THERMODIFFUSION IN LIQUID AND GASEOUS MULTICOMPONENT ISOTOPE MIXTURES

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The thermodiffusion process in isotopic mixtures of titanium, tin, and carbon tetrachloride has been studied experimentally. The results are analyzed here.

The idea of using a Clusius–Dickel thermodiffusion apparatus for separating the isotopes of a certain element in the liquid state was disclosed by those authors as early as in 1939 [1]. The very few subsequent experimental studies [2-5] with binary isotope mixtures have revealed that the magnitude of the thermodiffusion constant is noticeably higher than when the same mixtures are in the gaseous state. In view of this, according to [5, 6], thermodiffusion in the liquid state may be treated as a technological variant of the isotope concentration process applicable to various chemical elements.

Unfortunately, it has not been possible to calculate the thermodiffusion constant of liquid isotope mixtures on the basis of liquid-state theory, as it could be done in the case of gaseous mixture on the basis of the molecular-kinetic theory. Some results derived in [7, 8] from the thermodynamics of irreversible processes and from statistical mechanics have yielded a relation between the thermodiffusion constant and those characteristics of a binary mixture about which there are no reliable test data available yet (heat of evaporation of pure isotope components, heat of component evaporation from a solution, radial distribution function, etc.).

Since the thermodiffusion constant is a quantitative measure of the isotope effect involving the difference between the molecular masses of the components, hence obviously

$$\alpha=f(M_1,\ M_2) \tag{1}$$

for a binary mixture.

When the difference between the masses is small relative to the nominal mass of a molecule, i.e., when $M_2-M_1 \ll M_1$, then the right-hand side of (1) can be expanded into a Taylor series with respect to the small parameter M_2-M_1. The first term of the series is $f(M_1, M_1) = 0$ and, if only the second term is retained, the thermodiffusion constant and the mass difference should be related linearly. Thus, for example, the molecular-kinetic theory [12] yields for gases

$$\alpha_G= A_G\,\frac{M_2-M_1}{M_2+M_1}\,, \tag{2}$$

with A_G denoting a coefficient which accounts for the character of intermolecular forces, which indicates that the said relation is, indeed, linear.

Relation (2) is in complete agreement with test data.

Based on the kinetic theory of liquids, K. Wirtz in [9] has shown that for liquid binary isotope mixtures

$$\alpha_L=A_L\left(\sqrt{\frac{M_2}{M_1}}-1\right), \tag{3}$$

with A_L denoting a coefficient which accounts for the character of intermolecular forces but, because not enough is known about the coefficient A_L, this relation has not been confirmed experimentally.

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TABLE 1. Isotope Content of Titanium Tetrachloride Samples (%)

Top of column					Bottom of column				
Masses									
46	47	48	49	50	46	47	48	49	50
Steady state (22 h)									
8,66	7,84	73,05	5,4	5,05	7,3	7,04	73,7	5,91	6,05
Sample after 5.5 h									
8,50	7,78	73,02	5,5	5,2	7,65	7,28	73,27	5,9	5,9

When $M_2/M_1 - 1 \ll 1$, then formula (3) can be rewritten as

$$\alpha_L = A'_L(M_2 - M_1). \tag{4}$$

No theoretical formula is available for calculating the thermodiffusion constant in the case of multicomponent liquid isotope mixtures.

We assume in this case that, by analogy to (4), the same relation

$$\alpha_{ij} = A(M_i - M_j), \tag{5}$$

applies which E. Schumacher [10] has used for analyzing thermodiffusion in multicomponent gaseous isotope mixtures. Unlike (4), formula (5) can be verified experimentally even when no data on the coefficient A are available.

Using for this purpose convection free test cells is not feasible here, because slight shifts in concentration due to an elemental separation in such an apparatus cannot be recorded accurately enough by modern methods of mass-spectrometry.

Thermodiffusion columns, where the elemental effect is highly amplified, offer unquestionable advantages in this regard.

It has been shown in [10] that, when condition (5) is satisfied in a thermodiffusion column,

$$\ln q_{ij} \equiv \ln \frac{c_{iL} c_{j0}}{c_{i0} c_{jL}} = B' \alpha_{ij}, \tag{6}$$

with B' denoting a coefficient which accounts for the column geometry, for the physical characteristics of the mixture to be partitioned, and for the test temperatures.

A comparison of (5) and (6) yields

$$\ln q_{ij} = B''(M_i - M_j). \tag{7}$$

It must be emphasized that (6) corresponds to a steady state in a thermodiffusion column without reservoirs of finite volume at its ends.

Relation (7) was verified experimentally on carbon, titanium, and tin tetrachloride.

Titanium has five stable isotopes, tin has ten, carbon and chlorine have two each.

