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SEPARATION FACTORS AT SUBLIMATION REFINING OF SOME LANTHANIDES

A.I. Kravchenko
National Science Center "Kharkov Institute of Physics and Technology", Kharkiv, Ukraine
E-mail: alex@krawa.net

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. This does not contradict the conclusion on separation factors at distillation and sublimation of other substances. 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]. In particular, 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 factor β_i in the calculations of these processes. While the values of the effective separation factor β for real evaporation processes depend on many factors and cannot be calculated before the experiment, in ideal model of distillation it is easy to establish that $\beta_i=p_i/p$, where p and p_i are the vapor pressure of the base and impurity, respectively. The values of β_i are known for most binary systems over a wide temperature range - since the vapor pressures of almost all chemical elements are known. The effective separation coefficient β can be found from the results of the refining process. As follows from the distillation equation, at not too large degree of distillation $\beta \sim C/C_0$, where C is the impurity concentration in the condensate, C_0 is the initial impurity concentration in the substance being refined [2].

An analysis of the experimental data on the refining of a number of substances was carried out. A comparison was made between β and βi 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 $\sim 10^{-5}\ldots10^{-2}$ wt.%) was carried out at temperatures close to their melting points (melting points Sm, Eu, Tm, and Yb are 1350, 1099, 1818, and 1097 K, 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 in comparison with the data on the distillation and sublimation of other 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 factor β in various base-impurity systems was estimated ($\beta \sim C/C_0$). To calculate of 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 (total – for 36 base-impurity systems).

The conclusion that can be made about the ratio of β and βi by sublimation of the substances considered (Table) does not contradict the conclusion of [2] for distillation and sublimation.

At the same time, comparison of β and βi during distillation and sublimation (Table and [2]) allows us to re-address the question of the reasons for the divergence of β and β_i. Two circumstances are noteworthy. Firstly, the content of impurities does not decrease by more than 3 orders of magnitude – even at $\beta_i \ll 1$. Secondly, systems for which $\beta \sim \beta_i \sim 0.1$ and $\beta_i \sim 1$ are formed by elements with different valencies capable of forming chemical compounds with a vapor pressure substantially different from the vapor pressure of these elements. So, according to the data of Table and the data of [2], $\beta \sim \beta_i \sim 0.1$ and $\beta_i \sim 1$ in the systems Yb(III)-Ca(II), Ga(III)-Cu(I), Ga(III)-Si(IV), Tm(III)-Mn(VII), Pb(IV)-Ag(I), Pb(IV)-In(III), Pb(IV)-Sb(V), As(V)-Na(I), As(V)-Mg(II), Se(VI)-Cd(II) Mn(VII)-Fe(VIII), the basic valency of the element is indicated in parentheses. These circumstances indicate that the discrepancies between the effective and ideal separation coefficients in high-temperature evaporative refining processes are explained not by the chemical interaction of the components, but by other factors (possibly, the capture of impurities by the vapor of the main component).

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	$\sim10^{-2}$	$\sim10^{3}$	$\sim10^{-4}$	~1	$\sim10^{-1}$	$\sim10^{4}$	$\sim10^{-4}$
Al	~10	$\sim10^{-3}$	$\sim10^{5}$	$\sim10^{-5}$	$\sim10^{2}$	$\sim10^{-2}$	$\sim10^{4}$	$\sim10^{-5}$
Ni	$\sim10^{2}$	$\sim10^{-3}$	$\sim10^{5}$	$\sim10^{-5}$	$\sim10^{2}$	$\sim10^{-2}$	$\sim10^{5}$	$\sim10^{-5}$
Cu	~10	$\sim10^{-4}$	$\sim10^{6}$	$\sim10^{-6}$	$\sim10^{3}$	$\sim10^{-3}$	$\sim10^{6}$	$\sim10^{-6}$
Co	$\sim10^{2}$	$\sim10^{-4}$	$\sim10^{6}$	$\sim10^{-6}$	$\sim10^{3}$	$\sim10^{-3}$	$\sim10^{6}$	$\sim10^{-6}$
Si	$\sim10^{3}$	$\sim10^{-5}$	$\sim10^{6}$	$\sim10^{-7}$	$\sim10^{4}$	$\sim10^{-4}$	$\sim10^{6}$	$\sim10^{-7}$
Fe	$\sim10^{3}$	$\sim10^{-6}$	$\sim10^{6}$	$\sim10^{-8}$	$\sim10^{5}$	$\sim10^{-5}$	$\sim10^{7}$	$\sim10^{-8}$
La	$\sim10^{5}$	$\sim10^{-8}$	-	-	$\sim10^{7}$	$\sim10^{-7}$	$\sim10^{10}$	$\sim10^{-10}$
Ta	$>>10^{13}$	$<<10^{-13}$	$>>10^{13}$	$<<10^{-13}$	$>>10^{13}$	$<<10^{-13}$	$>>10^{13}$	$<<10^{-13}$

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 (βi) 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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КОЭФФИЦИЕНТЫ РАЗДЕЛЕНИЯ ПРИ СУБЛИМАЦИОННОМ РАФИНИРОВАНИИ НЕКОТОРЫХ ЛАНТАНОИДОВ

А.И. Кравченко

Показано, что применимость идеального коэффициента разделения в расчетах высокотемпературного сублимационного рафинирования Sm, Eu, Tm и Yb имеет ограниченный характер: в рассмотренных системах основа–примесь расхождение эффективного (β) и идеального (β_i) коэффициентов разделения растет с отклонением β_i от единицы и может быть весьма значительным; умеренное расхождение β и β_i (в пределах одного порядка) наблюдается при отклонении значений β_i от единицы не более чем на два порядка. Это не противоречит заключению о коэффициентах разделения при дистилляции и сублимации других веществ. Расхождения между эффективным и идеальным коэффициентами разделения в испарительных процессах рафинирования (дистилляция и сублимация) при малом содержании примесей не связаны с химическим взаимодействием компонентов.

КОЕФІЦІЄНТИ РОЗПОДІЛУ ПРИ СУБЛІМАЦІЙНОМУ РАФІНУВАННІ ДЕЯКИХ ЛАНТАНОЇДІВ

О.І. Кравченко

Показано, що застосовність ідеального коефіцієнта розподілу в розрахунках сублімаційного рафінування Sm, Eu, Tm і Yb має обмежений характер: у розглянутих системах основа–домішка розбіжність ефективного (β) і ідеального (β_i) коефіцієнтів розподілу зростає з відхиленням β_i від одиниці і може бути вельми значним; помірна розбіжність β і β_i (у межах одного порядку) спостерігається при відхиленні значень β_i від одиниці не більше ніж на два порядки. Це не суперечить висновку про коефіцієнти розподілу при дистиляції і сублімації інших речовин. Розбіжності між ефективним і ідеальним коефіцієнтами розподілу у випарних процесах рафінування (дистиляція і сублімація) не пов'язані з хімічною взаємодією компонентів.