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Thermal Diffusion Factor of He-N_2 Mixture Above 1 atm

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Abstract: The thermal diffusion factor α_T of He-N_2 mixture is determined by new thermal diffusion column method for a wide range of the light component concentrations ($x_{He} = 0$–1.0) at average temperatures 326 K and 347 K and pressures ranging from 0.193 to 0.88 MPa. It is found out that ${\alpha_T}^{-1}$ is a nonlinear function of the gas concentration at pressures above 0.35–0.38 MPa, the dependence of α_T on pressure has a minimum at 0.2–0.4 MPa and a maximum above 0.5 MPa, and the thermal diffusion factor of He-N_2 mixture is independent on gas concentration at 0.35–0.38 MPa.

Keywords: Gas mixture, He-N_2, thermal diffusion, thermal diffusion column, thermal diffusion factor

INTRODUCTION

The thermal diffusion factor α_T (TDF) is a fundamental parameter that characterizes the thermal diffusion (TD) process in fluids. The exact determination of its dependence on the mixture composition, temperature, and pressure for binary gas mixtures is a very important purpose of the investigations in the field. The knowledge of this dependence is important to comprehend the nature and the evaluation of the intermolecular interactions strength in these mixtures. On the other hand, the best possible knowledge of the TDF in a large interval of pressures, concentrations,

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and temperatures is necessary for the technological description of the TD process in gas separation installations or other TD equipment.

The TDF of He-N_2 mixture is studied by many researchers in wide ranges of temperature and pressure (1–7). Most of the quoted authors have been investigating the TDF as a function of the mixture composition at or near atmospheric pressure. The investigations above 1 atm. are insufficient and the dependence of α_T on pressure is studied only (3 and 4). There are no data about α_T as a function of the light component concentration at these conditions. The investigation of this dependence is very interesting because the research of some other mixtures show a non-linearity of the TDF dependence on concentration above 1 atm. (8).

The aim of the present work is to investigate the TDF of He-N_2 mixture as a function of the components concentration at different pressures above 1 atm.

EXPERIMENTAL METHOD AND SET-UP

The experimental method and set-up are based on a thermal diffusion column (TDC). The possibility of TDF experimental determination for binary gas mixture by a new TDC method is presented in Ref. 9. According to this paper the processes in the TDC can be described by the equation

$$\alpha_T = \ln[(N + \ln Q_L)/(N - \ln Q_H)]/\ln(T_H^*/T_C^*), \tag{1}$$

where

$$N = h/h_0, \tag{2}$$

$$Q_L = x_T/x_B, \tag{3}$$

$$Q_H = (1 - x_B)/(1 - x_T), \tag{4}$$

$$h_0 = (h_c + h_d)\,k_p, \tag{5}$$

$$h_c = (\rho\ g\ \Delta T\ \delta^4)/(1008\ \eta\ D\ \overline{T}), \tag{6}$$

$$h_d = (360\ \eta\ D\ \overline{T})/(\rho\ g\ \Delta T\ \delta^2), \tag{7}$$

$$\overline{T} = [T_H T_C/(T_H - T_C)]\ln(T_H/T_C), \tag{8}$$

$$T_H^* = (T_H + \overline{T})/2, \tag{9}$$

$$T_C^* = (T_C + \overline{T})/2, \tag{10}$$

$$\Delta T = T_H - T_C. \tag{11}$$

The following symbols are used in Eqs. (1–11):

ε – enrichment coefficient,
g – gravitational constant, m/sec^2,
ρ – mixture density, kg/m^3,
x – molar fraction of the lighter component,
T_H – temperature of the hot wall of the TDC, K,
T_C – temperature of the cold wall of the TDC, K,
T_H^* – average temperature of the hot gas flow in TDC, K,
T_C^* – average temperature of the cold gas flow in TDC, K,
δ – distance between hot and cold walls, m,
D – coefficient of mutual diffusion, m^2/sec,
η – dynamic viscosity, $n.sec/m^2$,
h – geometric height of TDC, m,
h_0 – mass transfer unit height, m,
h_c, h_d – components of h_0, corresponding to FJO coefficients K_c and K_d (see 10 and 11) about K_c and K_d, m,
k_p – coefficient for estimation the deviation of the TDC from and ideal one ($k_p = 1.0 - 1.2$ (9)),
N – number of mass transfer units along the height of the column,
Q_L – degree of enrichment of the light component (He),
Q_H – degree of enrichment of the heavy component (N_2).