The tests were performed in a cylindrical thermodiffusion apparatus closed on both ends. The design parameters of the column were as follows: $L = 0.35$ m, $\delta = 2.5 \cdot 10^{-4}$ m, $B = 0.105$ m. The inner cylinder was heated with vapor, the outer cylinder was cooled with running water. The temperature of the inside surface of the outer cylinder was checked with thermocouples and maintained at $T_2 = 308$°K. The

TABLE 2. Isotope Content of Tin Tetrachloride Samples (%)

Masses		112	114	115	116	117	118	119	120	122	124
Steady state (24 h)	top	1,06	0,76	0,43	14,6	7,57	24,4	8,42	32,62	4,52	5,62
	bottom	0,96	0,71	0,41	14,03	7,30	24,14	8,43	33,21	4,76	6,05
Sample after 11 h	top	1,04	0,73	0,41	14,61	7,61	24,34	8,44	32,64	4,50	5,68
	bottom	0,96	0,69	0,39	14,10	7,33	24,05	8,55	33,15	4,70	6,08

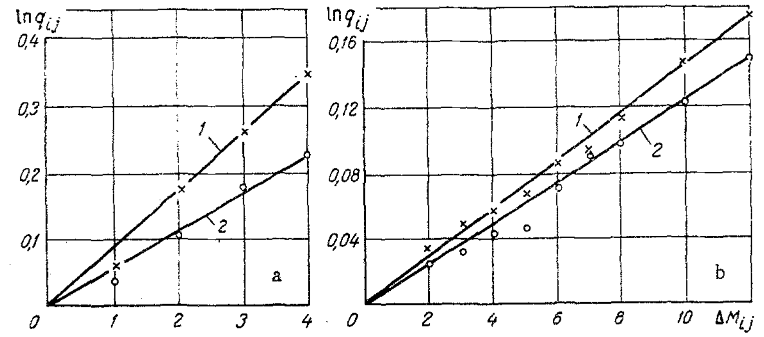

Fig. 1. Logarithm of the isotopes separation factor: (a) for titanium with masses $M_i = 47, 48, 49, 50$ and isotope with mass 46, as a function of the mass difference $\Delta M_{ij} = M_i - 46$; (b) for tin with masses $M_i = 114, 115, 116, 117, 118, 119, 120, 122, 124$ and isotope with mass 112, as a function of the mass difference $\Delta M_{ij} = M_i - 112$. 1) Steady state; 2) after 11 h.

temperature of the outside surface of the inner cylinder in the $TiCl_4$ test and in the $SnCl_4$ test was $T_1 = 380°K$, as calculated from the known saturated-vapor pressure and quantity of heat passing through the gap. On account of the tendency of $TiCl_4$ and $SnCl_4$ to interact with the air moisture, the column was filled with these substances under all necessary precautions. Samples for analysis were taken off the top and the bottom. The volume of each sample was approximately 0.02 ml. A total number of 4-6 samples was taken from both ends till steady state was reached, i.e., the total volume sampled from the column did not exceed 0.1 ml. Theoretically, formula (6) derived for a column operation without sampling would not be applicable here. According to estimates of the sample volume in dimensionless variables, however, under our specific test conditions the effect of the said sample volume was well within the limits of the measurement error. The isotopic content of samples was determined by mass-spectrometry with a model MKh-1303 instrument: measuring the atomic peaks of the respective elements in $TiCl_4$ and $SnCl_4$ analyses, and measuring the splinter CCl_3^+ and CCl^+ ions in the CCl_4 analyses (determination of the chlorine isotope content).

The results of titanium and tin measurements are given in Tables 1 and 2. These data have been evaluated in terms of relation (7) and, as can be seen in Fig. 1, they fit this relation closely enough.* Therefore, the direct proportionality between the thermodiffusion constant and the mass difference in multicomponent liquid isotope according to (5) is thus confirmed. The CCl_4 tests have shown that the splinter ions CCl_3^+ appearing in the mass-spectrometer are as subject to relation (7) as is also the separation of $C^{12}Cl^{35}_{n-1}Cl^{37}_{5-n}$ molecules.

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*The excursion of points $\Delta M = 1$ in Fig. 1a and $\Delta M = 5$ in Fig. 1b was due to a systematic error in the determination of rare isotopes.

TABLE 3. Percent Content of $C^{12}Cl^{35}_{m-1}Cl^{37}_{4-m}$ Masses after Thermodiffusive Partition of CCl_4, According to the Data of Mass-Spectrometric Analysis (Steady state), and of $C^{12}Cl^{35}_{n-1}Cl^{37}_{5-n}$ Masses*

	$C^{12}Cl^{35}_{m-1}Cl^{37}_{4-m}$				$C^{12}Cl^{35}_{n-1}Cl^{37}_{5-n}$				
Masses	117	119	121	123	152	154	156	158	160
Top of column	45,94	40,83	12,02	1,21	35,47	41,97	18,62	3,67	0,27
Bottom of column	41,37	42,61	14,36	1,66	30,84	42,18	21,63	4,93	0,42

*Percent content of these masses according to the formula

$$x_n = 100\ C_4^{5-n}\left(y_{Cl^{35}}\right)^{5-n}\left(1-y_{Cl^{35}}\right)^{n-1},$$

where C_4^{5-n} denotes the combinations of four elements of $(5-n)$ $(n = 1,2,3,4,5)$ and $y_{Cl^{35}}$ denotes the concentration of Cl^{35} determined from an analysis of $C^{12}Cl^{35}_{m-1}Cl^{37}_{4-m}$ $(m = 1,2,3,4)$ splinter groups.

