Effective and Ideal Separation Factors at Sublimation Refining of Sm, Eu, Tm, Yb

Kravchenko AI*

National Science Center "Kharkov Institute of Physics and Technology", Ukraine

Opinion

It is shown that the application of ideal separation factor in calculations of high-temperature sublimation refining of Sm, Eu, Tm and Yb has confined character: in considered base-impurity systems a difference between effective (β) and ideal (β_i) separation factors increases with deviation of β_i from unity and can be very significant; the measurable difference (in limited of a one order) between β and ideal β_i is observed at deviation of β_i from unity not more than 2 orders. The discrepancies between the effective and ideal separation factors in evaporative refining processes (distillation and sublimation at low impurity content) are not associated with the chemical interaction of the components.

Sublimation is one of the main methods for obtaining high-purity substances (as well as distillation and crystallization), in connection with which interest is shown in the theory of sublimation refining [1,2]. It was shown that high-temperature sublimation (at a temperature near the melting point) is described by the same simple equations as distillation.

One of the questions of the theory of distillation and sublimation is the question of the applicability of the ideal separation coefficient β_i in the calculations of these processes. The interest in using β_i in the calculations of distillation and sublimation refining of simple substances is related to the fact that β_i values are known for most binary systems in a wide temperature range - since vapor pressures of almost all chemical elements are known [1], while values of the effective separation coefficient β for real distillation or sublimation processes depend on many factors and cannot be calculated before the experiment ($\beta_i = p_i/p$, where p and p_i are the vapor pressure of the base and the impurity, respectively).

Using the basic equations of distillation, an analysis of the experimental data on the refining of a number of substances was carried out. A comparison was made between β and β_i in the refining of the base-impurity systems, in which Cd, Ga, Mn, Pb, S, Sb, Se, Te, Zn served as the basis for distillation (about 40 systems) and As, Cr, Mg, Mn for high-temperature sublimation (about 20 systems) [2]. It was shown that the applicability of β_i in the calculations of the distillation and sublimation refining of these systems is limited: the divergence of β and β_i increases with deviation of β_i from unity and can be quite significant; a moderate divergence of β and β_i (within the same order of magnitude) is observed when the values of β_i deviate from unity by no more than 3 orders of magnitude (in separate systems $\beta/\beta_i \sim 1$ and $\beta_i \sim 1$).

In pursuit of the fullness of knowledge about evaporative refining processes, attention was drawn to experimental data on the sublimation of Sm, Eu, Tm and Yb [3] - data that were not considered in a previous study [2]. The evaporation of these substances (with an initial impurity content of $\sim 10\text{-}5\text{-}10\text{-}2$wt%) was carried out at temperatures close to their melting points (melting points Sm, Eu, Tm, and Yb are 1350, 1099, 1818, and 1097K, respectively) . The purpose of this work was to study the ratio of the effective and ideal separation factors for the sublimation of lanthanides Sm, Eu, Tm and Yb and to determine the applicability of the ideal separation factor in the calculations of the sublimation refining of these substances.

According to the experimental data on the content of impurities in Sm, Eu, Tm and Yb during sublimation, the order of values of the effective separation coefficient β in various base-impurity systems was estimated. As in [2], only volatile impurities were considered. The

calculations took into account that for real distillation and high-temperature sublimation processes (with a degree of distillation usually not more than 90%) in the approximate calculations $\beta \sim C/C_0$, where C is the impurity concentration in the condensate, C_0 is the initial impurity concentration in the substance being refined [2]. To calculate β_i, we used data on the vapor pressure of pure components at the indicated temperatures [4]. The results of calculations of β and β_i are given in Table 1 (total - for 33 base-impurity systems).

Table 1: Separation factors at sublimation refining of Sm, Eu, Tm, Yb.

Impurity	β/β_i and β_i for Matters with Different Base							
	Sm		Eu		Tm		Yb	
	β/β_i	β_i	β/β_i	β_i	β/β_i	β_i	β/β_i	β_i
Ca	-	-	-	-	-	-	~1	0.2
Mn	~1	~10^{-2}	~10^3	~10^{-4}	~1	~10^{-1}	~10^4	~10^{-4}
Al	~10	~10^{-3}	~10^5	~10^{-5}	~10^2	~10^{-2}	~10^4	~10^{-5}
Ni	~10^2	~10^{-3}	~10^5	~10^{-5}	~10^2	~10^{-2}	~10^5	~10^{-5}
Cu	~10	~10^{-4}	~10^6	~10^{-6}	~10^3	~10^{-3}	~10^6	~10^{-6}
Co	~10^2	~10^{-4}	~10^6	~10^{-6}	~10^3	~10^{-3}	~10^6	~10^{-6}
Si	~10^3	~10^{-5}	~10^6	~10^{-7}	~10^4	~10^{-4}	~10^6	~10^{-7}
Fe	~10^3	~10^{-6}	~10^6	~10^{-8}	~10^5	~10^{-5}	~10^7	~10^{-8}
La	~10^5	~10^{-8}	-	-	~10^7	~10^{-7}	~10^{10}	~10^{-10}
Ta	>>10^{13}	<<10^{-13}	>>10^{13}	<<10^{-13}	>>10^{13}	<<10^{-13}	>>10^{13}	<<10^{-13}

As in [2], it is noteworthy that the content of impurities does not decrease by more than 3 orders of magnitude - even when $\beta_i \ll 1$ - and there is a relationship between β and β_i. In general, the data obtained supplement the data of work [2], and the conclusion that can be made about the ratio of β and β_i during sublimation of the considered systems does not contradict the conclusion of work [2] for distillation and sublimation.

It is important to note that, both during distillation and high-temperature sublimation (Table 1; [2]), β/β_i ratio depends on β_i, but does not depend on the nature of the components of the base-impurity system: the same β/β_i values are achieved in systems whose components are elements with different valences and are able to form chemical compounds with vapor pressure, significantly different from the vapor pressure of these elements. Therefore, the discrepancies between the effective and ideal separation coefficients in the evaporation refining processes (distillation and sublimation at low impurity content) are not due to chemical interaction of the components, but for other reasons (perhaps the entrapment of impurities by the main component vapor).

Conclusion

The applicability of the ideal separation ratio in the calculations of the high-temperature sublimation refining Sm, Eu, Tm and Yb is limited: in the considered base-impurity systems (with Ca, Mn, Al, Ni, Cu, Co, Si, Fe, La, Ta impurities) the divergence between the effective (β) and ideal (β_i) separation factors increases with deviation of β_i from unity and can be quite significant (by several orders of magnitude); a moderate divergence of β and β_i (within the same order of magnitude) is observed when the values of β_i deviate from unity by no more than 2 orders of magnitude.

The discrepancy between the effective and ideal separation coefficients in the evaporation refining processes (distillation and sublimation at low impurity content) is not due to chemical interaction of the components, but for other reasons (perhaps the entrapment of impurities by the main component vapor).

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