

STUDY OF THE THERMODIFFUSION CONSTANT OF AN Ar-Kr MIXTURE
AT LOW TEMPERATURES

V. L. Zhdanov and O. A. Kolenchits

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Reasons for divergence between theoretical and experimental values of the thermodiffusion constant of an Ar-Kr mixture at temperatures below 273°K are studied.

Experimental and theoretical studies of the temperature and concentration dependences of the thermodiffusion constant α_t of an Ar-Kr mixture have been performed in [1-8]. In the temperature range below 273°K the measurements of [1,2,4,6] indicate a monotonic decrease of α_t with decreasing temperature, while the data of [5] indicate the presence of a minimum in this function, which shifts toward higher temperatures with increasing krypton content. Similar anomalous behavior of the temperature dependence of α_t was observed by Grew and Mundy [3], who explained the presence of a minimum in their data as the effect of krypton adsorption in the measurement equipment.

Calculation of the thermodiffusion constant of an Ar-Kr mixture by the Chapman-Enskog method with the potential models (12-6), (exp-6) in the second approximation does not produce a temperature dependence adequately agreeing with experiment. Using the multiparameter potential function of [8], one can satisfactorily approximate the experimental dependence of α_t of an Ar-Kr mixture on temperature which was obtained in [5]; however these potentials cannot explain the shift of the minimum with increasing krypton content. Qualitatively this peculiarity of the experimental results is reflected by the α_t values calculated in [7] with consideration of the effect of krypton molecule dimerization, but these calculations do not agree quantitatively with experiment.

In our opinion these divergences may be produced by the following causes: errors in the experimental data; use of different methods for processing of experimental values of separation or the separation constant to determine α_t ; the effect on thermodiffusion separation produced by dimerization of gas molecules, which increases significantly at lower temperatures; convergence errors in the Chapman-Enskog approximations; inappropriate choice of potential model and molecular interaction parameters.

It is thus of interest to consider the possible degree of influence of the above factors on the thermodiffusion constant of an Ar-Kr mixture.

Experimental studies of α_t in the temperature range $\bar{T} = 168-272^\circ\text{K}$ were performed with a two-reservoir system, using the equipment described in [9], at an initial start-up pressure of 380 mm Hg at room temperature. The temperature of the upper reservoir T_u was maintained constant over the experiment while that of the lower reservoir T_l was adjusted. Under the influence of the constant temperature gradient thus produced, thermodiffusion separation of the binary gas mixture occurs, resulting in development of a concentration gradient, which in the stationary state is equal to [10]:

$$\nabla x_1 = k_t \nabla \ln T. \quad (1)$$

If we assume that the thermodiffusion constant is temperature independent over the small interval (T_u , T_l), then from Eq. (1) we obtain the integral value of the quantity α_t

$$\bar{\alpha}_t = \frac{S}{x_1 x_2 \ln(T_u/T_l)} \quad (2)$$

or

$$\bar{\alpha}_t = \frac{\ln q}{\ln(T_u/T_l)}, \quad (2')$$

where S and q are experimentally determined values.

