

G. D. Rabinovich, V. I. Shinkevich,
and K. K. Azroyan

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The thermal diffusion constant is determined for potassium isotopes in an aqueous solution of potassium iodide. Variants of the organization of the thermal diffusion separation process in solutions are discussed.

Thermal diffusion has been successfully used to separate isotopes of a number of elements in the gaseous phase. A detailed summary of the results achieved in this field is given in [1]. The possibility in principle of separating isotopes in the liquid phase was shown a long time ago [2,3], but only during World War II was this method applied for the enrichment of ^{235}U [4]. However, only after the appearance of [5,6] was the attention of researchers again attracted toward thermal diffusion separation of isotopes in the liquid phase using individual liquids as the working materials. Beginning in the 1970s a number of papers published in this field [7,8,9] showed that certain isotopes could be successfully enriched in liquids by thermal diffusion (^{34}S in CS_2 [9], ^{79}Br in $\text{C}_4\text{H}_9\text{Br}$ [7], ^{37}Cl in $\text{C}_6\text{H}_5\text{Cl}$ [8]).

Nevertheless it is difficult for thermal diffusion separation to compete economically with other methods of separation. Thus, it is interesting to study the possibility of isotopic separation in solutions of salts of various elements, since almost the only alternative in most cases is electromagnetic separation, which is characterized by low technicoeconomic indices because of its low productivity.

The first attempt to achieve such a process was by Korsching and Wirtz [10] who studied the separation of zinc isotopes in an aqueous solution of ZnSO_4 . The shift in the isotopic composition determined by the spectral analysis of hyperfine structure lines was within the limits of error of the measurements. In experiments on the separation of lithium isotopes Panson [11] found a considerable shift in isotopic composition in aqueous solutions of its chloride and nitrate. Abelson and Hoover [4] cite experiments performed with aqueous solutions of potassium salts in columns from 1 to 4 m long having a gap of 0.8 mm in which a separation factor $q = 1.2$ was reached for ^{41}K - ^{39}K . Recently [12] data were reported on the separation of potassium and rubidium in decinormal aqueous solutions of the chlorides of these elements in a packed column, which showed a certain isotopic shift. In 1970 we began a study of the separation of isotopes in solutions in order first to develop a technique for determining the thermal diffusion constant, the knowledge of which determines the prospects for the practical realization of the isotopic separation process in solutions, and second to develop schemes capable of ensuring the operation of columns connected in cascade.

Theory. We consider below the simplest case of an aqueous solution of an electrolyte with two kinds of ions (one cation and one anion) in which the cation occurs in two forms differing from one another in isotopic composition. In this case there is only one diffusion coefficient [13, p. 310], and since the solution is electrically neutral it can be considered as a three-component mixture. Taking account of the fact that the molar concentration of the solute is small, and denoting the solvent by subscript 1, and the molecules of the solute of different isotopic composition by 2 and 3, the system of transport equations [14]

$$\tau_i = x_i \sum_k H_{ik} x_k - K \frac{dx}{dz} + \sigma x_i$$

can be linearized and given the form

$$\tau_2 = H_{21} x_2 - K \frac{dx_2}{dz} + \sigma x_2, \quad \tau_3 = H_{31} x_3 - K \frac{dx_3}{dz} + \sigma x_3, \quad (1)$$

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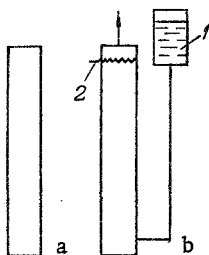


Fig. 1. Schematic diagram of thermal diffusion columns.

where the transport τ_i is expressed in moles per unit time, and

$$H_{ih} = \frac{\alpha_{ih} \rho_m^0 g \beta \delta^2 (\Delta T)^2 B}{6! \eta \bar{T}},$$

$$K = K_c + K_p, \quad (2)$$

$$K = \frac{g^2 \rho_m^0 \beta^2 \delta^2 (\Delta T)^2 B}{9! \eta^2 D},$$

where K_p is a coefficient which, according to [15], takes account of the effect of parasitic convection.

