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TEMPERATURE DEPENDENCES OF THE PECLET NUMBER IN SUBLIMATION PROCESSES OF SIMPLE SUBSTANCES

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The results of calculating the Peclet number $Pe = wr/(\rho D)$ (where D is the diffusion coefficient; w is the evaporation rate of the substance; ρ is the density of the substance; r is the size factor) in sublimation processes of simple substances with high values of vapor pressure (≈ 1 mm Hg and above at the melting temperature): As, Gd, Tm, Lu, Cr, Yb, Sm, Mg, Ra, Ca, Sr, Ni, Co, Eu, Mn, Ba. It is shown that the nature of the temperature dependence $Pe(T)$ is determined by the properties of the components of the sublimated system “base–impurity” (including the diffusion activation energy Q of impurity). For each substance for given Q and r, the dependence $Pe(T)$ is monotonic. A decrease in the process temperature can improve the purification of a substance from one of several impurities, accompanied by deterioration in the purification from another impurity.

INTRODUCTION

Sublimation is one of the methods for obtaining a number of high-purity substances, in connection with which there is an interest to the theory and practice of the method [1–9]. The advantage of the method over crystallization and distillation refining is the lower temperature of its implementation and, as a result, less contamination of the product by the container material. In this case, a special role in this method is played by the diffusion of impurities in the refined material.

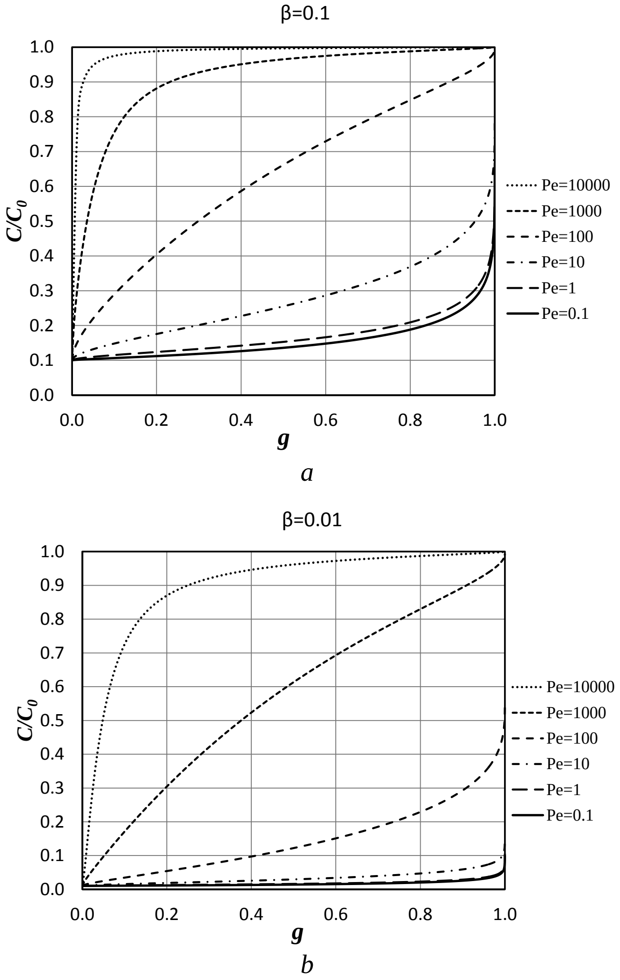
A method was developed for calculating the sublimation refining of a substance, taking into account the diffusion of impurities, in which the efficiency of the process with yield g is determined by two parameters (that depend on the temperature T): the separation coefficient $\beta(T)$ and the diffusion Peclet number

$$Pe(T) = \frac{w(T)r}{\rho D(T)}, \qquad (1)$$

where D is the diffusion coefficient; w is the rate of evaporation of the substance from a unit surface; ρ is the density of the substance; r is the dimensional factor of the material (for example, the initial radius of the evaporating sphere) – Figure [10]. The cleaning efficiency of the substance increases with a decrease in the Pe number. (For the same substance and at the same sublimation temperature, $Pe \sim r$). At $Pe = 0$, the C/C_0 dependence has the form of a distillation equation with ideal mixing of the evaporated liquid [10]:

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

Also, a technique was developed for calculating the temperature dependence of $Pe(T)$ and examples of calculating $Pe(T)$ for some simple substances (Mg, Cr, Sm, Eu) in small temperature ranges near the melting point T_m are given [11].



