REDUCED VALUE OF THERMODYNAMIC CONSTANTS

OF CHLORINE ISOTOPES IN

CARBON TETRACHLORIDE

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On the basis of the theory of packed thermodiffusion columns, the reduced value of the thermodynamic constants of chlorine isotopes in carbon tetrachloride are determined experimentally by a nonsteady method.

Liquid thermodiffusion was first used as a technological isotope-separation process for the enrichment of uranium 235 isotopes [1]. Interest in this method of separation then declined but was revived by the publication of a series of papers [2-5], in which thermodiffusion constants were determined in liquid isotopic mixtures of chlorine and bromine and, on this basis, the technical expediency of the use of thermodiffusion in the liquid phase was established. Note that, in realizing this process, great importance attaches to the choice of the material containing the required isotope. In the experiments of [3], for example, $\alpha = 0.04$ for bromine isotopes in phenyl bromide, $\alpha = 0.02$ in ethyl bromide [6], and $\alpha = 0.038$ in butyl bromide [7]. Therefore, in considering the technical realization of the thermodiffusion separation of chlorine isotopes in the liquid phase, it is important to choose the chlorine compound that has the largest thermodiffusion constant and is characterized by thermal stability and adequate chemical inertness. For chlorine isotopes in trichloroethylene [2], $\alpha = 0.1$, and in propyl chloride [6], $\alpha = 0.030$ (for experiments with a column operating in conditions of continuous sampling) and $\alpha = 0.021$ (without sampling). Such a large discrepancy between the results for different conditions of column operation may be due to parasitic convection arising as a result of temperature and concentration asymmetries [8, 9], since in [6] the means of ensuring uniformity of the gap through the insertion of wires did not eliminate the possibility of eccentricity between the axes of the two cylinders. In [8] it was shown that the sensitivity of thermodiffusion separation to parasitic convection increases with increase in the thermodiffusion constant and hence must be at its greatest in isotopic mixtures. Therefore, a column with an empty gap cannot be regarded as the best design for the determination of the thermodiffusion constant. A column with packing is more suitable, enabling the effect of parsitic convection to be reduced by at least an order of magnitude [10]. This type of column was first used in [3], in determining α for bromine isotopes in phenyl bromide. Unfortunately, no details of the calculation procedure adopted in [3] were given.

On the basis of the above considerations, the present experiments for the determination of the thermodiffusion constant were carried out using a cylindrical column of the type described in [11], the inner cylinder of which was heated by vapor and the outer by running water. The internal diameter of the outer cylinder was 30.020 ± 0.005 mm and the outer diameter of the inner cylinder was 26.970 ± 0.005 mm. Thus, the working gap was $\delta = 1.52 \pm 0.01$ mm. The gap was filled with small fractions of glass balls (diameter $d = 100-130\,\mu$). The filling height, corresponding to the working height, was $L = 35.0$ cm.

From the theory of packed columns [10, 12], it is known that in a column of this type the time to reach equilibrium is very large, and hence it is expedient to carry out the experimental determination of the thermodiffusion constant during the transient processes.

The material chosen for investigation was carbon tetrachloride or analytical grade, subjected to additional rectificational purification. Within the limits of sensitivity of the LKhM-7a chromatograph used to check the purity of the starting material, no impurities could be detected, which means that they are present in amounts of not more than $10^{-4}\%$.

Carbon tetrachloride is chemically inert and may therefore be suitable as a starting material for the extraction of chlorine isotopes. Its distinguishing feature is that it is a multicomponent isotopic mixture formed by ten masses $^{12}C^{35}Cl_m^{37}Cl_{4-m}$ and $^{13}C^{35}Cl_m^{37}Cl_{4-m}$, where $m = 0.4$. Neglecting the components with ^{13}C because

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of their low concentrations (altogether not more than 1.1%), carbon tetrachloride may be regarded as a five-component mixture. It is necessary to ask whether the asymptotic solution derived for a binary mixture in [13] may be used in this case. An interesting possibility is offered by the approximation of [14], in which the transfer equation for a multicomponent system

$$ J_i = H_0 c_i \sum_{j=1}^{k} m_{ij} c_j - K \frac{\partial c_i}{\partial z} $$

is simplified by the introduction of the approximate solution

$$ \sum_{j=1}^{k} m_{ij} c_j \approx \sum_{j=1}^{k} m_{ij} c_{j0}, \tag{1} $$

where the relative mass difference $m_{ij} = (M_i - M_j)/(M_i + M_j)$, and c_{j0} is the initial concentration of the j-th component of the mixture. Using this approximation, the transient processes in a multicomponent system may be described using the expression in [13], replacing the Soret coefficient by $\alpha_0 \sum_{j=1}^{k} m_{ij} c_{j0}/\overline{T}$ and setting b = 1.