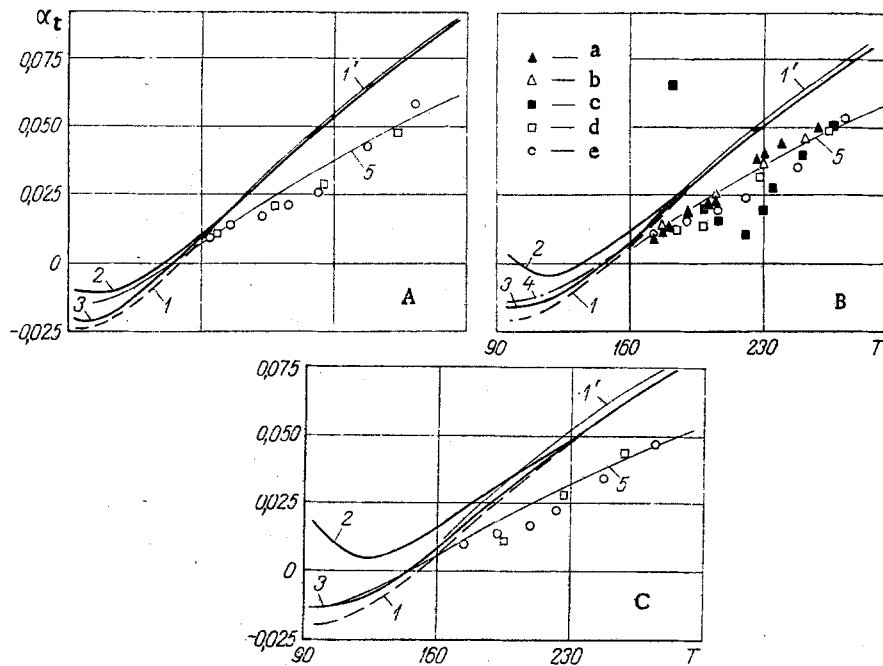


Fig. 1. Temperature dependence of α_t of Ar-Kr mixture for various krypton contents: A) 25%; B) 50%; C) 75%. Calculated values obtained as follows: 1, 1') second approximation of Chapman-Enskog theory using (12-6), (exp-6) potentials with parameters of [7], [18]; 2, 4, 3) Eq. (4) at 380 and 100 mm Hg with consideration of pressure change, (12-6) potential, and parameters of [7]; 5) third approximation of Chapman-Enskog theory with (exp-6) potential and parameters from [18]. Experimental data: a) 46.5% [1]; b) 54.1% [2]; c) 49.98% [5]; d) 49.98% (data of [5] processed by present authors; e) 50% (data of present authors) [12].

However, in practice the assumption of a small temperature gradient is not satisfied in the two-reservoir apparatus, and determination of the thermodiffusion constant with Eq. (2) is not correct. Thus to determine α_t we must use a differential method of processing the measurement results

$$\alpha_t = \frac{1}{x_1 x_2} \frac{dS}{d \ln(T_u/T_l)} \quad (3)$$

or

$$\alpha_t = \frac{d \ln q}{d \ln(T_u/T_l)} \quad (3')$$

The values of α_t obtained from Eq. (3) are more "sensitive" to the character of the thermodiffusion separation process than those of Eq. (2).

Measured values of the thermodiffusion separation S and its temperature dependence were processed by the method of least squares in the form of a polynomial, subsequent differentiation of which was used to determine α_t values (Fig. 1). We estimate the uncertainty in separation measurement to be 4% at the 0.95 confidence level. The α_t values obtained refer to a mean temperature \bar{T} [11], since the value of the thermodiffusion separation, while being a function of temperature of the lower vessel, also depends on the temperature of the upper.

For a correct comparison of the data of the various authors it is necessary that the α_t values be obtained by processing the experimentally measured values (S or q) by one and the same method. Figure 1 presents α_t values from data of [1, 2] obtained with Eq. (3). Since in [6] the concentration dependence of thermodiffusion separation was the measured quantity, these data cannot be processed by an analogous method and so were not used in the comparison of experimental results.

As is evident from Fig. 1, the temperature dependence of α_t obtained by the present authors, as well as the data of [1, 2], show no minimum over the parameter range limiting the

gaseous state of the mixture. In this region α_t decreases monotonically with temperature reduction, with its decrease being nonlinear, gradually disappearing with approach to the phase transition region, as is especially noticeable in mixtures with a high krypton content. With further decrease in temperature (in the region near the krypton saturation line) we observed a sharp increase in α_t for all compositions studied [12], similar to the anomaly observed in [5]. However, in this range of parameters for Ar-Kr mixtures (as was indicated in [12]) the observed minimum in the α_t dependence is produced by partial condensation of the krypton.

Analysis of the conditions under which the experiments of [5] were performed shows that at the temperature producing the minimum value of α_t the mixture studied was quite far from the phase transition region. In [7] an attempt was made to explain the presence and character of the minimum in the experimental temperature dependence of α_t found in [5] through the effect of krypton molecule dimerization on the process of thermodiffusion separation.

The effect of gas molecule dimerization, experimentally established in [13,14], should have an influence on transfer processes, since it leads to the appearance of a new component and converts a pure gas into a binary mixture, and an initial binary mixture into a multi-component system. A method for calculating the thermodiffusion constant of binary gas mixtures with consideration of the effect of dimerization was presented in [13]. The process of formation of dimers from molecules of component A was considered as a chemical reaction of the type $2A \rightleftharpoons A_2$, the rate of which is comparable to the thermodiffusion separation process, such that a local equilibrium is established between dimers and monomers in the mixture.