The high degrees of separation, which are a disadvantage of the known TDC methods, when mixtures of gases with considerably different physical properties are investigated, could turn advantageous. For this purpose the quoted method is developed further more as follows:

The concentration variation of the light component along the TDC height, when the column is sufficiently high, would appear as shown in Fig. 1. Practically, the whole curve could hardly be observed but considerable fragments of it can be realized. On the other hand, it is well known that Eq. (1) describes the physical processes not only in the whole column but in any single section of it, as well (10,11). Hence, if the concentration variation along the TDC height is known it can be divided into sections (microcolumns, micro-TDC). Then the concentration variations in each of them will be sufficiently small and the value of α_T in this section can be estimated more precisely by using Eqs. (1–11). Practically, it means that the experiment is carried out simultaneously in four different columns with four different gas mixture compositions. Thus, the value of α_T can be defined for any section (microcolumn) and the dependence $\alpha_T^{-1}(x_0)$ in the interval from x_B to x_T can be determined in one only experiment (at $\overline{T}$ = const and p = const), where x_0 is the mean concentration of the light component in the micro-TDC during the experiment.

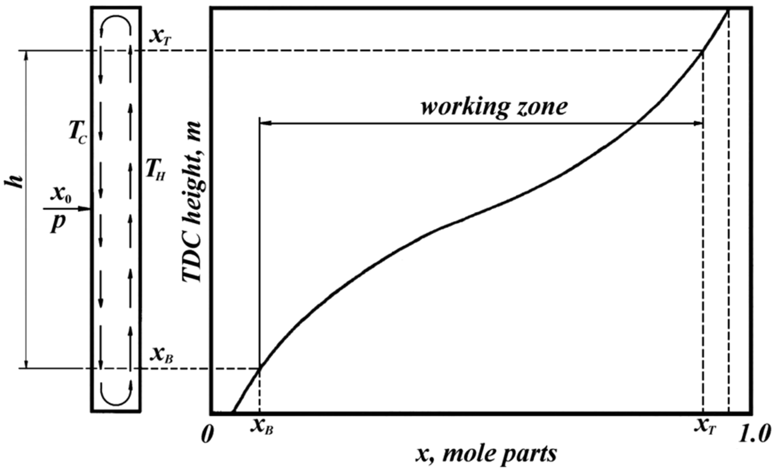

Figure 1. The concentration variation of the light component along the TDC height.

This allows to investigate the dependence $\alpha_T^{-1}(x_0)$ ($\overline{T} = \text{const}$ and $p = \text{const}$) over the whole interval $x_0 = 0$–1.0 within 3–4 experiments by using mixtures with different gas composition.

This is the principle difference between this method and the conventional methods. By comparison, the conventional column methods available allow to determine only one point from the curve in one experiment.

To avoid the edge effects, both ends of the curve have to be neglected (see Fig. 1). The term "working zone" is used in the figure in order to label the employed part of the curve.

The principal scheme of an experimental setup that realizes the method is shown in Fig. 2. As the TDC is the most important element of the experimental setup its schematic plan is drawn in Fig. 3. Positions from 1 to 5 are the same as in Fig. 2.

The TDC is made by two concentric 2400 mm long tubes 2 and 4 (see Figs. 2 and 3). The outer diameter of the inner tube 2 is 32 mm. and the inner diameter of the outer tube 4 is 38 mm. The colinearity between tubes 2 and 4 is achieved by the guide bush 6 and the conflate flanges 1. The outer tube 4 is stainless steel and the inner one consist of stainless steel tube Ø30 × 1 stuffed in a brass tube Ø32 × 0.9 mm (see positions 2 in Fig. 3). This is done to increase the heat conductivity of the inner tube 2 to ensure higher uniformity of the temperature field along the inner tube. The temperature gradient along the column height is less than 2 K for the higher values of T_H. The distance between the inner (hot) and outer (cold) walls of the column is fixed to be $\delta = 3 \pm 0.1$ mm. This value of δ