Here α_0 is the reduced value of the thermodiffusion coefficient, related to that for each pair of isotopes by the expression

$$ \alpha_{ij} = \alpha_0 \frac{M_i - M_j}{M_i + M_j}. \tag{2} $$

The solution given in [13] may be written in the form

$$ \Delta c_i = c_{i0} f(x, k), \tag{3} $$

where

$$ f(x, k) = \frac{2k}{2k+1} \left\{ x + \left(x + \frac{2k+1}{2k} \right) \mathrm{erf}\, \sqrt{kx} + \sqrt{\frac{x}{\pi k}} \exp(-kx) + \frac{k+1}{2k+1} \left[\exp\left(\frac{2k+1}{k} x \right) \mathrm{erfc}\left(\frac{k+1}{k} \sqrt{kx} \right) - 1 \right] \right\} $$

and

$$ x = \frac{H}{2M} t, \quad k = \frac{HM}{2mK}. $$

Computer analysis of experimental data by the least-squares method, using Eqs. (3) and (4) leads to values of the two parameters h = H/M and n = HM/mK, and hence the following formula is obtained for the reduced value of the thermodiffusion constant:

$$ \alpha_0 = \frac{\delta \overline{T}}{\Delta T \sum\limits_{j=1}^{k} m_{ij} c_{j0}} \sqrt{\frac{6 \varepsilon h n}{5 D_{\mathrm{eff}}}}. \tag{5} $$

For the experimental fraction of glass balls, D_{eff}/D is [10] 0.167 ± 0.018 when the porosity ε = 0.39.

In the experiments using the packed column, one end of which was connected to a thermosyphon with a large-volume reservoir (90 cm^3), the temperature at the hot and cold surfaces was measured by calibrated copper—Constantan thermocouples: T_1 = 367°K, T_2 = 286°K; hence ΔT = 81°C. By means of the reservoir, an excess pressure of 4 atm was maintained in the working gap, in view of the low boiling point of carbon tetrachloride. Samples for analysis were removed through a lower sampling vent. The isotopic composition of the samples was determined on a MKh-1303 mass spectrometer from the fragment peaks $^{12}C^{35}Cl_3^+$ and $^{12}C^{35}Cl_2^{37}Cl^+$. Since the distribution of chlorine atoms in the carbon tetrachloride molecule conforms to a binomial probability law, it is possible from these peaks to find the content of one of the isotopes in the sample. If the ^{35}Cl content is a, the fraction of $^{12}C^{35}Cl_3^+$ entering the ion collector is a^3 and the fraction of $^{12}C^{35}Cl_2^{37}Cl^+$ ions is $3a^2(1-a)$. This, if the measured ratio is p

$$ p = \frac{a^3}{3a^2(1-a)} = \frac{a}{3(1-a)}, \tag{6} $$

from which a may be determined, and hence the fraction of each kind of molecule $^{12}C^{35}Cl_m^{37}Cl_{m-4}$ in the carbon tetrachloride may be calculated. The appropriate fraction is a^4 for $^{12}C^{35}Cl_4$, $4a^3(1-a)$ for $^{12}C^{35}Cl_3^{37}Cl$,

TABLE 1. Change over Time in Concentration (%) of ^{35}Cl and Relative Concentrations of $^{12}C^{35}Cl_m^{37}Cl_{m-4}$

t, h	a	Mass			
		152	156	158	160
0	75,56	0	0	0	0
29	75,20	1,89	1,99	3,97	6,03
35	75,17	2,05	2,17	4,32	6,53
65	74,90	3,45	3,64	7,37	11,24
70	74,90	3,45	3,64	6,37	11,24
100	74,72	4,37	4,63	9,44	14,46
107	74,66	4,68	4,96	10,13	15,53
140	74,53	5,35	5,67	11,62	17,91