Dependence of C/C_0 on the product (condensate) from yield g at different values of the Pe number and β:
a – β = 0.1; b – β = 0.01 [10].
(C/C_0 is the ratio of the average impurity concentration in the condensate to the initial impurity concentration)

Numerical determination of Pe values at temperature T for a material in the form of a ball with an initial radius r, cm was carried out according to the formula:

$$Pe(T) = \frac{0.058\,p\left(\dfrac{M}{T}\right)^{1/2} r}{\rho D^* \exp\left[\dfrac{Q}{R}\left(\dfrac{1}{T_m} - \dfrac{1}{T}\right)\right]}, \qquad (2)$$

where T is process temperature, K; T_m is the melting point of the substance, K; p is the vapor pressure of the substance, mm Hg, at temperature T; M is the atomic mass of the substance, at. mass unit; ρ is the density of the substance, g/cm^3; Q/R is the ratio of the activation energy of impurity diffusion to the universal gas constant, K (for most impurities in simple substances, the Q/R values are in the range from $0.5 \cdot 10^4$ to $3 \cdot 10^4$ K [11]); D^* is the diffusion coefficient, cm^2/s, of the impurity in the sublimated substance at temperature T_m. (For most impurities in simple substances at a temperature near T_m, the diffusion coefficient of an impurity in a liquid is $D_m \sim 10^{-5}$ cm^2/s, and in a solid $D^* \sim 10^{-6}$ cm^2/s [11]).

Meanwhile, it is of interest to examine in more detail the temperature dependences of $Pe(T)$: for a larger number of substances (allowing sublimation refining for practical purposes) and in an extended temperature range – to reveal patterns. This was the purpose of the work.

PERFORMANCE OF CALCULATIONS

The Peclet number in the processes of sublimation refining of simple substances with a vapor pressure of ≈ 1 mm Hg and above at the melting temperature T_m (i.e., substances were considered, the sublimation of which can be carried out at a sufficiently high rate) was calculated. The temperatures at which the vapor pressure of the substance is greater than 0.001 mm Hg (when a practical interest in the process remains) were considered. The calculation of the Pe number in a solid at a temperature near T_m (at which the diffusion coefficient is D^* and the order of its value is known) was carried out using formula (1). To calculate Pe at lower temperatures, formula (2) was used. The data on the vapor pressure of substances at temperature T were found from the monograph by Nesmeyanov [12]. For comparability of the results, the calculations were carried out at $r = 1$ cm, and the results were denoted as Pe_1. As in [11], the calculations were carried out at a value of $D^* = 5 \cdot 10^{-6}$ cm^2/s and three values of the activation energy of impurity diffusion. A computer program was used to perform the calculations.

RESULTS AND DISCUSSION

The calculation results are presented in Tables 1–3 (for arsenic, it is taken into account that its vapor consists mainly of As_4 molecules; for comparison, Table 1 shows the calculated Pe_1 values for some substances with low vapor pressure and for two complex substances: for ice [13] and naphthalene [14]). The data in Tables 1 and 2 can be compared with the graphs in Figure.

At a temperature near T_m, for substances with a $p \approx 1$ mm Hg and higher, $Pe_1 \sim 10^2 \ldots 10^8$ and for substances with a low p, $Pe_1 \approx 0$ (see Table 1).

As can be seen from the Table 2, the nature of the temperature dependence $Pe_1(T)$ is determined by the nature of the components of the sublimated system “base–impurity”. In each considered system “base–impurity” at a given value of Q/R, the dependence $Pe_1(T)$ is monotonic.