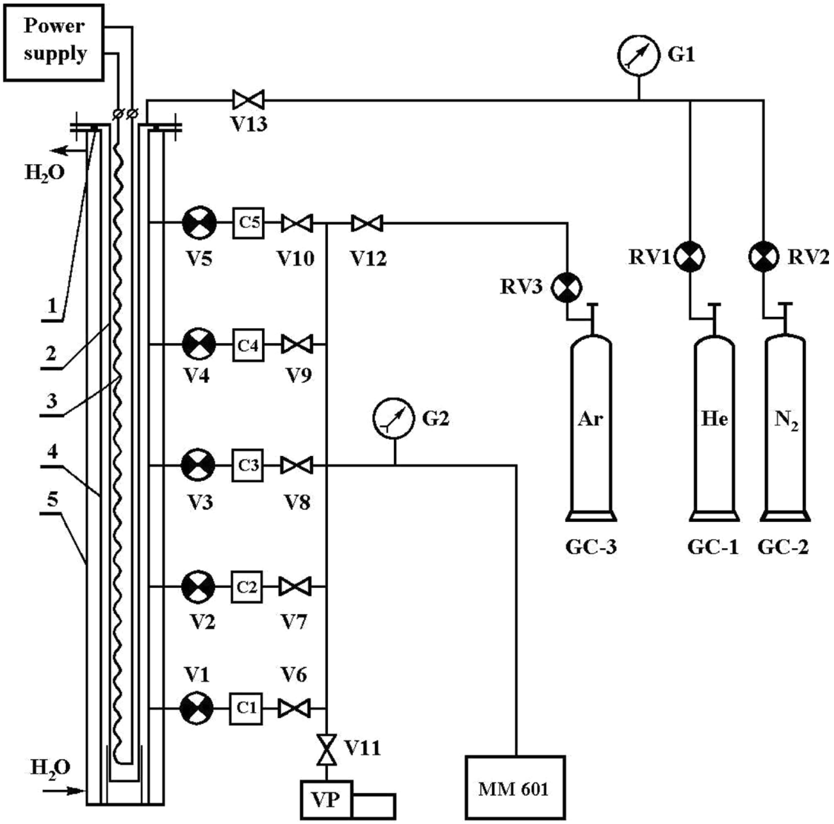

Figure 2. Principal scheme of the experimental set-up.

is chosen so that the Q(p) dependence maximum is between 0.3 and 0.6 MPa at $\overline{T} = 320 - 460\,K$ for the investigated N_2-He mixture. This construction, when necessary, allows a variation of the distance δ by changing the outer tube of the column. The ratio outer/inner diameters is less than 1.2 that is sufficiently low to consider that the column geometry is pseudoplane. An electrical heater 3 is mounted in the inner tube 2. It is connected to the power supply PS-1 (see Fig. 2) which permits a variation of the power from 0 to 12 kW. The heater is made of 8 parallel connected Cantal A rods with a diameter 4 mm. (see positions 8 in Fig. 3), fixed along the length of the inner tube 2 (see cross section in Fig. 3). The power supply is connected to the bottom of the column via copper tube 5 mm in diameter and 1 mm thick fitted tightly in a Ø6 × 0.4 mm stainless steel tube 9 to avoid the oxidation of the copper at high temperatures during the experiments.

