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ON THE THEORY OF EVAPORATION REFINING

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The theory of sublimation and distillation refining, which takes into account the diffusion of impurities, is considered. The conceptual nature of the theory is noted due to the large number of parameters whose values are unknown.

INTRODUCTION

Distillation and sublimation are the main methods for obtaining high-purity substances (as well as directional crystallization) for applications in electronics, and therefore there is an interest in the theory and practice of evaporation refining [1–12].

According to current concepts [7–11], the dependence of the efficiency of refining the "base – impurity" substance on the degree of distillation at a given temperature T of the process in the general case, taking into account the diffusion of impurities in the evaporated material (but without taking into account other possible factors, for example, such as the capture impurities by the vapor of the main component or the chemical interaction of the components of the substance with the formation of volatile or non-volatile compounds) – is determined by two parameters: the equilibrium separation factor β_0 (which is considered constant) and the Peclet diffusion number

$$Pe = wX/\rho D, \quad (1)$$

where w is the rate of evaporation of the substance from a unit surface; D is the diffusion coefficient of the impurity; ρ is the density of the substance; X is the size factor of the evaporated material (for example, the thickness of the material layer in the crucible and the radius of the evaporated ball) [7–10].

The speed w is determined using the formula for numerical calculations

$$w = 0.058p(M/T)^{1/2}, \quad (2)$$

where p is the vapor pressure, mm Hg at a temperature T, K; M is the atomic (or molar) mass of a vapor of a substance (a.e.m. or g/mol) [4]. The temperature dependence of the diffusion coefficient of an impurity is determined by the equation

$$D(T) = D_m exp[(Q/R)(T_m^{-1} - T^{-1})], \quad (3)$$

where T_m is the melting point of the substance; D_m is the impurity diffusion coefficient at temperature T_m; Q is the activation energy of impurity diffusion in the substance under consideration, and R is the universal gas constant [9, 10]. It is generally accepted that $D_m \sim 10^{-5}$ cm^2/s during distillation and $\sim 10^{-6}$ cm^2/s during sublimation.

There is a fundamental possibility of calculating the dependences $\beta(T)$ and $\beta(g)$, where g is the degree of distillation, is shown [13]. These calculations are based on the use of the Burton-Prim-Slichter equation

$$\beta = [1 + (\beta_0^{-1} - 1)exp(-v\delta/D)]^{-1}, \quad (4)$$

where β is the effective separation coefficient; β_0 is the equilibrium separation coefficient; v is the linear velocity of the evaporation surface; δ is the diffusion layer thickness, – as well as on calculations of the impurity distribution in the evaporating material [8]. (If the crucible has a simple shape, then $v = w/\rho$ [11]).

Taking into account the dependence $\beta(g)$, the following equation is valid:

$$C / C_0 = [1 - (1 - g)^{\beta}] / g, \quad (5)$$

where C/C_0 is the relative average concentration of an impurity in the condensate and C_0 is initial impurity concentration. If $w/D \approx 0$ (i.e., under conditions of ideal mixing of the evaporated substance), then $Pe \approx 0$, and $\beta \approx \beta_0$.

Meanwhile, it is noteworthy that the parameters β and Pe are themselves determined by other parameters. The possibility of their use in calculations of evaporative refining is the subject of consideration in this paper.

PARAMETERS AND THEIR FEATURES

As can be seen from equations (1)–(3), Pe depends on the vapor pressure of the main component (p), on the activation energy of impurity diffusion (Q) in the evaporated substance, on the coefficient D_m of impurity diffusion in the substance under consideration, and also on the size factor of the material (X).

The Pe number is included in the calculations of the dependencies $\beta(T)$ and $\beta(g)$, i.e. these calculations are performed using the same parameters p, D_m, Q, and X. Also δ is included in the calculations. The impurity concentration in the diffusion layer decreases monotonically from the value of C_s near the interface to $C_\delta = \eta C_s$ at a distance δ from this surface, where η is a conditionally given number ($0 < \eta << 1$).

Thus, taking into account the diffusion of an impurity significantly complicates the theory, requiring the use of eight parameters (not counting η for finding δ), in comparison with a theory that takes into account only the difference in vapor pressure of the components according to equation (5) with one parameter. The required parameters are generally poorly understood – although there are data on the vapor pressure of simple substances in wide temperature ranges [3] and data on β_0 for some "base–impurity" substances [5].

Separately, it can be noted that the considered theory of evaporation refining with two main parameters (β_0 and *Pe*) does not take into account the convection of the evaporated liquid, and also does not explain two experimental observations: 1) a decrease in the purification efficiency with a decrease in the initial impurity content [14] and 2) a discrepancy between the effective coefficient β and the ideal separation coefficient β_i [15].