In work with solutions of solids either of the two variants shown schematically in Fig. 1 is possible. In the variant shown in Fig. 1a the solution is placed in a column closed at both ends. In addition to the separation of the solute from the solvent, the components of the solute are separated from one another. As a result the solute is concentrated at the bottom of the column and the solvent at the top. Although the heavy components of the mixture are separated from one another, the upper part of a sufficiently tall column may turn out to contain practically pure solvent. In other words, by increasing the length of the column in this method of operation it is impossible to obtain appreciable amounts of separated solid components at the top of the apparatus. This was noted by Korsching who proposed and tried the scheme shown in Fig. 1b [16]. In this scheme the solvent is supplied continuously from the reservoir 1, while at the top of the column solvent is evaporated by the heater 2 and leaves the column as vapor.

Thus, there is a continuous flow from the bottom to the top of the column which prevents the separation of the solute from the solvent. Of course this flow cannot be larger than the convective flows which arise in the column as a result of the temperature difference between its hot and cold surfaces, since in this case these would be a violation of the reflux principle which determines the efficiency of the thermal diffusion apparatus of Clusius and Dickel; i.e., the relation

$$\sigma < \rho B \bar{w} \quad (2')$$

must hold, where \bar{w} is the average velocity of convective flows.

In the variants of Fig. 1 the process proceeds in such a way that the amounts of solute and solvent in the column remain constant. This is true also in scheme 1b, since although the solvent is evaporated from the upper end of the column, it is exactly compensated by the feed into the lower end of the column.

Thus, in the problem under consideration the condition

$$\int_0^{y_e} x_i dy = x_{i0} y_e \quad (3)$$

must be satisfied, where x_{i0} is the initial concentration of the i -th component.

A positive value of the thermal diffusion constant corresponds to the motion of the light component toward the hot wall of the column; $H_{12} > 0$ and $H_{13} > 0$. Using the fact that $H_{ij} = H_{ji}$, we obtain instead of (1)

$$\frac{dx_2}{dy} - (\kappa - 1) x_2 = 0, \quad \frac{dx_3}{dy} - (\kappa - h) x_3 = 0, \quad (4)$$

TABLE 1. Characteristics of a 20% Solution of Potassium Iodide and Results of Separation in the Thermal Diffusion Column in the Steady State

Isotopic ratio $^{39}\text{K}/^{41}\text{K}$		Physical characteristics at $T=330^\circ\text{K}$			
top of column	bottom of column	dynamic viscosity, $\eta \cdot 10^3$, $\text{N} \cdot \text{sec}/\text{m}^2$	diffusion coeff. $D \cdot 10^9$, m^2/sec	Volume coeff. of expansion $\beta \cdot 10^3$, deg^{-1}	density $\rho \cdot 10^{-3}$, kg/m^3
18,046	13,93	0,49	2,62	0,41	1,151

Note. The values of the dynamic viscosity, volume coefficient of expansion, and density were taken from [20], the diffusion coefficient was found from $D_T = D_0 [1 + \gamma(t - t_0)]$, where $D_0 = 1.58 \cdot 10^{-9} \text{ m}^2/\text{sec}$ for a normal solution at 18°C [21], and $\gamma = 3.55 \eta^{1/2} \rho^{-1/3}$.

where

$$y = \frac{H_{12}z}{K}, \quad x = \frac{\sigma}{H_{12}}, \quad h = \frac{H_{13}}{H_{12}}. \quad (5)$$

The solutions of Eqs. (4) which satisfy condition (3) have the form

$$x_2 = x_{20} y_e \frac{(x-1) e^{(x-1)y}}{e^{(x-1)y_e} - 1}, \quad (6)$$

$$x_3 = x_{30} y_e \frac{(x-h) e^{(x-h)y}}{e^{(x-h)y_e} - 1}. \quad (7)$$

We note that the solution obtained presupposes that the α_{ij} assume constant values over the height of the column, i.e., in (6) and (7) there must be substituted the average value of α corresponding to the initial concentration of the solution.