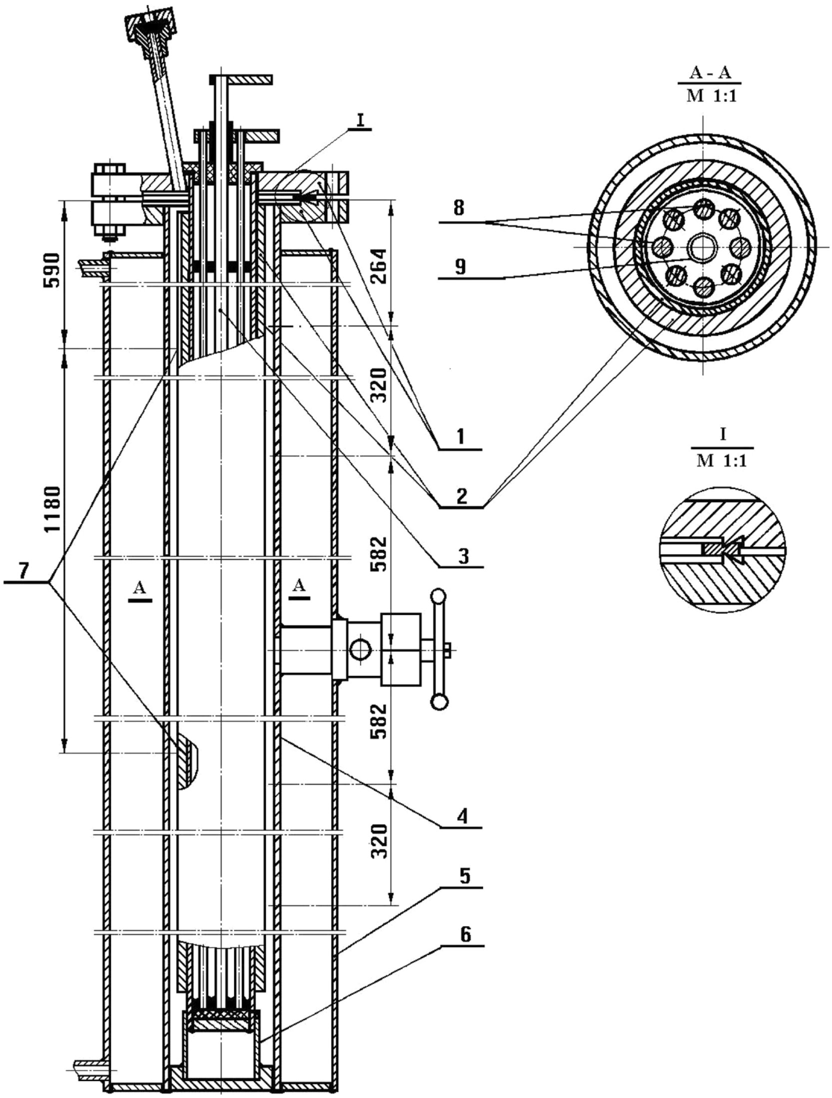

Figure 3. Thermal diffusion column plan.

The TDC hot wall temperature T_H is regulated by changing of the power supply. It can be varied from 300 K up to 800 K. This temperature is controlled by two Ni-Ni/Cr thermocouples (not visible on a schematic plan in Fig. 3) with an accuracy of ± 1 K. The thermocouples are put into a channel built in the inner stainless steel tube 2 along its length, covered by the brass tube and filled with ceramic isolation. So they are fixed at two different heights in the rectangular channel formed between the inner stainless steel tube and the outer brass tube (see positions 2 in Fig. 3). The distance between them is 1180 mm (see positions 7 in Fig. 3).

The outer tube 4 of the TDC is surrounded by water jacket 5. The temperature T_c can be kept between 280 K and 290 K by regulation of the water flow with an accuracy of ±0.5 K.

The concentration of the gas mixture is accomplished for any single experiment. First the TDC is evacuated two times through valves V1 ÷ V5 by a vacuum pump VP. It is filled with any of the investigated gases between both evacuations. The column is filled with the investigated gases from the gas cylinders GC-1 and GC-2 through the reduction valves RV1 and RV2. The ratio between two components is realized using a manometer G1 with accuracy 0.6%. The working pressure can be in the range 0.2 ÷ 1.2 MPa. First, the cameras C1 ÷ C5 are evacuated twice down to 1 Pa with the vacuum pump VP. The pressure therein is measured with the manometer G2. The cameras are filled with Ar or other neutral gas from the gas cylinder GC-3 between two evacuations. Gas samples for analysis are taken from 5 points at different heights through valves V1 ÷ V5 (see Figs. 2 and 3). The cameras C1 ÷ C5 are filled with gas from the TDC. Their volume (2 ÷ 3 cm^3 for each of them) is substantially less than the column volume (about 1200 cm^3). Therefore, the extraction of the gas samples does not affect observable the TDC process. The gas from cameras C1 ÷ C5 goes for analysis through valves V6 ÷ V10 into the mass spectrometer Micromass MM601 which sensitivity is of the order of 1 ppm.