Assuming that dimers are formed in the mixture only from the heavier component A, and that the pressure remains constant, the thermodiffusion constant of a mixture consisting of components A and C can be calculated from the relationships of [7]

$$\alpha_t(A, C) = \frac{Y_2(1 + 2\mu + 2\mu x_C) - Y_1 x_A (nK_2)'_t T}{(1 + \mu + \mu x_C)(1 + 2\mu) Z}, \quad (4)$$

where

$$\begin{aligned} Y_1 &= x_A D_{13} D_{23} - 2D_{12} D_{23} + (1 + x_C) D_{12} D_{13}, \\ Y_2 &= (D_{13} - 2D_{23}) \mu \alpha_{12}^{(3)} x_A D_{12} + (1 + 2\mu) x_A D_{13} D_{23} (\alpha_{13}^{(3)} + \mu \alpha_{23}^{(3)}) + (1 + 2\mu) x_C D_{12} (\alpha_{13}^{(3)} + 2\mu \alpha_{23}^{(3)} D_{23}), \\ Z &= (1 + 2\mu) x_A D_{13} D_{23} + x_C D_{12} D_{13} + 4\mu D_{12} D_{23}, \\ \mu &= \{[1 + 4(1 - x_C^2) nK_2]^{1/2} - 1\} / 2(1 + x_C). \end{aligned}$$

The numerator of Eq. (4) consists of two terms: the first generated by the process of thermodiffusion of the ternary gas mixture, and the second by formation of double molecules.

The diffusion coefficient of a binary mixture is calculated by the formula of [10]

$$D_{ij} = 2.68 \cdot 10^{-7} \frac{T^{3/2} \left(\frac{M_i + M_j}{2M_i M_j} \right)^{1/2}}{p \sigma_{ij}^2 \Omega_{ij}^{(1,1)*} (T_{ij}^*)}, \quad (5)$$

while the thermodiffusion constant of the components i and j of a ternary mixture is given by [16]

$$\alpha_{i,j}^{(3)} = - \frac{\begin{vmatrix} a_{11} & a_{12} & a_{13} & 1 \\ a_{21} & a_{22} & a_{23} & 1 \\ a_{31} & a_{32} & a_{33} & 1 \\ b_{1,ij} & b_{2,ij} & b_{3,ij} & 0 \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}}, \quad (6)$$

where

$$\begin{aligned} a_{rs} &= x_s M_{rs} M_{sr} \frac{F'_{rs}}{E_{sr}} + \delta_{rs} \sum_l x_l \frac{F_{sl}}{E_{sl}}, \\ b_{i,ij} &= -(1 - x_h) M_{ji} \frac{6C_{ij}^* - 5}{E_{ij}} - x_h M_{hi} \frac{6C_{ih}^* - 5}{E_{ih}}, \\ b_{j,ij} &= (1 - x_h) M_{ij} \frac{6C_{ij}^* - 5}{E_{ji}} + x_h M_{hj} \frac{6C_{jh}^* - 5}{E_{jh}}, \end{aligned}$$

$$b_{k,ij} = x_k M_{ik} \frac{6C_{ki}^* - 5}{E_{ki}} - x_k M_{jk} \frac{6C_{kj}^* - 5}{E_{kj}},$$

$$F_{ij} = 6M_{ij}^2 + \left(5 - \frac{12}{5} B_{ij}^*\right) M_{ji}^2 + \frac{16}{5} M_{ij} M_{ji} A_{ij}^*, \quad F'_{ij} = -11 + \frac{12}{5} B_{ij}^* + \frac{16}{5} A_{ij},$$

$$E_{ij} = \frac{2}{5} \sqrt{\frac{2}{M_{ij}}} \frac{\Omega_{ij}^{(2,2)*}}{\Omega_{ij}^{(1,1)*}} \left(\frac{\sigma_{ii}}{\sigma_{ij}}\right)^2, \quad M_{ij} = \frac{M_i}{M_i + M_j}, \quad M_{ji} = \frac{M_j}{M_i + M_j}.$$

The quantity nK_2 (where K_2 is the equilibrium constant of the chemical reaction) is defined for every temperature by the components of the second virial coefficient $B_b^*(T^*)$ and $B_m^*(T^*)$, produced by the presence within the mixture of stable and metastable dimers, respectively [17]:

$$nK_2 = -\frac{p}{kT} b_0 [B_b^*(T_A^*) + B_m^*(T_A^*)], \quad b_0 = \frac{2}{3} \pi N_A \sigma_A^3. \quad (7)$$

The dependence of the quantities B_b^* and B_m^* on reduced temperature was tabulated and approximated by a seventh-order polynomial in [17].

