecting operation temperature, pressure and time in lithium refining.

2 INFLUENCES OF TEMPERATURE AND PRESSURE ON EVAPORATION RATE

2.1 Relationship between maximum evaporation rate and temperature

When the total chamber pressure (p) is less than the saturation vapor pressure of a pure element (p_i^*), and the mean free path (λ) of the vaporized molecule is greater than the effective dimension (l , the distance between evaporating and condensing surface) of the unit, the evaporation rate of the distilled element is maximum, which can be described as

$$\omega_{\max} = 2.623 \times 10^{-2} \alpha p_i^* (M/T)^{1/2} \quad (1)$$

where ω_{\max} stands for the maximum evaporation rate, $\text{g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$; α is the distillation coefficient, M is relative molecular mass of the distilled element. The saturation vapor pressure of the distilled element is p_i^* , Pa; when the molten surface temperature is T , K.

Relationships between saturation vapor pressure of pure elements (p_i^* , Pa) in the crude lithium and temperature (T , K) are listed in as^[5,6]

$$\begin{aligned} \lg p_{\text{Li}}^* &= -8415 T^{-1} - \lg T + 13.465 \\ &\quad (453.6 \sim 1615 \text{ K}) \\ \lg p_{\text{Na}}^* &= -5780 T^{-1} - 1.18 \lg T + 13.625 \end{aligned} \quad (2)$$

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$$(298 \sim 1156 \text{ K}) \quad (3)$$

$$\lg p_K^* = -4470 T^{-1} - 1.37 \lg T + 13.705$$

$$(350 \sim 1050 \text{ K}) \quad (4)$$

$$\lg p_{Mg}^* = -7780 T^{-1} - 0.855 \lg T + 13.535$$

$$(298 \sim 923 \text{ K}) \quad (5)$$

$$\lg p_{Mg}^* = -7550 T^{-1} - 1.41 \lg T + 14.915$$

$$(923 \sim 1363 \text{ K}) \quad (6)$$

$$\lg p_{Ca}^* = -9350 T^{-1} - 1.39 \lg T + 14.945$$

$$(298 \sim 1115 \text{ K}) \quad (7)$$

$$\lg p_{Ca}^* = -8920 T^{-1} - 1.39 \lg T + 14.575$$

$$(1115 \sim 1767 \text{ K}) \quad (8)$$

$$\lg p_{Al}^* = -16380 T^{-1} - \lg T + 14.445$$

$$(934 \sim 2523 \text{ K}) \quad (9)$$

$$\lg p_{Si}^* = -23550 T^{-1} - 0.565 \lg T + 14.475$$

$$(298 \sim 1687 \text{ K}) \quad (10)$$

$$\lg p_{Fe}^* = -21080 T^{-1} - 2.14 \lg T + 19.015$$

$$(298 \sim 1808 \text{ K}) \quad (11)$$

$$\lg p_{Ni}^* = -22500 T^{-1} - 0.96 \lg T + 15.725$$

$$(298 \sim 1728 \text{ K}) \quad (12)$$

Supposing that the distillation coefficient α_i is 1, the maximum evaporation rate of each element containing in the crude lithium was calculated in the temperature range of 673 ~ 1273 K according to Eqns. (1) ~ (12), as presented in Table 1.

It can be seen from Table 1 that the maximum evaporation rate is affected remarkably by distillation temperature, which enhances several or even tens times with the increase at the temperature of 100 K. It is concluded that Na and K are volatilized quickly and concentrated into vapor phase. It is easy to separate K and Na from the lithium completely because the values of $\omega_{\max, K}$ and $\omega_{\max, Na}$ are 100~ 1000 times greater than that of $\omega_{\max, Li}$ in refining the crude lithium