The distance between valves V1 and V5 is 1804 mm. This is the working zone of the TDC (see Fig. 1). There are two sections on both sides of the working zone in which the composition of the gas mixture is not controlled. The upper one is 264 mm long and the lower 312 mm long (see Fig. 3).

The column was filled with the investigated gas mixture with chosen gas concentration under chosen pressure. The cooling water and the heater 3 (see Fig. 2) kept up the chosen temperatures T_H and T_C. When the separating process was stabilized (the relaxation time was experimentally obtained previously), samples for analysis are taken through valves V1 ÷ V5. After that the new experiment with the other mixture can be done.

The valves V1 ÷ V5 divide the working zone of TDC into 4 "micro-TDC", which top and bottom concentrations x_{Ti} and x_{Bi} are determined by a masspectrometer MM 601. The experiments showed that it was enough usually to have micro-TDCs in which the concentration variation along the height of the column was linear or almost linear and its gradient was sufficiently small. If the concentration variation in the micro-TDC was linear or almost linear it could be accepted that the mean concentration in the i-th micro-TDC was

$$x_{0i} = (x_{Ti} - x_{Bi})/2 \qquad (13)$$

otherwise the determination of x_{0i} became more difficult. Our estimations and preliminary experiments showed that the concentration gradient could be considered sufficiently small in most cases if

$$\Delta x = x_T - x_B \leq 0.15. \qquad (14)$$

If this condition was fulfilled the gas properties along the height of micro-TDC could be considered almost constant. Further decrease of Δx did not lead to significant improvement of the results. If the concentration variation along the height of any of the micro-TDC was too large then the micro-TDC had to be divided into two or more parts. The He concentrations in the dividing points between these new microcolumns could be calculated using a mathematical description of the law of a concentrations variation along the height of the whole TDC.

The total inaccuracy in determining α_T through the factors N, Q_L and Q_H and by the ratio (T_H/T_C) was estimated to be less than 5%. The values of ρ, η, and D were deduced for the values of x_0, T and p for each of the defined micro-TDC. T and p were uniform for all micro-TDC for any single experiment. The TDF was calculated using Eqs. (1–11) for each micro-TDC.

EXPERIMENTAL RESULTS AND DISCUSSION

The gas mixtures were studied at the following conditions in the TDC:

Cold wall temperature of the TDC – $T_C = 287.5 \pm 0.5$ K (287–288 K),

- Hot wall temperature of the TDC – $T_H = 373$ K and 423 K,
- Logarithmical average temperature – $\overline{T} = 326$ K and 347 K, and
- Gas mixture pressure in the TDC – $p = 0.193 - 0.88$ MPa.

Experiments were carried out with 3–4 gas mixtures at 326 K and p = const, changing consecutively the pressure from 0.193 MPa to 0.88 MPa. Then the procedure was repeated at $\overline{T} = 347$ K. The following parameters were measured during the experiments:

- Temperatures of the hot and the cold walls of the TDC – T_H and T_C,
- Pressure in the TDC – p,
- Concentrations of the light component (He) taken for analysis through valves V1 ÷ V5 to define x_{Bi} and x_{Ti} for each microcolumn and the dependence x(h), if necessary.

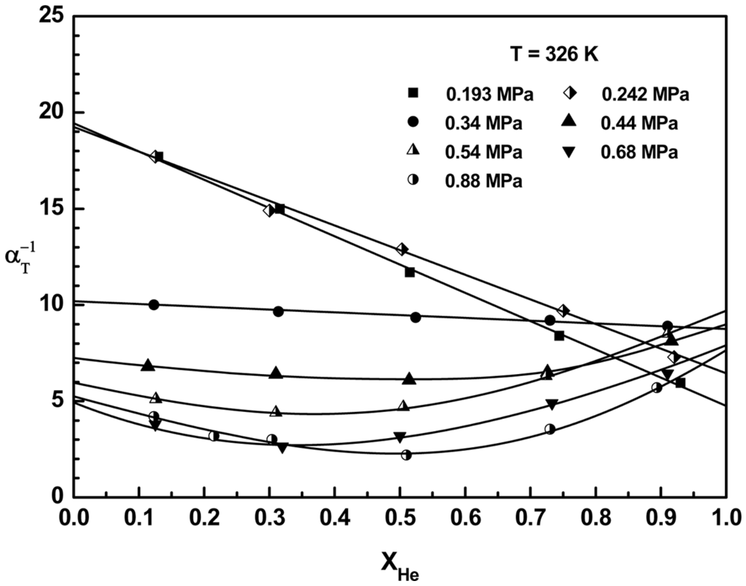

Figure 4. Experimental values of α_T as a function of mean concentration x_0 at $\overline{T} = 326$ K and $p = 0.193$, 0.242, 0.34, 0.44, 0.54, 0.68 and 0.88 MPa.