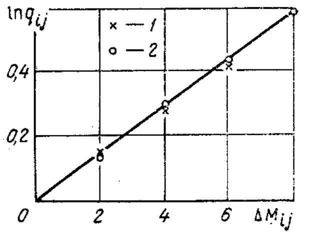

Fig. 2

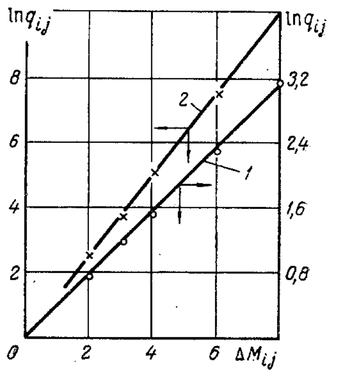

Fig. 3

Fig. 2. Logarithm of the separation factor during steady state conditions: 1) between masses $M_i = C^{12}Cl^{35}_{m-1}Cl^{37}_{4-m}$ (m = 2, 3, 4) and mass 117, as a function of the mass difference $\Delta M_{ij} = M_i - 117$; 2) between masses $M_i = C^{12}Cl^{35}_{n-1}$-$Cl^{37}_{5-n}$ (n = 2, 3, 4, 5) and mass 152, as a function of the mass difference $\Delta M_{ij} = M_i - 152$.

Fig. 3. Logarithm of the separation factor, during steady state conditions, between the krypton isotope with mass 86 and masses M_j = 84, 83, 82, 80, 78, as a function of the mass difference $\Delta M_{ij} = 86 - M_j$, in a column with reservoirs at the ends. Calculations by the authors based on the test results in [11, 12] and according to (8): 1) V_0 = 2.4 liters, V_L = 2.5 liters, and $y^* = 0.4$; 2) $V_0 = V_L$ = 0.25 liters and $y^* = 1.25$.

These results are shown in Table 3 and in Fig. 2. In this way, during thermodiffusive separation, each of the $C^{12}Cl^{35}_{n-1}Cl^{37}_{5-n}$ masses behaves like an isotope of a fictitious element of mass 162 − 2n (n = 1, 2, 3, 4, 5).

When the test data are evaluated in the form

$$\ln q_{ij} = A' \frac{M_i - M_j}{M_i + M_j} \qquad (8)$$

the logarithm of the separation factor remains almost a linear function of the relative mass difference, because the small variation of the denominator in (18) has made it impossible to ascertain its effect.

We must further note, in conclusion, that relation (7) is very general and applies not only to the steady state in a thermodiffusion column with both ends closed but also to the transient state and to thermodiffusion columns with reservoirs at the ends.

According to Fig. 1a, b, the linearity of Eq. (7) is fully retained during a transient. This does not agree with the theoretical conclusions in [13], where the author analyzes the transient process of separation in thermodiffusion columns and concludes that, for example, in a ternary mixture of components differing by a unit of mass the relation between separation factors q_{12} and q_{13} should be $2C \ln q_{12} = \ln q_{13}$ with $C < 1$. According to our experiments $C = 1$ at any instant of time. As to the apparatus with reservoirs at the ends, we have used data from tests with krypton [11]. We have evaluated those data according to relation (7) and the results shown in Fig. 3 convincingly confirm the validity of this formula. We will only note that the separation factor for isotopes Kr^{86}–Kr^{78} has not been plotted with curve 2 because of the poor accuracy of the Kr^{78} concentration measurement at the bottom of the column. Based on the linear relation in Fig. 1b, the concentration of the krypton Kr^{78} isotope in this experiment should have been equal to $7 \cdot 10^{-4}\%$ rather than the 0.01% indicated in [11].

Thus, relation (7) represents a rather general process characteristic of separating isotopes from a multicomponent mixture under conditions of a temperature gradient, and it can be stated in terms of the following rule: in a multicomponent isotope mixture under conditions of a temperature gradient, the logarithm of the separation factor for each pair of components is directly proportional to the respective mass difference.

This rule leads to the following practical conclusions. First of all, with the aid of this rule, it is possible to determine all separation factors from test data on the separation of two isotopes, which is especially important when one component exists in such small quantities as to make it very difficult to determine the change in its isotope content. Secondly, on the basis of data on the separation kinetics involving two components, it is possible to calculate the transients for all other components.

NOTATION

α_{ij}	is the thermodiffusion constant involving components i and j;
M_i	is the mass of i-th component;
q_{ij}	see relation (6);
V	is the volume of reservoir;
L	is the length of column;
$y^* = H^*L/K$;	
H^*	is the referred coefficient in the transfer equation for a multicomponent mixture;
K	is the transfer coefficient.

Subscripts

0, L	refer to the respective column ends;
i, j	refer to the components of the mixture.

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