in the temperature range of 673 ~ 873 K. The maximum evaporation rate of lithium, however, is 10^5 times more than those of Al, Si, Fe and Ni in the range of 973 ~ 1273 K, respectively. Thus, these four impurities are easy to be separated from the crude lithium and concentrated in the distilled residual liquid while the lithium is enriched in vapor. In addition, it can be also derived from Table 1 that the ratios of $\omega_{\max, Mg}$ to $\omega_{\max, Li}$ are 49.64, 38.24 and 31.33 at 673 K, 773 K, and 873 K, respectively, the ratios of $\omega_{\max, Ca}$ to $\omega_{\max, Li}$ are 0.234, 0.33 and 0.44, respectively. Lithium will co-volatilize in removing Mg and Ca. As mentioned in our previous work^[4], the mass content of Mg or Ca in the crude lithium is less than 1%. If the co-volatilization amount of lithium is 3% ~ 5%, Mg and Ca would be evaporated and separated from the crude lithium completely in the temperature range of 673~ 873 K. Therefore, a fractional vacuum distillation should be taken to obtain lithium with high purity. The result is consistent with that of the thermodynamics^[4]. Metal K, Na, Mg and Ca are volatilized at their maximum evaporation rates when the co-volatilization amount of lithium reaches 3% ~ 5% in the temperature range of 673~ 873 K, and the values of $\omega_{\max, Li}$ are $3.620 \times 10^{-5} \sim 1.794 \times 10^{-2} \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$. The lithium is volatilized at the maximum rate of $1.492 \times 10^{-1} \sim 8.244 \times 10^{-1} \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ in the temperature of 973~ 1073 K.

2.2 Influence of pressure on evaporation rate

Vacuum can promote the evaporation of metals or alloys. Many studies^[7~ 11] showed that the evaporation rate (ω) increases with the decrease in cham-

Table 1 Relationship between maximum evaporation rate $\omega_{\max}(\text{g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1})$ of each element and temperature

T / K	$\omega_{\max, K}$	$\omega_{\max, Na}$	$\omega_{\max, Li}$	$\omega_{\max, Mg}$	$\omega_{\max, Ca}$
673	9.762	2.427×10^{-1}	3.620×10^{-5}	1.797×10^{-3}	8.460×10^{-6}
773	5.448×10^1	2.483	1.219×10^{-3}	4.661×10^{-2}	4.081×10^{-4}
873	1.994×10^2	1.455×10^1	1.794×10^{-2}	5.620×10^{-1}	7.878×10^{-3}
973	5.470×10^2	5.810×10^1	1.492×10^{-1}	2.261	8.094×10^{-2}
1073	—	1.763×10^2	8.244×10^{-1}	1.036×10^1	5.290×10^{-1}
1173	—	—	3.362	3.608×10^1	2.453
1273	—	—	1.089×10^1	1.019×10^2	8.316
T / K	$\omega_{\max, Al}$	$\omega_{\max, Si}$	$\omega_{\max, Fe}$	$\omega_{\max, Ni}$	
973	1.831×10^{-8}	1.707×10^{-14}	5.672×10^{-12}	3.477×10^{-13}	
1073	5.859×10^{-7}	2.771×10^{-12}	4.578×10^{-10}	4.308×10^{-11}	
1173	1.026×10^{-5}	1.873×10^{-10}	1.711×10^{-8}	2.319×10^{-9}	
1273	1.135×10^{-4}	6.483×10^{-9}	3.558×10^{-7}	6.612×10^{-8}	

ber pressure (p) in a higher area ($p > p_{\text{crit}}$, as shown in Fig. 1). When p reduces to a specific value p_{crit} or below ($p \leq p_{\text{crit}}$), the ω does not increase any more or just increases at an ignorable amount. This specific value p_{crit} is called as critical pressure p_{crit} , which is of great help for the selection of optimized pressure. The critical pressure means that ω is the ω_{max} in practice. It rises with enhancing temperature.