Table 1

Pe_1 for substances in the solid phase at a temperature near T_m ($D = D^* \sim 10^{-6}$ cm^2/s)

Substance	T_m, K	p, mm Hg	Pe_1
As	1090	$\sim 10^5$	$\sim 10^8$
Gd	1586	189	$\sim 10^5$
Tm	1818	180	$\sim 10^5$
Lu	1936	19.1	$\sim 10^3$
Cr	2130	7.7	$\sim 10^3$
Sm	1350	4.4	$\sim 10^3$
Yb	1097	3.1	$\sim 10^3$
Mg	923	2.8	$\sim 10^4$
Ra	1233	2.5	$\sim 10^4$
Ca	1112	2.0	$\sim 10^4$
Sr	1042	1.9	$\sim 10^4$
Ni	1726	1.8	$\sim 10^2$
Co	1768	1.4	$\sim 10^2$
Eu	1099	1.1	$\sim 10^4$
Mn	1517	0.9	$\sim 10^2$
Ba	1002	0.8	$\sim 10^3$
Fe	1812	$\sim 10^{-2}$	~ 1
Cu	1357	$\sim 10^{-4}$	$\sim 10^{-2}$
Al	934	$\sim 10^{-9}$	$\sim 10^{-6}$
In	430	$\sim 10^{-19}$	$\sim 10^{-17}$
Ga	303	$\sim 10^{-38}$	$\sim 10^{-34}$
$C_{10}H_8$	353	8	$\sim 10^4$
H_2O	273	5	$\sim 10^4$

Table 2

Dependence $Pe_1(T)$ for various substances and impurities with different values of the diffusion activation energy (T_m, K, of the substance is indicated near the chemical symbols)

Sub-stance	T, K	p, mm Hg	Pe_1 at different values of Q/R		
			$1\cdot10^4$ K	$2\cdot10^4$ K	$3\cdot10^4$ K
As 1090	600	0.15	$\sim10^5$	$\sim10^8$	$\sim10^{12}$
	700	7.3	$\sim10^6$	$\sim10^8$	$\sim10^{10}$
	800	121	$\sim10^6$	$\sim10^8$	$\sim10^9$
	900	$\sim10^3$	$\sim10^6$	$\sim10^7$	$\sim10^8$
	1000	$\sim10^4$	$\sim10^7$	$\sim10^7$	$\sim10^8$
Gd 1586	1000	0.01	328	$1\cdot10^4$	$5\cdot10^5$
	1200	1	$4\cdot10^3$	$3\cdot10^4$	$2\cdot10^5$
	1300	5	$1\cdot10^4$	$4\cdot10^4$	$2\cdot10^5$
	1400	20	$2\cdot10^4$	$5\cdot10^4$	$1\cdot10^5$
	1500	67	$5\cdot10^4$	$7\cdot10^4$	$9\cdot10^4$
Tm 1818	1100	$\sim10^{-3}$	102	$4\cdot10^3$	$1.4\cdot10^5$
	1200	0.05	414	$7\cdot10^3$	$1.2\cdot10^5$
	1300	0.3	$1\cdot10^3$	$1\cdot10^4$	$1.1\cdot10^5$
	1400	2	$4\cdot10^3$	$2\cdot10^4$	$1.0\cdot10^5$
	1500	6	$9\cdot10^3$	$3\cdot10^4$	$9\cdot10^4$
	1600	21	$2\cdot10^4$	$4\cdot10^4$	$8\cdot10^4$
	1700	62	$4\cdot10^4$	$5\cdot10^4$	$8\cdot10^4$
	1800	180	$7\cdot10^4$	$8\cdot10^4$	$8\cdot10^4$
Lu 1936	1400	$\sim10^{-3}$	18	131	947
	1500	0.04	73	326	$1.5\cdot10^3$
	1600	0.2	232	685	$2.0\cdot10^3$
	1700	0.7	545	$1\cdot10^3$	$2.3\cdot10^3$
	1800	2	$1\cdot10^3$	$2\cdot10^3$	$2.9\cdot10^3$
	1900	7	$3\cdot10^3$	$3\cdot10^3$	$4\cdot10^3$
Cr 2130	1600	$\sim10^{-3}$	9	33	154
	1700	0.03	28	91	298
	1800	0.1	65	153	362
	1900	0.4	188	332	587
	2000	1	458	622	844
Sm 1350	1000	$\sim10^{-3}$	78	$1\cdot10^3$	$1\cdot10^4$
	1100	0.09	289	$2\cdot10^3$	$8\cdot10^3$
	1200	0.9	$1\cdot10^3$	$3\cdot10^3$	$8\cdot10^3$
	1300	3	$2\cdot10^3$	$3\cdot10^3$	$4\cdot10^3$
Yb 1097	800	$\sim10^{-3}$	91	$2.7\cdot10^3$	$8\cdot10^4$
	900	0.06	321	$2.4\cdot10^3$	$2\cdot10^4$
	1000	0.5	834	$2.0\cdot10^3$	$5\cdot10^3$
Mg 923	700	$\sim10^{-3}$	281	$9\cdot10^3$	$8\cdot10^5$
	800	0.2	$1\cdot10^3$	$7\cdot10^3$	$4\cdot10^4$
	900	1.7	$3\cdot10^3$	$3\cdot10^3$	$4\cdot10^3$
Ra 1233	800	$\sim10^{-3}$	442	$4\cdot10^4$	$9\cdot10^6$
	900	0.05	$1\cdot10^3$	$3\cdot10^4$	$5\cdot10^5$
	1000	0.4	$3\cdot10^3$	$2\cdot10^4$	$1\cdot10^5$
	1100	2	$6\cdot10^3$	$2\cdot10^4$	$4\cdot10^4$
	1200	7	$1\cdot10^4$	$1\cdot10^4$	$2\cdot10^4$
Ca 1112	800	$\sim10^{-3}$	56	$2\cdot10^3$	$6\cdot10^4$
	900	0.01	131	$1\cdot10^3$	$9\cdot10^3$
	1000	0.1	410	$1\cdot10^3$	$3\cdot10^3$
	1100	6	$9\cdot10^3$	$1\cdot10^4$	$1\cdot10^4$
Sr 1042	800	$\sim10^{-3}$	224	$4\cdot10^3$	$7\cdot10^4$
	900	0.1	658	$3\cdot10^3$	$1\cdot10^4$
	1000	0.9	$2\cdot10^3$	$3\cdot10^3$	$4\cdot10^3$
Ni 1726	1300	$\sim10^{-3}$	4	25	165
	1400	$9\cdot10^{-3}$	9	36	138
	1500	0.06	37	89	213
	1600	0.3	118	187	295
	1700	1.3	345	377	412
Co 1768	1300	$\sim10^{-3}$	4	33	250
	1400	$9\cdot10^{-3}$	11	47	208
	1500	0.02	43	117	322
	1600	0.1	136	246	446
	1700	0.7	396	496	622
Eu 1099	900	0.02	137	$1\cdot10^3$	$8\cdot10^3$
	1000	0.2	428	$1\cdot10^3$	$3\cdot10^3$
Mn 1517	1200	$\sim10^{-3}$	8	44	254
	1300	0.03	30	89	267
	1400	0.2	110	190	330
	1500	0.8	264	284	306
Ba 1002	900	0.01	40	124	385
	1000	0.1	125	128	130

