EXPERIMENTAL STUDY OF THE THERMAL DIFFUSION CONSTANT OF $Kr-N_2O$ AND NH_3-CO_2 MIXTURES

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Some new experimental data regarding the thermal-diffusion constants of $Kr-N_2O$ and NH_3-CO_2 mixtures, obtained in a two-cylinder experimental apparatus, are presented.

Research into the thermal-diffusion separation of binary gas mixtures has shown [1-11] that the greatest difference between theoretical and experimental results in relation to the thermal-diffusion constant occurs for mixtures of polyatomic gases, especially those containing a polar component. The thermal-diffusion constant α_T, being a function of the difference between the masses and sizes of the molecules, depends very substantially on the dynamic characteristics of collisions between these molecules, including the effects of inelastic collisions. However, allowance for the dipole moment and inelastic collisions when calculating the thermal-diffusion constant does not always lead to satisfactory results.

The experimental and theoretical analysis of the thermal-diffusion constants of $Kr-N_2O$ and NH_3-CO_2 mixtures which we shall present in this paper has shown that the theory incorporating the inelastic collisions of molecules agrees less closely with experiment than that which only allows for elastic collisions.

We made an experimental determination of the thermal-diffusion constant with the aid of a two-bulb apparatus, the construction of which was described in [12]. The gas was analyzed by the thermal-conductivity method, using sensitive thermoresistor units of the STI-19 type. The gases in question had the following purities: Kr — 99.97% Kr; N_2O — medically pure; CO_2 — 99.8% CO_2; NH_3 — 99.8% NH_3.

$\underline{Kr-N_2O}$. The temperature dependence of the thermal-diffusion constant of the $Kr-N_2O$ mixture was studied by Datta et al. [9] for the case $x_1 = x_2$ in the temperature range $\bar{T}$ = 362-485°K. Since α_T falls sharply with falling temperature at 400-363°K, these authors suggest that at a temperature on the order of $\bar{T}$ = 325°K α_T may assume a zero value, and at lower temperatures it may even change sign.

We studied the thermal-diffusion constant α_T of the $Kr-N_2O$ mixture at $\bar{T}$ = 309-356°K. In this case T_1 = 293.5°K and T_2 = 323, 348, 373, 393, 415, 423, 457 (Fig. 1). The error of the results was ±4%.

We see from Fig. 1 that the value of α_T is positive over the whole temperature range studied and increases with rising temperature, first rapidly and then in the range T = 348-356°K more slowly. Our experimental results agree with those of [9].

We calculated the thermal-diffusion constant in accordance with the Chapman — Enskog theory, using the Lennard-Jones (12-6) and (12-6-5) potentials [14, 15]. The N_2O molecule has a weak dipole moment, and as indicated in Fig. 1 its influence may be neglected. Earlier calculations [15] showed that the quadrupole moment of this molecule could only make an appreciable contribution to α_T at low temperatures, at which inversion was encountered.

Allowance for the inelastic collisions was made by the Monchick et al. method [16], based on the quantum-mechanical theory of Wang-Chang and Uhlenbeck [17, 18]. We also used experimental values of the thermal conductivity of pure K_r and N_2O gases taken from [19, 20]. We

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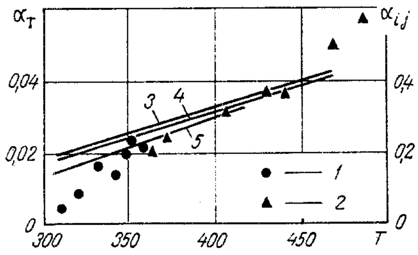

Fig. 1

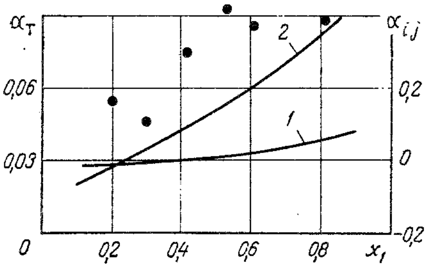

Fig. 2

Fig. 1. Thermal-diffusion constant as a function of temperature (°K) for a $Kr-N_2O$ mixture ($x_1 = x_2$). Experimental data: 1) author's; 2) [9]. Calculated data: 3) by the Lennard-Jones (12-16) potential; 4) the (12-6-5) potential; 5) α_{ij} allowing for inelastic collisions.

Fig. 2. Concentration dependence of the thermal-diffusion constant α_T for an NH_3-CO_2 mixture at $\bar{T}$ = 330°K. Points) experimental data. Calculated data: 1) using the (12-6-3) potential [13]; 2) α_{ij} allowing for inelastic collisions.

see on comparing the calculated data with experiment (Fig. 1) that the α_T data obtained after allowing for the inelastic collisions of the molecules be an order of magnitude above the experimental results. The Chapman–Enskog theory gives results agreeing more closely with experiment.

NH_3-CO_2. For the NH_3-CO_2 mixture no published data regarding the thermal-diffusion constant are available. It should be noted that very few investigations have yet been carried out for mixtures of NH_3 with other gases; NH_3 is one of a number of gases in which the molecules have a high dipole moment, so that a study of thermal-diffusion separation in mixtures of NH_3 with other gases might produce useful information regarding the effect of the dipole moment on the value of α_T.