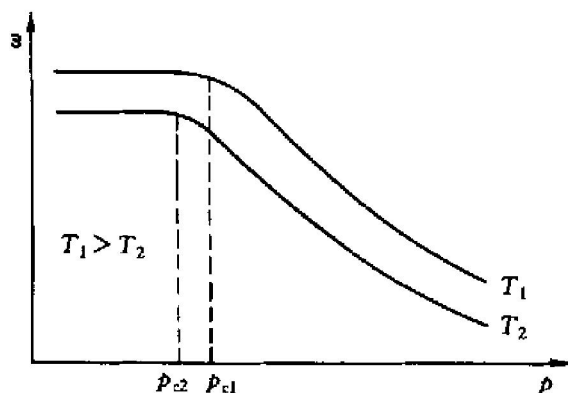


Fig. 1 Relationship of evaporation rate with chamber pressure

The critical pressure is determined by a useful scattering cross-section of vapor molecular and its mass as^[5]

$$p_{\text{crit}} = \frac{\kappa T}{\lambda \sigma \sqrt{1 + M_{\text{m}}/M_{\text{g}}}} \quad (13)$$

$$\sigma = \frac{\pi}{4} \left(\frac{d_{\text{m}} + d_{\text{g}}}{2} \right)^2 \quad (14)$$

where M is the relative molecular mass of the vapor (subscript m stands for metal and g stands for residual gas), d is the diameter of the vapor molecular, σ is the mean useful cross-section of the vapor molecule, κ is Boltzmann constant ($\kappa = 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$), λ is the mean free path.

Because argon is used as the protective gas and the distance between evaporating and condensing surface is 2 cm in refining the crude lithium, it is considered that argon is the residual gas and λ is 2 cm. Thus, the critical pressures of the elements in the

crude lithium were calculated by Eqns. 13 and 14 on basis of the values of M_{m} , M_{g} , d_{m} and d_{g} as listed in Table 2.

It is shown from Table 2 that the critical pressure is related to evaporation temperature, and p_{crit} enhances with the increase in temperature. The values of $p_{\text{crit, Na}}$ and $p_{\text{crit, K}}$ are 1.30~2.19 Pa in the temperature of 673~873 K. The minimum chamber pressure should be less than 1.30 Pa to volatilize Na and K, which ensures that the maximum evaporation rates of Na and K reach the range of $2.427 \times 10^{-1} \sim 1.455 \times 10^1 \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ and $9.762 \sim 1.994 \times 10^2 \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$, respectively. The values of $p_{\text{crit, Mg}}$ and $p_{\text{crit, Ca}}$ are in the range of 1.85~2.40 Pa and 1.44~1.87 Pa in 673~873 K, respectively. When Na and K evaporate from the crude lithium under the pressure less than 1.30 Pa, Mg and Ca volatilize at their maximum evaporation rates of $1.797 \times 10^{-3} \sim 5.620 \times 10^{-1} \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ and $8.460 \times 10^{-6} \sim 7.878 \times 10^{-3} \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$, respectively. If the mass loss amount of 3%~5% Li is taken, Mg and Ca can be removed completely in the process of removing of K and Na. In addition, the value of $p_{\text{crit, Li}}$ is 3.23~3.67 Pa in the range of 973~1073 K, which is greater than the values of p_{crit} of Al, Si, Fe and Ni. The minimum chamber pressure can be selected in the range of 3.0~3.2 Pa when lithium is distilled at a higher temperature. The pressure range ensures that the evaporation of lithium at its maximum evaporation rate of $1.942 \times 10^{-1} \sim 8.244 \times 10^{-1} \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ while the four impurities volatilize at lower rate far less than the respective ω_{max} . Because the value of $\omega_{\text{max, Li}}$ is about 10^6 times of Al, Si, Fe and Ni, respectively, the impurities hardly evaporate and remained in the residual and are separated from lithium completely.

2.3 Effect of temperature and pressure on mean free path

As stated above, the mean free path (λ) of the distilled vapor molecule is greater than or equals to the effective dimension (l) of the chamber, under

Table 2 Relationship between critical pressure p_{crit} (Pa) of pure metals and temperature