Table 3

Comparison of $Pe_1(0.5T_\mathrm{m})$ and $Pe_1(T_\mathrm{m})$ at different values of the activation energy of impurity diffusion

Sub-stance	$\approx T_m$	$\approx 0.5T_m$	$Pe_1(0.5T_\mathrm{m})/Pe_1(T_\mathrm{m})$ at different values of Q/R		
			$1\cdot10^4$ K	$2\cdot10^4$ K	$3\cdot10^4$ K
As	1000	600	$\sim10^{-2}$	~10	$\sim10^4$
Gd	1500	800	$\sim10^{-3}$	~1	~10
Tm	1800	900	$\sim10^{-4}$	$\sim10^{-3}$	~1
Lu	1900	1000	$\sim10^{-6}$	$\sim10^{-4}$	~0.1
Cr	2000	1000	$\sim10^{-7}$	$\sim10^{-5}$	$\sim10^{-4}$
Sm	1300	700	$\sim10^{-5}$	~0.1	$\sim10^2$
Yb	1000	700	$\sim10^{-2}$	~1	$\sim10^2$
Mg	900	500	$\sim10^{-3}$	~10	$\sim10^5$
Ra	1200	600	$\sim10^{-4}$	~1	~10
Ca	1100	600	$\sim10^{-4}$	~0.1	$\sim10^3$
Sr	1000	500	$\sim10^{-4}$	~1	$\sim10^4$
Ni	1700	900	$\sim10^{-7}$	$\sim10^{-5}$	$\sim10^{-3}$
Co	1700	900	$\sim10^{-7}$	$\sim10^{-5}$	$\sim10^{-3}$
Eu	1000	600	$\sim10^{-3}$	~0.1	$\sim10^2$
Mn	1500	800	$\sim10^{-6}$	$\sim10^{-4}$	~0.1
Ba	1000	500	$\sim10^{-5}$	~0.1	$\sim10^4$