The calculation of α_t values performed in [7] with use of the (12-6) potential over a parameter range corresponding to the experiments of [5] (at a pressure of 100 mm Hg) revealed that consideration of dimerization produces values which at low temperatures significantly exceed those produced by calculating the thermodiffusion constant of a binary mixture using the second approximation of the Chapman-Enskog theory, with the divergence increasing with increasing krypton content. Qualitatively, the theoretical dependence obtained in this manner is similar to the experimental one: there is a minimum, which shifts toward higher temperatures with increase in krypton content [7] (Fig. 1, curve 4). On this basis [7] concluded that the increase in the thermodiffusion constant of an Ar-Kr mixture observed experimentally in [5] could be explained by the effect of dimerization on thermodiffusion separation, although in experiment the minimum occurs in the region of positive α_t values and at a higher temperature, where theory indicates practically no effect from dimerization on the thermodiffusion process. It should be noted that the calculation of the thermodiffusion constant in [7] was performed with constant pressure over the entire temperature range considered, while in the experiments of [5] one and the same quantity of gas mixture was subjected to thermodiffusion separation at different equipment temperatures, so that a different pressure was established for each concrete temperature difference. Since the number of dimers in the mixture is proportional to the pressure, consideration of its change in accordance with real conditions in the measurement apparatus while performing calculations with Eq. (4) would undoubtedly produce some other temperature dependence of the thermodiffusion constant than that obtained in [7].

Therefore the present authors performed a calculation of the temperature dependence of α_t with consideration of the change in pressure, using Eqs. (4)-(7) and the (12-6) potential, with the same potential parameters used in [7], and also in the second approximation of the Chapman-Enskog theory using the (12-6) and (exp-6) potentials with parameters taken from [7] and [18] respectively. The parameters for interaction of the differing types of molecules were calculated with the usual combination rules [10]. Mixture pressure in the apparatus at various temperatures was determined from the equation of state.

It is evident from Fig. 1 that the divergence of the α_t values calculated with and without consideration of dimerization is decreased significantly if the change in pressure during experiment is considered. Thus dimerization of krypton molecules proves to have a more significant effect on the thermodiffusion process occurring in the two-reservoir apparatus during measurement of the temperature dependence of α_t of an Ar-Kr mixture than was assumed when [7] explained the observed experimental minimum as the product of dimerization.

Despite the fact that Fig. 1b presents experimental values of α_t relating to different Ar-Kr mixture compositions (maximum concentration difference does not exceed 8%) it is of interest to compare these data, since they were obtained at significantly differing mixture pressures (700 mm Hg [1]; 20 mm Hg [2]; 120 mm Hg [5]; 380 mm Hg in the present experiments). Since the number of dimers in the mixture increases with increasing pressure and decreasing temperature, one would expect an increase in divergence of experimental α_t values obtained at various pressures as temperature decreases, if the dimerization process does have a significant effect on thermodiffusion separation. However, evaluation of the experimental

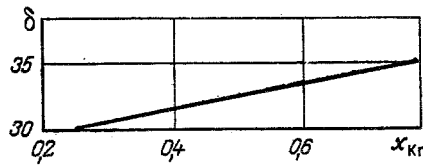


Fig. 2. Contribution of third approximation to value of the thermodiffusion constant calculated in the second approximation of the Chapman-Enskog theory [$\delta = (\alpha_t(2) - \alpha_t(3))/\alpha_t(2) \cdot 100\%$], versus krypton concentration.

results shown in Fig. 1 indicates that with decrease in temperature the agreement of the data of various authors does not deteriorate (the uncertainty in determination of the thermodiffusion separation or constant does not exceed 5% for all data).

The α_t values obtained by the present authors by processing the results of [5] on thermodiffusion separation in the form of a polynomial without consideration of extremal S values, which produced the minimum in α_t , also correspond to the general character of the temperature dependence (Fig. 1).

Thus, analysis of the experimental facts has shown no effect of krypton molecule dimerization on thermodiffusion separation of Ar-Kr mixtures, so that the divergence of theoretical α_t values from experiment in the temperature range under consideration cannot be explained by the presence of dimers in the mixture.

It is known that the strict Chapman-Enskog molecular-kinetic theory [10], even in the first approximation (with consideration of one term in the expansion in Sonin polynomials), conforms well to all experimental facts concerning viscosity coefficient, while for the diffusion constant the results are also satisfactory. The thermal conductivity and thermodiffusion coefficients do not appear in this case. To describe the processes of thermal conductivity and thermodiffusion, and also to obtain the dependence of the diffusion coefficient on concentration it is necessary to use two terms in the expansion in Sonin polynomials (in Devoto's terminology [19] this is the second approximation of the Chapman-Enskog theory for transfer coefficients, which corresponds to the term "first" approximation used in [10] in the sense of the first nonzero approximation). We note that, like the first, all higher approximations of the transfer coefficients refer to systems with a low temperature gradient, since the heat flux and temperature gradient are related linearly.