The value of k_p was accepted to be $k_p = 1.05$ because the TDC was manufactured very precisely.

The results for $\alpha_T{}^{-1}(x_0)$ at $\overline{T} = \text{const}$ and $p = \text{const}$ are shown in Figs. 4 and 5. It is well seen that the dependence of $\alpha_T{}^{-1}(x_0)$ is linear in the pressure range 0.193–0.34 MPa and can be described by equation

$$\alpha_T{}^{-1} = b - m x_0 \tag{15}$$

where

$$b = \alpha_T{}^{-1}(0), \tag{16}$$

$$m = \alpha_T{}^{-1}(0) - \alpha_T{}^{-1}(1). \tag{17}$$

On the other hand, it is nonlinear above 0.44 MPa and a minimum is observed between $x_0 = 0.3$ and $x_0 = 0.6$. Therefore in Eq. (15) appears a nonlinear term $\Delta(x_0)$ and it transforms to

$$\alpha_T{}^{-1} = b - m\ x_0 - \Delta(x_0). \tag{18}$$

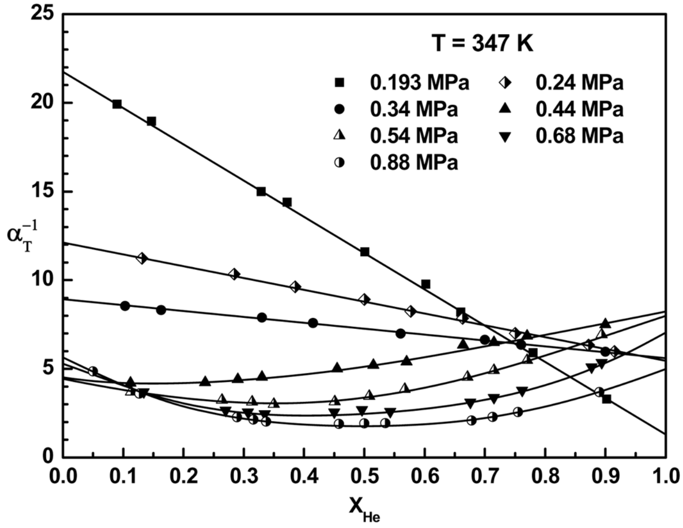

Figure 5. Experimental values of α_T as a function of mean concentration x_0 at $\overline{T} = 347\,K$ and $p = 0.193$, 0.242, 0.34, 0.44, 0.54, 0.68, and 0.88 MPa.

In this case ($p > 0.44$ MPa), the value of ${\alpha_T}^{-1}(1)$ becomes higher than ${\alpha_T}^{-1}(0)$ while ${\alpha_T}^{-1}(1) < {\alpha_T}^{-1}(0)$ in the lower pressure range. It is obvious that there is a point in the range 0.34–0.44 MPa where

$${\alpha_T}^{-1}(0) = {\alpha_T}^{-1}(1)$$

and coefficient m in Eqs. (15) and (18) becomes equal to 0. This fact is illustrated in Fig. 6, where the dependence of m(p) is shown for both temperatures 326 K and 347 K. It is calculated by using Eq. (17). The coefficient $m > 0$ at 0.193–0.34 MPa, $m < 0$ in the upper range and $m = 0$ in the region of $p \approx 0.35$–0.38 MPa.

