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EVALUATING THE EFFICIENCY OF EVAPORATIVE REFINING USING THE BURTON-PRIM-SLICHTER EQUATION

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The efficiency of distillation or sublimation is assessed by the value β/β_0, calculated at the melting temperature of the substance being refined using the Burton-Prim-Slichter equation (β and β_0 are effective and equilibrium separation factors). Examples of calculations are given for a number of substances with a simple base: Sb, Yb, Mg, Eu, Te, Zn, Cd, Be.

INTRODUCTION

Distillation and sublimation are among the main methods for obtaining high-purity substances, and therefore there is interest in their theory [1–15]. 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, 9]. 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 [13]:

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

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 [16–18]

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

where δ is the thickness of the near-surface layer with varying impurity concentration in the evaporated material. For a given β_0, the closer β/β_0 is to unity, the lower is the refining efficiency.

Equation (1) was derived by considering crystallization. Later it was noted that there are no fundamental prohibitions on using this equation in relation to distillation [3, 8, 12, 13]. In general, the similarity of equations describing various mass transfer processes was noted [3, 8, 9, 14].

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 value $\delta/D \sim 10^2 \ldots 10^3$ s/cm [1–4, 16–18]. At the same time, T_m is a common temperature for distillation and sublimation.

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 [12]. However, it was later found that this assumption is incorrect [13], in connection with which it is necessary to rethink the results of the work [12].

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

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 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 ($g \cdot cm^{-2} \cdot s^{-1}$) 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).

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. 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, 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 $T = T_m$ (while in the technological processes of refining these substances, T differs from T_m by 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 $D(T)$. It has been shown that with increasing temperature the value β/β_0 changes towards unity, however, the dependence of β/β_0 on temperature is not a simple task [13].

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 carried out in a container with a finite volume.

It is useful to note that the Burton-Prim-Slichter equation (1) can be reduced to a form that has a clearer physical meaning:

$$B = B_0 \exp(-v\frac{\delta}{D}),$$

where $B = \beta^{-1} - 1$ and $B_0 = \beta_0^{-1} - 1$.

β/β_0 for substances with known melting points T_m and various 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 various β_0			β/β_0 at δ/D = 1000 s/cm and various 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

CONCLUSIONS

The possibility of estimating the efficiency of evaporative refining is shown by calculating the value β/β_0 at the melting point of the refined substance with using the Burton-Prim-Slichter equation at values of parameter δ/D known from the study of crystallization processes. The calculations are performing without using the Peclet number (as in [8, 9]), the value of which for a particular substance "base – impurity" is usually unknown [15]. Examples are given of calculating β/β_0 for a number of substances "base–impurity" with a simple base (Sb, Yb, Mg, Eu, Te, Zn, Cd, Be) at $T = T_m$. In most examples $\beta \approx \beta_0$; in some examples (at large values of δ/D) $\beta \approx 1$ (i.e. the purification of substance is no). 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 [12] taking into account subsequent research of dependence $\beta(T, g)$ [13] – with clarification of the meaning of the separation coefficient used in the theory of evaporative refining [9, 12] and refusal to consider evaporative processes at $T \neq T_m$.

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ОЦІНКА ЕФЕКТИВНОСТІ ВИПАРНОГО РАФІНУВАННЯ ЗА ДОПОМОГОЮ РІВНЯННЯ БАРТОНА-ПРІМА-СЛІХТЕРА

О.І. Кравченко

Ефективність випарного рафінування (дистиляція або сублімація) оцінюється за величиною β/β_0, розрахованою за температури плавлення речовини, що рафінується, за допомогою рівняння Бартона-Прима-Сліхтера (β та β_0 – ефективний та рівноважний коефіцієнти поділу). Наведено приклади розрахунків для ряду речовин із простою основою: Sb, Yb, Mg, Eu, Te, Zn, Cd, Be.