The separation factor of the two isotopes can be found from (6) and (7)

$$q = \frac{x_{2e} x_{3i}}{x_{2i} x_{3e}} = e^{(h-1)y_e}. \quad (8)$$

Equation (8) yields the important result that the separation factor does not depend on the rate of evaporation of the solvent when condition (2') is satisfied.

Experiment. The first problem in the experimental investigation was to confirm the possibility in principle of separating potassium isotopes in an aqueous solution, and the second was to determine the value of the thermal diffusion constant.

The experiments were performed without withdrawal on a flat thermal diffusion column with a working height of 17.5 cm, a width of 4 cm, and a gap of 0.26 ± 0.01 cm. The column was inclined at an angle of 3° with the vertical with the hot side uppermost to stabilize convective flows. Thermostats were used for heating and cooling. Temperatures were measured with copper-Constantan thermocouples. An aqueous solution of potassium iodide was chosen as the working material. The experiments were performed for $T_2 = 344^\circ\text{K}$ and $T_1 = 330^\circ\text{K}$, and lasted for 30 h, which ensured that a steady state was reached. At the end of the experiment the concentration of the solute at the top and bottom of the column was determined by a refractometer, and the isotopic ratio $^{39}\text{K}/^{41}\text{K}$ was measured with an MI-1305 mass spectrometer. For our spectrometer the standard ratio was $^{39}\text{K}/^{41}\text{K} = 14.01$.

Discussion of Results. Table 1 shows the average values of several experiments performed with a solution of potassium iodide having an initial concentration $1 - x_{10} = 0.0264$ (0.2 mass fraction). The mass fractions in mole fractions were calculated from the expression

$$x = \frac{(mM_2 + M_3) c_1}{M_1(1+m)(1-c_1) + (mM_2 + M_3) c_1}, \quad (9)$$

where m is the $^{39}\text{K}/^{41}\text{K}$ ratio determined by mass spectrometric analysis, and the M_i are the molecular masses of the components.

We rewrite the exponent in (8) by using the notation

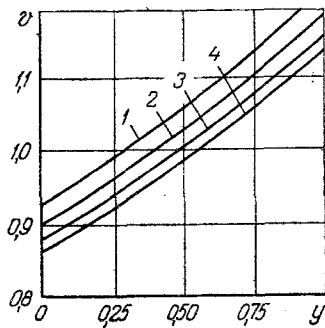


Fig. 2

Fig. 2. $v = x_2 x_{30} / x_3 x_{20}$ as a function of the dimensionless column length y for $y_e = 2.76$ and $h = 1.098$ for various values of the dimensionless evaporation parameter κ : 1) $\kappa = 0$; 2) 0.5; 3) 1; 4) 1.5.

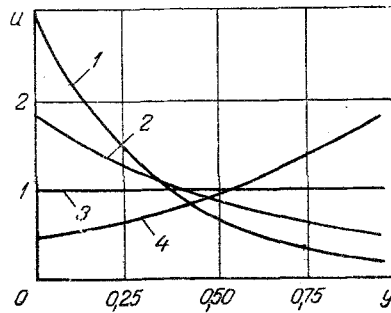


Fig. 3

Fig. 3. $u = (x_2 + x_3) / (x_{20} + x_{30})$ as a function of the dimensionless column length y for $y_e = 2.76$ and $h = 1.098$; the values of the evaporation parameter are the same as in Fig. 2.

$$(h - 1) y_e = 504 \frac{(\alpha_{13} - \alpha_{12}) \eta DL}{g \rho \beta \delta^* \bar{T} [1 + (K_p / K_c)]} \quad (10)$$

It is clear from (8) that the left-hand side of this expression can be determined from the known value of the separation factor q . Since according to Table 1 $q = 1.295$, $(h - 1)y_e = 0.259$. Substituting this value into (10) and using data on the physical characteristics of the potassium iodide solution given in Table 1 and data on the working height of the column and the size of the gap, we obtain

$$\alpha_{13} - \alpha_{12} = \alpha_{23} = (0.0153 \pm 0.0025) \left(1 + \frac{K_p}{K_c} \right) \quad (11)$$