Laranjeira, using Chapman's r.e.s. first approximation, has proved theoretically the nonlinearity of the ${\alpha_T}^{-1}(x_0)$ dependence (12). He has shown that Eq. (18) is valid at any pressure. According to him the nonlinear term in Eq. (18) for inert gas mixtures is defined as

$$\Delta(x_0) = a\ x_0(1 - x_0)/(x_0 + c) \tag{19}$$

where a and c are temperature and pressure dependent coefficients specific for every mixture. Laranjeira has estimated the value of $\Delta(x_0)$ to be less than 1% of the ${\alpha_T}^{-1}$ value and can be neglected. Our results and the results of T. Makita (8) show that it increases with pressure increasing

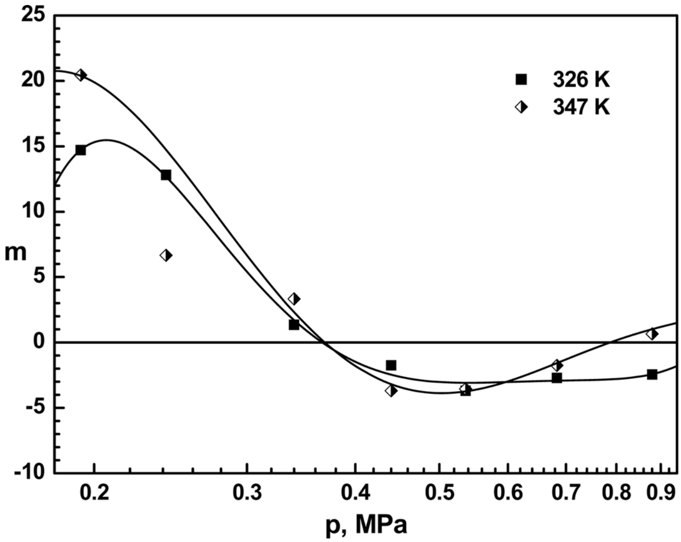

Figure 6. Coefficient m dependence on pressure at $\overline{T} = 326\,K$ and 347 K.

and cannot be neglected above some "critical" pressure p_c. This critical value for the He-N_2 mixture is $p_c \approx 0.35$–0.38 MPa, according to the experimental data (see Fig. 6). The results for $\alpha_T(p)$ at $\overline{T} = \text{const}$ and $x_0 = \text{const}$, shown in Figs. 7 and 8, confirm this conclusion. The data for $\alpha_T(p)$ are calculated by interpolation of the experimental data shown in Figs. 4 and 5. It is well seen that $\alpha_T(p)$ curves overlap in a point, approximately. This fact means that α_T does not depend on the concentration at this pressure or the dependence is negligible. So, when the pressure becomes $p = p_c$

$$\alpha_T^{-1}(x_0) = \text{const}$$

and respectively

$$m = 0 \text{ and } \Delta(x_0) = 0.$$

The overlap of the $\alpha_T(p)$ curves is observed also by C.A. Velds et al. for He-CO_2 mixture (13).

It is well known that the thermal diffusion is a II order effect due to the intermolecular collisions, as well as on the nature of the force field between molecules, and on their masses and collision diameters. Obviously, the multimolecular interactions, the size and the mass of the gas molecules, and the force field between them begin to have a more considerable influence on the properties of the gases and their mixtures

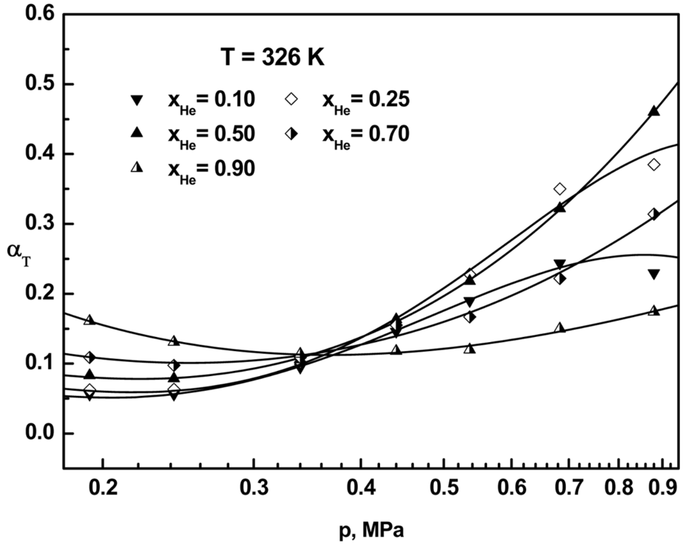

Figure 7. TD factor α_T as a function of pressure at $\overline{T} = 326\,K$ and $X_0 = 0.1, 0.25, 0.50, 0.70,$ and 0.90.