We studied the concentration dependence of the thermal-diffusion constant of the NH_3-CO_2 mixture at a mean temperature of $\bar{T}$ = 330°K (T_1 = 293.5°K; T_2 = 373°K) (Fig. 2). The accuracy of the resultant data was estimated as ±4.6%.

It follows from Fig. 2 that, despite the considerable scatter in the experimental data, the general behavior of the concentration dependence of α_T is characterized by a positive deviation from the linear relationship and does not obey the relationship proposed in [10]. Data calculated by the Chapman–Enskog theory using the (12-6-3) potential [13] fail to describe the experimental results; the same applies to the theory of Monchick et al. [16] allowing for the inelastic collisions of the molecules.

This disagreement between theory and experiment may be associated with the fact that the NH_3 is paired with CO_2. Experiments [21-24] have shown that the behavior of the thermal-diffusion coefficient α_T of mixtures of CO_2 even with certain inert gases ($Ar-CO_2$, $Ne-CO_2$, $Xe-CO_2$) exhibits a number of singularities which have never yet received a proper physical explanation.

As in the case of the $Kr-N_2O$ mixture, the theory allowing for inelastic collisions between the molecules in the NH_3-CO_2 mixture disagrees more seriously with experiment than the Chapman–Enskog theory.

LITERATURE CITED

1. W. W. Watson and D. Woernley, Phys. Rev., 63, 181 (1943).
2. K. E. Grew, Phil. Mag., 7, 35, 30 (1944).
3. K. E. Clusius and M. Z. Huber, Naturforsch., 10a, 556 (1955).
4. E. A. Mason and L., Monchick, J. Chem. Phys., 36, 2746 (1962).
5. B. P. Mathur and W. W. Watson, J. Chem. Phys., 49, No. 12, 5537 (1968).
6. A. K. Chosh, A. K. Batabyal, and A. K. Barua, J. Chem. Phys., 47, No. 2, 452 (1967).
7. E. W. Becker and E. Dörnenberg, Naturwissens., 37, 165 (1950).
8. E. W. Becker and W. Beyrich, J. Phys. Chem., 56, 911 (1952).
9. K. K. Datta, Seal Parag, and A. K. Barua, J. Phys. Soc. Japan, 37, 4 (1974).

10. A. F. Zolotukhina and O. A. Kolenchits, in: Heat and Mass Transfer and Thermophysical Properties of Materials [in Russian], ITMO, Akad. Nauk BelorusSSR, Minsk (1974).
11. A. F. Zolotukhina, in: Properties of Heat and Mass Transfer in Materials [in Russian], ITMO, Akad. Nauk BelorusSSR, Minsk (1975).
12. A. F. Zolotukhina, in: Heat and Mass Transfer and the Transport Properties of Materials [in Russian], ITMO, Akad. Nauk BelorusSSR, Minsk (1972).
13. E. A. Mason and L. Monchick, J. Chem. Phys., 36, 6 (1962).
14. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids Wiley (1964).
15. F. J. Smith, R. J. Munn, and E. A. Mason, J. Chem. Phys., 46, 317 (1967).
16. L. Monchick, R. J. Munn, and E. A. Mason, J. Chem. Phys., 45, 3051 (1966).
17. C. S. Wang-Chang and G. E. Uhlenbeck, Transport Phenomena in Polyatomic Gases, University of Michigan Engineering Research Report, NO S-M. 681 (1951).
18. C. S. Wang-Chang, G. E. Uhlenbeck, and J. de Boer, Studies in Statistical Mechanics (1964).
19. N. B. Vargaftik, Handbook on the Thermophysical Properties of Gases and Liquids [in Russian], FM, Moscow (1972).
20. A. G. Shashkov and F. P. Kamchatov, Izv. Akad. Nauk BelorusSSR, Ser. Fiz.-Énerg. Nauk, No. 4 (1973).
21. L. Z. Waldmann, Naturforsch., 4a, 105 (1949).
22. S. Weissmann, S. C. Saxena, and E. A. Mason, Phys. Fluids, 3, 510 (1960); 4, 643 (1961).
23. J. R. Cozens and K. E. Grew, Phys. Fluids, 7, 1395 (1964).
24. A. K. Batabyal and A. K. Barua, J. Chem. Phys., 48, 2557 (1968).

COMPARISON OF METHODS OF DESCRIBING MASS TRANSFER IN MULTICOMPONENT MIXTURES

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The accuracy of three basic approximate methods of describing mass transfer in multicomponent mixtures is estimated by using a mathematical model of intraphase mass transfer.

One of the main trends in the improvement of methods of calculating separation processes in multicomponent mixtures (MCM) in chemical engineering involves taking account of the kinetic equations of mass transfer. In spite of the considerable number of papers which have been published in this field, the kinetics of mass transfer has not been adequately studied. As a result of the extreme complexity of convective mass-transfer problems and the inadequate study of molecular and turbulent diffusion, all the methods of describing multicomponent mass transfer so far developed are approximate. The question of accuracy and the limits of applicability of these methods remains debatable, since physical experiments [1, 2] and their comparison with calculational methods proposed in the literature [3] so far cannot give a comprehensive answer.

The present paper is devoted to an analysis of the accuracy of various approximate methods of describing mass transfer and the development of recommendations for their use in mathematical models.

The equations describing mass transfer in multicomponent mixtures have the form [4]

$$N_i = \sum_{j=1}^{n} \mathbf{B}_{ij} (y_{jf} - y_j). \tag{1}$$

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