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Research Article

On Parameters of Evaporation Refining

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Abstract: The previously presented 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) is analyzed. The complexity of the theory is noted: to calculate the refining efficiency depending on the yield at a given temperature, a large number of parameters (nine) 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 impurity diffusion activation energy in the refined substance Q, the impurity diffusion coefficient D_m at temperature T_m and the material size factor X. The conceptual character of the theory under consideration is noted due to the lack of knowledge of most of these parameters and the neglect of all process factors.

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

1. 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 [1–11].

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 initial thickness of the material layer in the crucible and the radius of the evaporated ball) [7–10]. The evaporation process is described by a system of equations, the solution of which can be found by numerical methods. This dependence and the distribution of impurities in the condensate during the condensation of steam into a solid phase is illustrated in Figure 1 [11, 12].

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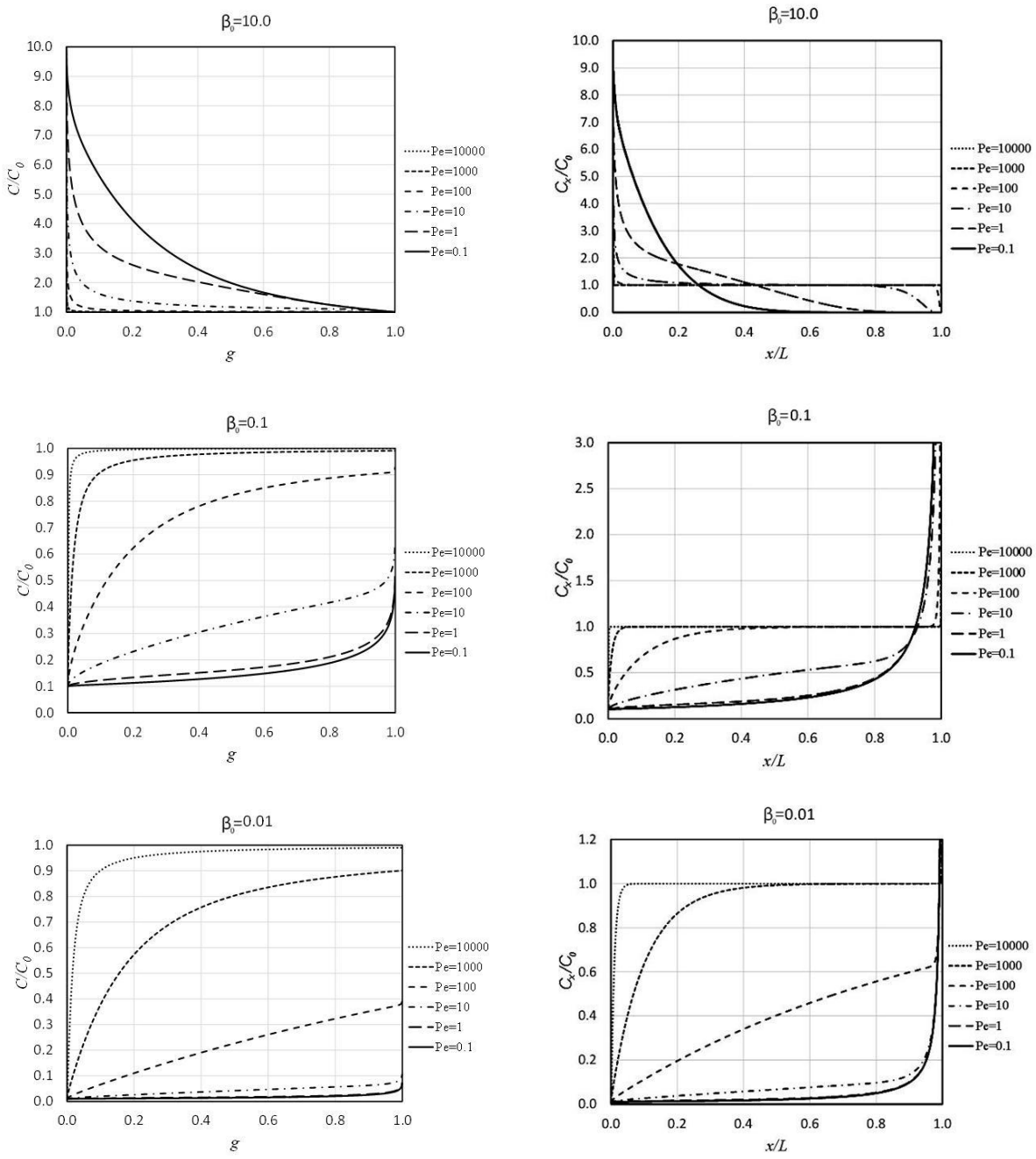

Figure 1. Dependence of the relative average concentration C/C_0 of an impurity in the condensate on the degree g of distillation of the material in the form of a flat layer during its one-sided evaporation in vacuum and dependence of C_x/C_0 on x/L in the condensate - at different values of the equilibrium separation factor β_0 and of the Peclet number (Pe). (C_0 is initial impurity concentration, C_x is the concentration of impurities in the condensate at a distance x from the substrate, L is the thickness of the condensate) [8, 11–13]

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 β(T) and β(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 (the speed of movement of the evaporation surface relative to the container), δ is the thickness of the boundary layer in a crystallizing or evaporating material near the interface (thickness of the layer in which a noticeable change in the composition of the evaporating liquid is observed, - 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 of β on 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.

Meanwhile, it is noteworthy that the parameters β and *Pe* are themselves determined by other parameters. The dependences of β and *Pe* on other parameters are the subject of consideration in this paper.

2. 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 β(T) and β(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 (the enhancement of convection is equivalent to an increase in the diffusion coefficient in the above equations), 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].

3. 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.

Conflict of interest

There is no conflict of interest for this study.

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