CONCLUSIONS

The Peclet number (*Pe*) was considered as one of the two main parameters of sublimation refining (the purification efficiency increases with a decrease in the Peclet number). At various values of the process temperature and the activation energy of the impurity diffusion, the Peclet numbers were calculated for a number of simple substances with high vapor pressures (≈ 1 mm Hg and higher at the melting point of the substance): As, Gd, Tm, Lu, Cr, Yb, Sm, Mg, Ra, Ca, Sr, Ni, Co, Eu, Mn, Ba. For comparability of the results, the calculations were performed for a material in the form of a ball with a unit initial value of the radius at a given value of the diffusion coefficient of an impurity in a solid near the melting point $D^* = 5\cdot10^{-6}$ cm^2/s. It was found that the nature of the $Pe_1(T)$ dependence is determined by the properties of the components of the “base–impurity” system (including the activation energy of impurity diffusion): a decrease in the process temperature can improve the purification of a substance from one of several impurities, accompanied by a deterioration in the purification from another impurity.

A simple possibility of estimating the Peclet number for materials in the solid phase at a temperature near the melting point when $Pe = wr/(\rho D^*)$ is noted – Table 1.

In the general case, to clarify the dependence of C/C_0 from T in the sublimation process with given g, it is necessary to take into account both $\beta(T)$ and $Pe(T)$.

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ТЕМПЕРАТУРНЫЕ ЗАВИСИМОСТИ ЧИСЛА ПЕКЛЕ В СУБЛИМАЦИОННЫХ ПРОЦЕССАХ РАФИНИРОВАНИЯ ПРОСТЫХ ВЕЩЕСТВ

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Представлены результаты вычислений числа Пекле $Pe = wr/(\rho D)$ (где D – коэффициент диффузии; w – скорость испарения вещества; ρ – плотность вещества; r – размерный фактор) в процессах сублимации простых веществ с высокими значениями давления пара (≈ 1 мм рт. ст. и выше при температуре плавления): As, Gd, Tm, Lu, Cr, Yb, Sm, Mg, Ra, Ca, Sr, Ni, Co, Eu, Mn, Ba. Показано, что характер температурной зависимости $Pe(T)$ определяется свойствами компонентов сублимируемой системы «основа–примесь» (включая энергию активации диффузии Q примеси). Для каждого вещества при заданных Q и r зависимость $Pe(T)$ монотонна. Снижение температуры процесса может улучшать очистку вещества от одной из нескольких примесей, сопровождаясь ухудшением очистки от другой примеси.

ТЕМПЕРАТУРНІ ЗАЛЕЖНОСТІ ЧИСЛА ПЕКЛЕ В СУБЛІМАЦІЙНИХ ПРОЦЕСАХ РАФІНУВАННЯ ПРОСТИХ РЕЧОВИН

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Представлено результати обчислень числа Пекле $Pe = wr/(\rho D)$ (де D – коефіцієнт дифузії; w – швидкість випаровування речовини; ρ – щільність речовини; r – розмірний фактор) у процесах сублімації простих речовин з високими значеннями тиску пари (≈ 1 мм рт. ст. і вище при температурі плавлення): As, Gd, Tm, Lu, Cr, Yb, Sm, Mg, Ra, Ca, Sr, Ni, Co, Eu, Mn, Ba. Показано, що характер температурної залежності $Pe(T)$ визначається властивостями компонентів системи «основа–домішка» (включаючи енергію активації дифузії Q домішки). Для кожної речовини при заданих Q і r залежність $Pe(T)$ монотонна. Зниження температури процесу може покращувати очищення речовини від однієї з кількох домішок, супроводжуючись погіршенням очищення від іншої домішки.