In [20,21] it was shown that the number of approximations necessary to realize correct theoretical values of the thermodiffusion constant of a gas mixture must be not less than three, while use of a larger number of terms in the expansion in Sonin polynomials ensures rapid convergence of the series. In accordance with this, the authors calculated the thermodiffusion constant of an Ar-Kr mixture in the third approximation using the (exp-6) potential function and potential parameters of [18] (for the (12-6) potential the collision integrals needed for this case are unavailable) using the method of [19]

$$\alpha_t(3) = \frac{5}{2} \frac{1}{x_1 x_2 n} \frac{Q_{D_i}^T}{Q_{D_{12}}}$$

where

$$Q_{D_i}^T = \begin{vmatrix} \bar{q}_{hk}^{-00} & \bar{q}_{hk}^{-01} & \bar{q}_{hk}^{-02} & 0 \\ \bar{q}_{hk}^{-10} & \bar{q}_{hk}^{-11} & \bar{q}_{hk}^{-12} & n_h \\ \bar{q}_{hk}^{-20} & \bar{q}_{hk}^{-21} & \bar{q}_{hk}^{-22} & 0 \\ \delta_{ih} & 0 & 0 & 0 \end{vmatrix}, \quad Q_{D_{ij}} = \begin{vmatrix} \bar{q}_{hk}^{-00} & \bar{q}_{hk}^{-01} & \bar{q}_{hk}^{-02} & \delta_{hj} \\ \bar{q}_{hk}^{-10} & \bar{q}_{hk}^{-11} & \bar{q}_{hk}^{-12} & -\delta_{hi} \\ \bar{q}_{hk}^{-20} & \bar{q}_{hk}^{-21} & \bar{q}_{hk}^{-22} & 0 \\ \delta_{ik} & 0 & 0 & 0 \end{vmatrix}.$$

The elements \bar{q}_{ij}^{mp} for a binary mixture are a matrix of form

$$\bar{q}_{12}^{mp} = \begin{vmatrix} q_{11}^{mp} & q_{12}^{mp} \\ q_{21}^{mp} & q_{22}^{mp} \end{vmatrix}$$

and are functions of the numerical density of the components, the molecular mass of the components, the potential parameters, and the collision integrals [19]. To obtain the second approximation the elements with $m, p = 2$ are cancelled from the determinants $Q_{D_i^T}$ and $Q_{D_{ij}}$.

The contribution of the third approximation to the quantity $\alpha_t(2)$, calculated in the second approximation, increases with growth in concentration and varies insignificantly over the temperature interval 185–300°K (Fig. 2).

It is evident from Fig. 1 that use of the third approximation of the Chapman–Enskog method produces a significant improvement in the agreement between theory and experiment, both qualitatively and quantitatively.

NOTATION

$\alpha_t = k_t/x_1(1 - x_1)$, thermodiffusion constant of binary gas mixture; k_t , thermodiffusion ratio of binary gas mixture; x_1 , concentration of lighter component; T , temperature, °K; $S = (x_1^{T_u} - x_1^{T_l})$, thermodiffusion separation; $x_1^{T_u}, x_1^{T_l}$, concentration of lighter component at temperatures T_u, T_l , respectively; $q = [x_1^{T_u}/(1 - x_1^{T_u})]/[x_1^{T_l}/(1 - x_1^{T_l})]$, separation constant; $T = (T_u T_l / (T_u - T_l)) \cdot \ln(T_u / T_l)$, Brown temperature, °K; p , pressure, atm; n , numerical density of mixture molecules, m^{-3} ; M_i , molecular weight of i -th component of mixture, kg/kmol; $\Omega_{ij}^{(l,s)*}(T_{ij}^*)$ reduced collision integral; the quantities A^*, B^*, C^* being combinations of the collision integrals of [10]; $T_{ij} = kT/\epsilon_{ij}$, reduced temperature; $\epsilon_{ij}/k, \sigma_{ij}$, interaction potential parameters, °K and Å; N_A , Avogadro's number, $kmol^{-1}$; D_{ij} , diffusion coefficient, m^2/sec ; k , Boltzmann's constant, $J/°K$.

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