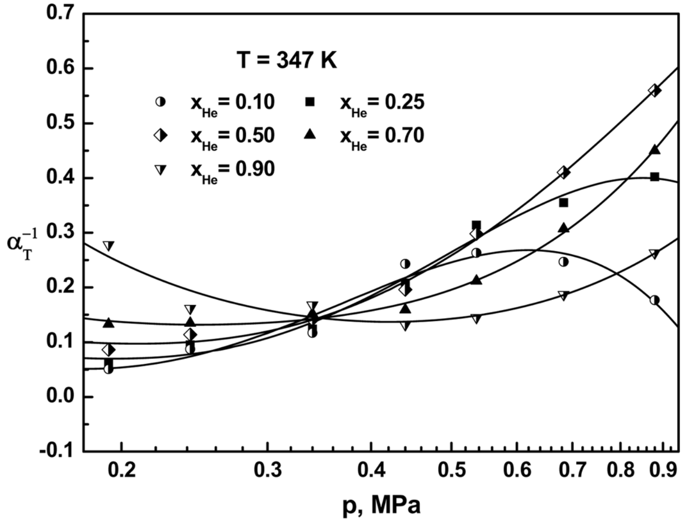

Figure 8. TD factor α_T as a function of pressure at $\overline{T} = 347\,K$ and $X_0 = 0.1, 0.25, 0.50, 0.70,$ and 0.90.

at higher pressures. We consider that this is the main cause for the nonlinearity of $\alpha_T^{-1}(x_0)$ above p_c.

Another interesting fact is that all $\alpha_T(p)$ curves pass through a minimum at $p = 0.2–0.6$ MPa and through a maximum above 0.5 MPa, which are shifted to the pressures so the concentration of the light component (He) increases (see Figs. 7 and 8). At low pressures ($p < p_c$) α_T is greater for higher concentration of the light component. At higher pressures ($p > p_c$ or a little higher) the greatest values of α_T are for $x_0 \approx 0.5$.

Presence of a minimum of the $\alpha_T(p)$ curves have been observed by C.A. Velds et al. for He-CO_2 mixture (13) and by Van Ee for He-N_2 mixture. The results of Van Ee were quoted by W.A. Oost et al. in Ref. 3. Working on his doctoral degree, he studied He-N_2 mixture, containing 49.2% He at pressures 0.1–15 atm and temperatures 77–290 K. Numerically our results are analogous to the results of Van Ee. The main difference is that according to his observations the minimum is smaller and probably at lower pressure (the right value cannot be found precisely because of the lack of data between 0.1 and 1.9 atm and below 0.1 atm).

CONCLUSIONS

Some interesting results are obtained during our investigations, described in this paper. The thermal diffusion factor of the He-N_2 mixture is determined at $p = 0.193–0.88$ MPa, $x_0 = 0–1.0$ and mean temperatures 326 K and 347 K. This experimental result can be useful for the practice (TDC designing for example) or for research aims. The presence of a minimum on $\alpha_T(p)$ for He-N_2 mixture, observed by Van Ee (3), is confirmed. It is shown that the nonlinear term in Eq. (15), proved theoretically by Laranjeira (12), has a considerable values above p_c and cannot be neglected. Therefore, the $\alpha_T^{-1}(x_0)$ dependence of He-N_2 mixture is nonlinear above p_c. It is found out that $\alpha_T(p)$ dependences overlap to a point, approximately, which means that α_T does not depend on the concentration at $p = p_c$. The nature of this effect is not clear, the importance is obvious and its explanation lies ahead.

The proposed new experimental method and set-up allow getting the reliable experimental results in a large temperature and pressure ranges, for arbitrary concentrations and physical properties of the investigated gas mixtures.

We believe our results and the new experimental method will be useful for other researchers working in the field, especially concerning the process analysis in the thermal diffusion columns and for better comprehension of the nature and the evaluation of the intermolecular interactions strength.

ACKNOWLEGEMENTS

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