TABLE 2. Results for Reduced Value of Thermodynamic Constant

Mass	$\sum\limits_{j=1}^{k} m_{ij}c_0 \cdot 10^2$	$\sum\limits_{j=1}^{k} m_{ij}c_i \cdot 10^2$	α_0	α_{0m}
152	—0,66	—0,64	3,1	
154	—0,01	+0,013	—	
156	0,64	0,66	3,25	$3,4\pm0,7$
158	1,27	1,30	3,4	
160	1,90	1,92	3,6	

$6a^2(1-a)^2$ for $^{12}C^{35}Cl_2^{37}Cl_2$, and so on. Table 1 gives the ^{35}Cl concentration a and the corresponding variation of each component concentration with respect to its initial value at various times; the intermediate mass 154 is excluded from consideration since in this case Eq. (1) is not satisfied (Table 2). These results were used to find the parameters L and n. The value of the self-diffusion coefficient required in Eq. (5) is D = $2.05 \cdot 10^{-9}$ $m^2 \cdot sec^{-1}$ at $\overline{T}$ = 326°K [15]. The results of the calculation are shown in Table 2, from which it is evident that the difference between the values of α_0 for the various masses falls within the limits of experimental error and a mean value of α_0 = 3.4 ± 0.7 may be taken. Particularly noteworthy is the good agreement between columns 2 and 3 of Table 2, which indicates the use of the approximation in Eq. (1).

Using this value of α_0 and Eq. (2) it is simple to determine α_{ij} and on this basis to carry out the calculation for the separating equipment.

Unfortunately, there are no data in the literature on the reduced thermodiffusion constant of chlorine isotopes in carbon tetrachlorides. Of some interest in this connection is the experiment of [16], in which a straight-line dependence of $\ln q_{ij}$ on ΔM_{ij} was obtained for the given mixture. In the experiment, a steady-state method was used in an empty-gap column. The slope of the experimental straight line was proportional to α_0. Using this dependence the reduced thermodiffusion coefficient is found to be α_0 = 2.4. As is evident, the value obtained in the packed-column is larger, which confirms that parasitic convection is absent from such a column.

NOTATION

c_i	is the concentration of i-th component;
α_0	is the reduced value of thermodiffusion coefficient;
J	is the flux of i-th component;
t	is the time;
M	is the molecular weight;
$\overline{T}$	is the mean temperature;
D_{eff}	is the effective diffusion coefficient;
ε	is the porosity;
q	is the separation coefficient;
ρ	is the density;
β	is the volume-expansion coefficient;
δ	is the gap width;
ΔT	is the temperature difference between hot and cold surfaces;

B	is the gap perimeter;
η	is the viscosity;
z	is the vertical coordinate;

$H_0 = \alpha_0 k \rho^2 g \beta (\Delta T)^2 B \delta / 12 \eta \bar{T}$; $K = g^2 k^2 \rho^2 \beta^2 (\Delta T)^2 \cdot B \delta^3 / 120 \eta^2 D_{eff}$;

k	is the permeability.

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RADIATIVE ANGULAR COEFFICIENTS IN
AXISYMMETRIC SYSTEM

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A method is proposed for the calculation of the angular coefficients from an analytic determination of the region of visibility.

The design of furnaces, high-temperature chemical equipment, high-temperature energy–conversion apparatus, and cryogenic systems involves calculations of radiative heat transfer.

Because of the complexity of radiative heat transfer and the lack of accurate values of the emissive characteristics of surfaces, it is usual in calculations to consider models and shells with simple surface properties.

In calculating the radiative heat transfer between diffusely emitting and diffusely reflecting surfaces separated by a diathermal medium, it is necessary to determine the angular coefficients of the radiation, which determines the proportion of the energy transfer transmitted from one surface to another.

There are a considerable number of works in which the angular coefficients are calculated analytically for various configurations ([1-4], etc.). The present paper proposes an algorithm for the computer calculation of radiative angular coefficients.