CONCLUSIONS

The previously presented in a number of articles [7–12] theory of evaporation refining which takes into account the difference in the vapor pressure of the components and the diffusion of impurities (but not other possible factors, for example, such as the capture of impurities by the vapor of the main component) is analyzed. It is noted that to calculate the efficiency of refining depending on the yield at a given temperature, taking into account the diffusion of impurities, a large number (nine, not counting η) of parameters of the substance and material are required: molar mass *M*, density ρ, melting point T_m, equilibrium separation factor β_0, vapor pressure of the main component *p*, the activation energy of impurity diffusion in the refined substance *Q*, the diffusion coefficient D_m of the impurity at temperature T_m and the size factor of the material *X*, – while the theory, which takes into account only the difference in the vapor pressure of the components, uses only one parameter close to β_0 (equation (5)). Most of these parameters are poorly understood (and the parameter δ is also conditionally determined), as a result of which the theory of evaporative refining under consideration should be considered conceptual (i.e., giving an idea of the nature of the dependence of the refining efficiency on the process output at a given temperature, but not allowing specific calculations to be performed). At the same time, the theory under consideration does not take into account the convection of the evaporating liquid and does not explain some experimental observations that are obviously not related to the diffusion of impurities.

REFERENCES

1. G.G. Devyatykh, Yu.E. Elliev. *Glubokaya ochistka veshchestv*. M.: "Vysshaya Shkola", 1990 (in Russian).

2. Yu.I. Dytnerskii. *Processes and apparatus of chemical technology*: Textbook for high schools / Ed. 2. In two books. P. 2. *Mass exchange processes and apparatus*). M.: "Himiya, 1995.

3. A.N. Nesmeyanov. *Davlenie par a khimicheskikh elementov*. M.: "Akad. Nauk SSSR", 1961 (in Russian).

4. V.A. Pazukhin, A.Ya. Fisher. *Razdelenie i rafinirovanie metallov v vakuume* M.: "Metallurgiya", 1969 (in Russian).

5. L.A. Nisel'son, A.G. Yaroshevski. *Mezhfazovye koeffitsienty raspredeleniya*. M.: "Nauka", 1992, 399 p. (in Russian).

6. B.S. Bokshtein, A.B. Yaroslavtsev. *Diffuziya atomov i ionov v tvyordykh telakh*. M.: MISiS, 2005 (in Russian).

7. Y.P. Kirillov, L.A. Kuznetsov, V.A. Shaposhnikov, M.F.Churbanov. Effect of diffusion on the purification of substances by distillation // *Inorganic materials*. 2015, v. 51, N 11, p. 1092-1097; DOI: 10.7868/S002337X15100088

8. A.I. Zhukov, A.I. Kravchenko. Calculation of sublimation with taking into account of diffusion of impurity // *Inorganic materials*. 2017, v. 53, N 6, p. 648-653; DOI: 10.1134/S0020168517060164

9. A.I. Zhukov, A.I. Kravchenko. Temperature dependence of the Peclet diffusion number in the processes of sublimation of some simple substances // *Inorganic materials.* 2021, v. 57, N 7, p. 753-759; DOI: 10.1134/S0020168521070104

10. A.I. Kravchenko, A.I. Zhukov, O.A. Datsenko. Temperature dependences of the Peclet number in sublimation processes of simple substances // *Problems of Atomic Science and Technology*. 2022, N 1, p. 13-16.

11. A.I. Kravchenko, A.I. Zhukov. Separation factors and Peclet numbers in evaporation refining of elemental substances near their melting point // *Inorganic materials.* 2022, v. 58, N 8, p. 860-865; DOI: 10.31857/S0002337X22080076

12. A.I. Zhukov, A.I. Kravchenko Calculation of impurity distribution in solidified condensate with taking into account of Peclet number // *Problems of Atomic Science and Technology.* 2024, N 1(149), p. 25-28.

13. A.I. Kravchenko, A.I. Zhukov. Influence of the evaporation temperature and degree of distillation on the effective separation factor // *Inorganic Materials,* 2023, v. 59, N 8, p. 883-888; DOI: 10.31857/S0002337X23080083

14. A.I. Kravchenko. Relationship between Effective and Ideal Separation Factors for Distillation and Sublimation // *Inorganic Materials*, 2016, v. 52, N 4, p. 378-385; DOI: 10.7868/S0002337X16040099

15. A.I. Kravchenko. Separation factors at sublimation refining of some lanthanides // *Problems of Atomic Science and Technology*. 2020, N 1, p. 35-37.

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ПРО ТЕОРІЮ ВИПАРНОГО РАФІНУВАННЯ

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Розглянуто теорію випарного рафінування, що враховує дифузію домішок. Відзначено концептуальний характер теорії внаслідок великої кількості параметрів, значення яких невідомі.