The large value of the error arises mainly from the inaccuracy in measuring the gap width which enters Eq. (10) to the fourth power. To determine a more accurate value of α_{23} it is necessary to take account of the effect of parasitic convection, which can be done by considering the separation of the potassium iodide as a whole from the solvent. A refractometric measurement of the concentration gave the following values: at the top of the column $1 - x_{1e} = 0.113$ mole %, and at the bottom $1 - x_{1i} = 11.904$ mole %, which corresponds to $q^0 = 104.7$. We denote by y_e^0 the natural logarithm of the separation factor of the water-solute system, i.e., $y_e^0 = \ln q^0 = 4.65$. Since

$$y_e^0 = 504 \frac{\alpha_0 \eta DL}{g \rho \beta \delta^* \bar{T} [1 + (K_p / K_c)]} \quad (12)$$

knowing α_0 and using the values of the remaining physical quantities listed in Table 1 it is possible to find the factor which takes account of parasitic convection.

According to Tanner's data [17], at $T = 310^\circ\text{K}$ and $x_{10} = 0.0245$, $\alpha_0 = 0.33$. Since the average temperature was higher in our experiments, our value of α_0 should be somewhat higher than the value in [17] since the thermal diffusion constant for the solution under study increases with increasing temperature. If we take $\alpha_0 = 0.33$ as the minimum value and substitute it into (12) we find $1 + K_p / K_c = 1.21 \pm 0.16$. Then taking account of (11) we obtain finally

$$\alpha_{23} = 0.019 \pm 0.005.$$

It is interesting to compare this result with data on the thermal diffusion constant for potassium isotopes obtained in experiments by Lodding and Ott [18] on the separation of this metal in solution. Their value of $\alpha_{23} = 0.0309 \pm 0.0025$ is larger than ours, which can be accounted for by the difference in the character of the intermolecular interactions: in the first case the effect of separation is determined directly by the interaction of isotopes of atoms or groups of atoms, and in the second case by a different interaction of the solute of a different isotopic composition with the solvent.

A comparison of our data on α_{23} with values known for binary isotopic liquid mixtures [5,19] shows that further technicoeconomic development of the possibility of the enrichment of potassium isotopes in solutions is of practical interest.

Let us consider now how separation may be affected by the recirculation of solvent as in the scheme of Fig. 1b. To do this we use Eqs. (6) and (7) to determine x_2x_{30}/x_3x_{20} and $(x_2 + x_3)/(x_{20} + x_{30})$ as functions of the dimensionless withdrawal κ and the dimensionless column length y . The calculated values of L , δ , ΔT , and x_{10} in our experiments are listed in Figs. 2 and 3, which show that as κ increases, the ratio of the concentrations of the two isotopes decreases at the top and bottom of the column, although the separation factor determined by (8) remains unchanged (Fig. 2), and the concentration of the solute for $\kappa = 1$ remains practically equal to its initial value (Fig. 3). This means that the weight of the enriched product which can be removed is sharply larger than in a column without recirculation, with a certain decrease in the degree of enrichment of the light component and an increase in the degree of enrichment of the heavy component. In realizing this scheme which ensures the maintenance of a constant concentration of solute over the whole height of the column equal to its initial value, there is the possibility of combining columns in a cascade of ordinary thermosiphon loops and in principle achieving any given degree of enrichment.

NOTATION

x , molar concentration; τ , number of moles of component transported to positive end of column per unit time; σ , number of moles of solvent evaporated from column per unit time; y_e , value of y at $z = L$; z , vertical coordinate; L , length of column; α_{23} , thermal diffusion constant; $\rho_M = \rho \sum_i c_i / M_i$, molar density; c_i , mass fraction of component i ; M_i , molecular weight; T_1 , T_2 , temperatures of cold and hot surfaces of column; $\Delta T = T_2 - T_1$; ρ , mass density; $\bar{T} = (T_1 + T_2)/2$; η , D , β , dynamic viscosity, diffusion coefficient, coefficient of volume expansion; δ , gap width; B , width of column. Subscripts: e , i , values at positive and negative ends of column; 0 , initial value; 1 , 2 , 3 , solvent, first isotope, second isotope.

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