T/K	$p_{\text{crit, Li}}$	$p_{\text{crit, Na}}$	$p_{\text{crit, K}}$	$p_{\text{crit, Mg}}$	$p_{\text{crit, Ca}}$	$p_{\text{crit, Al}}$	$p_{\text{crit, Fe}}$	$p_{\text{crit, Ni}}$
673	2.30	1.69	1.30	1.85	1.44	1.94	1.74	1.73
773	2.64	1.94	1.49	2.12	1.65	2.23	2.00	1.99
873	2.98	2.19	1.68	2.40	1.87	2.52	2.26	2.25
973	3.23	2.44	1.88	2.67	2.08	2.81	2.52	2.51
1073	3.67	2.70	2.07	2.95	2.29	3.10	2.78	2.76
1173	4.01	2.95	2.26	3.22	2.51	3.38	3.04	3.02
1273	4.35	3.20	2.45	3.50	2.72	3.67	3.30	3.28

which the evaporation rate is not affected by chamber pressure any more. When the vapor molecule of distilled lithium is considered as monoatomic one, the effect of temperature and pressure on mean free path can be described as^[12]

$$\lambda = 3.11 \times 10^{-18} T / (d^2 p) \quad (15)$$

where p is chamber pressure, Pa; d is the diameter of lithium vapor molecule, $d_{\text{Li}} = 2.90 \times 10^{-8}$ cm.

According to Eqn. 15, the mean free path values of distilled lithium vapor molecular were calculated in the range of 673 ~ 1273 K and 0.01 ~ 10 Pa, as shown in Fig. 2.

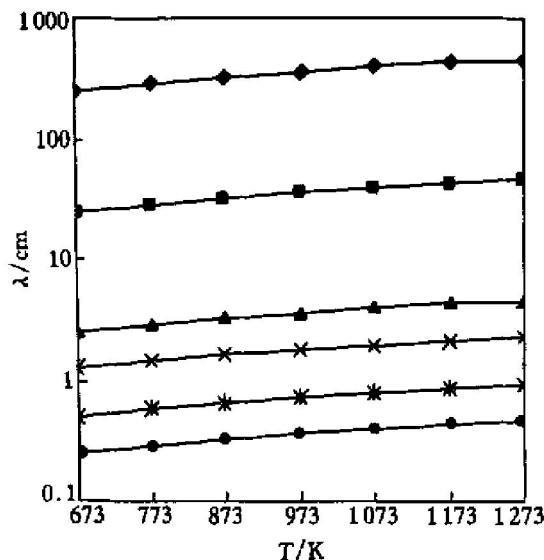


Fig. 2 Mean free path of distilled lithium vapor molecular

◆—0.01 Pa; ■—0.1 Pa; ▲—1 Pa;
×—2 Pa; *—5 Pa; ●—10 Pa

It can be seen from Fig. 2 that the minimum distillation pressure can be controlled in 1 ~ 2 Pa for λ matching l in the temperature of 973 ~ 1073 K. The minimum pressure is considered as the critical pressure of the condition above. Lithium evaporates quickly at the maximum rate of $1.492 \times 10^{-1} \sim 8.244 \times 10^{-1} \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$. The evaporation rate does not increase with lowering distillation pressure. Also from Fig. 2, λ increases with enhancing temperature, which indicates that p_{crit} behaviors the same.

Therefore, the evaporation rate of metal relates to distillation temperature as well as the value of residual pressure. It is necessary to control elevated temperature and low chamber pressure for separating impurities efficiently from the crude lithium in the process of refining lithium.

3 CONCLUSION

A fractional vacuum distillation should be taken to obtain lithium with high purity. Metal K, Na, Mg

and Ca volatilize at the respective maximum evaporation rate of $9.762 \sim 1.994 \times 10^2$, $2.427 \times 10^{-1} \sim 1.455 \times 10^1$, $1.797 \times 10^{-3} \sim 5.620 \times 10^{-1}$ and $8.460 \times 10^{-6} \sim 7.878 \times 10^{-3} \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ in lower temperature of 673 ~ 873 K and the pressure below 1.30 Pa. Metal Mg and Ca can be removed completely with the mass loss amount of lithium 3% ~ 5%. Lithium is distilled in higher temperature of 973 ~ 1073 K and the pressure of 3.0 ~ 3.2 Pa, which ensure that lithium is volatilized at the maximum rate of $1.492 \times 10^{-1} \sim 8.244 \times 10^{-1} \text{ g} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ while Al, Si, Fe and Ni are remained in the residuals.

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