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Research Article

On Application of Burton-Prim-Slichter Equation in Calculations of Evaporation Refining

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Abstract: Using examples of substances with a simple base (Sb, Yb, Mg, Eu, Te, Zn, Cd, Be), the application of the Burton-Prim-Slichter equation is shown to assess the possibility of evaporative refining of substances by calculations at the values of the parameter δ/D, known from the study of crystallization (δ is the thickness of the surface layer in the evaporated material, *D* is the diffusion coefficient of the impurity). Calculations of β/β_0 were performed for the indicated substances at melting points. (β and β_0 are the effective and equilibrium separation coefficients.)

***Keywords*:** distillation; sublimation; separation factor; Burton-Prim-Slichter equation

1. Introduction

Distillation and sublimation are among the main methods for obtaining high-purity substances, and therefore there is interest in their theory [1–11]. In the general case, these processes are described by a system of equations with two parameters: with the equilibrium separation factor β_0 and with the Peclet number

$$Pe = vX/D,$$

where *v* is the linear velocity of the evaporation surface, *D* is the impurity diffusion coefficient, *X* is the dimensional factor of the evaporated material (for example, the initial thickness of the liquid layer in the crucible). Due to the complexity of the equations, their solutions cannot be obtained in an analytical form, but can be found by numerical methods [8-11]. At the same time, to describe distillation and sublimation, a simple equation is applicable with an effective separation factor β depending on the degree of distillation *g* [10, 11]:

$$\frac{C}{C_0} = \frac{1-(1-g)^{\beta}}{g},$$

where *C* is the average impurity concentration in the condensate, C_0 is the initial impurity concentration. (β is the ratio of the impurity concentration in the vapor leaving the evaporation surface to its concentration in the substance near the evaporation surface.)

The question of the ratio of β and β_0 in distillation and sublimation processes can be considered - similar to how the ratio between the effective and equilibrium distribution coefficients in crystallization processes is considered using the Burton-Prim-Slichter equation [12, 13]. It was noted that there are no fundamental prohibitions on using this equation, which was originally derived when considering crystallization, to consider distillation processes too, in the form

$$\beta = \frac{\beta_0}{\beta_0 + (1-\beta_0)\exp\left(-v\frac{\delta}{D}\right)}, \quad (1)$$

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where δ is the thickness of the near-surface layer with varying impurity concentration in the evaporated material. The similarity of the equations describing various mass transfer processes, including both crystallization and distillation, was noted [3, 8, 10].

However, there is a difficulty in using equation (1) in calculations of evaporation processes with an arbitrary temperature T. The difficulty is due to the fact that the values of δ and D are unknown at temperature T. Meanwhile, from the study of crystallization, it is known that at the melting point T_m of a substance $\delta/D \sim 10^2 - 10^3$ s/cm [10, 11]. At the same time, T_m is a special distillation and sublimation temperature.

The Burton-Prim-Slichter equation was used in calculations of evaporative refining at temperatures $T = T_m \pm 200$ K under the assumption of constant δ in the specified temperature range [10]. However, it was later found that this assumption is incorrect [14] in connection with which it is necessary to rethink the results of the work [10].

The aim of this work is to present the result of the correct application of Burton-Prim-Slichter equation to calculation of effective separation factor in processes of evaporation refining.

2. Performance of Calculations

The evaporation at T_m of substances with a simple base was considered, for which distillation and sublimation as refining processes have practical meaning [7].

Calculations were performed using equation (1) at δ/D = 100 s/cm and 1000 s/cm (as in crystallization processes). For simplicity of calculations, it was assumed that the material and the container have simple shapes for which $v = w/\rho$. The speed of evaporation w [g·cm^{-2}·s^{-1}] was calculated according to the Langmuir equation using the well-known formula for numerical calculations [5]

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

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.u.m. or g/mol].

Reference data on the pressure p of all substances were taken from monograph [6] (for Te, the peculiarity of this substance to evaporate in the form of Te_4 molecules was taken into account).

3. Results and Discussion

The results of calculations of β/β_0 at melting points and the indicated values of δ/D and $\beta_0 < 1$ are given in Table 1. It is noteworthy that in some cases β/β_0 strongly depends on the choice of the value of δ/D (100 or 1000 s/cm). Table 1, constructed using a simple equation (1), - without the use of complex calculations within the framework of the theory with β_0 and the Peclet number [9], - gives an idea of the possible values of β/β_0 for the particular case $T = T_m$ (when the temperatures of technological refining processes differ of these substances from T_m by about 100-200 K). The deviation of T from T_m is reflected in the value of β/β_0 due to the temperature dependences $v(T)$, $\delta(T)$, and $D(T)$ for the considered substance but accounting for these dependencies is not an easy task.

It is important to note that equation (1) describes the discrepancy β/β_0 as a consequence of the non-zero rate of the process in a container with an infinite volume, but does not take into account the fact that this discrepancy may be a consequence of the action of other factors, primarily a consequence of the dependence of β/β_0 on g in process in a container with a finite volume [14].

It is useful to note that the Burton-Prym-Slichter equation (1) can be reduced to a form that gives a better understanding of the relationship between β and β_0:

$$\beta^{-1} - 1 = (\beta_0^{-1} - 1)exp(-v\delta / D).$$

Table 1. Ratio β/β_0 for substances at melting points and different values of β_0 and δ/D

Sub-stance	T_m, K	p_m, mm Hg	M, a.u.m.	ρ, g·cm^{-3}	w, g·cm^{-2}·s^{-1}	v, cm/s	β/β_0 at δ/D = 100 s/cm and different β_0			β/β_0 at δ/D = 1000 s/cm and different β_0		
							β_0 = 0.1	β_0 = 0.01	β_0 = 0.001	β_0 = 0.1	β_0 = 0.01	β_0 = 0.001
Sm	1350	4.4	150	7.5	0.08	0.011	3	3	3	10	100	1000
Yb	1097	3.1	173	7.0	0.07	0.010	2	3	3	10	100	1000
Mg	923	2.8	24	1.7	0.03	0.018	4	6	6	10	100	1000
Eu	1099	1.1	152	5.2	0.02	0.004	1.4	1.5	1.5	9	36	53
Te	723	0.18	128 x 4	6.2	0.006	0.0009	1.1	1.1	1.1	1.1	1.1	1.1

Zn	693	0.15	65	7.1	0.003	0.0004	1.0	1.0	1.0	1.0	1.0	1.0
Cd	594	0.12	112	8.7	0.003	0.0004	1.0	1.0	1.0	1.0	1.0	1.0
Be	1551	0.032	9	1.8	0.00014	0.00008	1.0	1.0	1.0	1.1	1.1	1.1

4. Conclusions

Using the Burton-Prim-Slichter equation at values of the parameter δ/D characteristic of crystallization processes, the discrepancies between the effective (β) and equilibrium (β_0) separation factors in the evaporative refining processes of a number of substances "base-impurity" with a simple base (Sb, Yb, Mg, Eu, Te, Zn, Cd, Be) at melting points. In most examples, $\beta/\beta_0 \sim 1$; in some examples (at large values of δ/D) the discrepancy is large: $\beta/\beta_0 \sim 10\text{-}10^3$, with $\beta \approx 1$ (i.e., without purification of substance). Calculations of the value of β/β_0 at the melting point of the substance to be refined are useful as a simple preliminary assessment of the possibilities of refining.

The presented article is the result of a rethinking the work [10] taking into account subsequent research [14] – with clarification of the meaning of the separation coefficient used in the theory of evaporative refining [9, 10] and refusal to consider processes at $T \neq T_m$.

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