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On the Determination of the Thermal Diffusion Factor from Column Measurements

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A new method for experimental determination of the thermal diffusion factor α_T for binary gas mixtures with a thermal diffusion column (TDC) is developed, based on A. M. Rozen's equation of TDC. The experimental results for α_T are obtained in a reduced form in this approximation. An experimental reference point, determined in the same TDC with a standard gas mixture, is used for the transformation of the results for α_T in absolute units. The proposed method is applicable for arbitrary gas mixtures, irrespective of the mass difference of the components.

KEY WORDS: gas mixtures; thermal diffusion; thermal diffusion factor.

1. INTRODUCTION

Thermal diffusion (TD) was theoretically predicted by Enskog [1] and Chapman [2] independently in 1911 and 1912. The effect was experimentally confirmed in 1917 by Chapman and Doutson [3] on H_2–CO_2 and H_2–SO_2 mixtures using the two-bulb method. The detailed investigation of this effect was started with the works of Ibbs [4] and other investigators 2 years later. More recently a sufficiently rigorous point of view on the physical aspects of TD was given by Monchik and Mason [5] (see also Ref. 6).

Up to the discovery of the thermal diffusion column (TDC) by Clusius and Dickel [7], TD aroused only academic interest. The remarkable conclusion of Clusius and Dickel, that it is possible to create a continuous mass transfer by the thermal diffusion effect in conjunction with the vertical

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convection flows, led to the practical use of the TDC for separation of liquid and gas mixtures.

The theory of TDC was developed by Clusius and Dickel [8], Waldmann [9], and Van der Grinten [10]. A more general theory was lated proposed by Bardeen [11].

Exact solutions for the TDC with a flat geometry were given by Furry et al. (FJO) [12]. The coaxial cylindrical column, more suitable for practice, was considered by Furry and Jones [13]. In all the former cases very idealized models were used—a Maxwellian gas or a gas of hard spheres, one-component systems, and others. The theories of TDC are reviewed in an elementary, but physically clear way in the article by Jones and Furry [14].

All these early theories are based on the kinetic theory of gases, the kinetic coefficients being obtained from kinetic equations derived in terms of collision cross section and mean free path. The FJO theory was modified by Rutherford and co-workers [15, 16] for the purpose of including the case of the light-isotope mixture separation in TDC with an annular space geometry. Relations, derived in Ref. 16, have been used by this author for obtaining the TD factor α_T of dilute Ne–Xe mixtures in the TDC, the separation process being confined between two vertical, concentric tubes [17]. In more recent papers [18, 19], Rutherford extended his theoretical treatment of the problem, obtaining numerical evaluation for TDC equations under conditions of large temperature differences and when the properties of the gas mixture components strongly depend on the temperature.

On the other hand, Rozen [20] showed that the problem for separation of gas mixtures in a TDC can be considered in the framework of the general phenomenological theory of mass transfer using the concept of transfer unit height (TUH).

2. THERMAL DIFFUSION FACTOR: METHODS FOR ITS DETERMINATION

According to nonequilibrium thermodynamics [21], the overall mass diffusion flow j along the coordinate s in an n-component system at the absence of any external forces is given by

$$j_k = -\rho \left[\sum_{j=1}^{n} D_{kj}\, \partial x_j/\partial s - D_{Tk}\, \partial(\ln T)/\partial s \right] \qquad (1)$$

where ρ is the density of the gas mixture, x_j is the concentration of the corresponding component of the mixture, D_{Tk} is the thermodiffusion coefficient of the kth component, and D_{kj} is the matrix element of the coefficient of mutual diffusion.

At equilibrium the overall flow is equal to zero, and from Eq. (1) follows

$$dx_j = \left(D_{\mathrm{T}k} \bigg/ \sum_{j=1}^{n} D_{kj} \right) d(\ln T) \tag{2}$$

Usually instead of $D_{\mathrm{T}k}$ the thermal diffusion factor α_{T} is used. The latter is defined by

$$D_{\mathrm{T}k} = \alpha_{\mathrm{T}kj} x_j \sum_{j=1}^{n} (x_k D_{kj}) \tag{3}$$

In the case of a binary gas mixture, one obtains from Eqs. (2) and (3) the following expression for α_{T}:

$$\alpha_{\mathrm{T}} = d\left(\ln \frac{x}{1-x} \right) \bigg/ d(\ln T) \tag{4}$$

If α_{T} is independent of the temperature T, the integration of Eq. (4) between two points at which the temperatures are T_1 and T_2 and the concentration of the light component, x_1 and x_2, respectively, leads to

$$\alpha_{\mathrm{T}} = \ln q / \ln(T_2/T_1) \tag{5}$$

where q is defined as a coefficient of separation for a gas mixture at the stated conditions

$$q = x_2(1-x_1)/x_1(1-x_2) = (T_2/T_1)^{\alpha_{\mathrm{T}}} \tag{6}$$

The thermal diffusion factor α_{T} can be determined by Eq. (5) or (6), using the two-bulb method [3] or swing separator [22].

The two-bulb method was historically the first to be used and now is considered classical. However, it is affected by several serious drawbacks. In order to get reliable data, large temperature differences must be used because of the small concentration changes. The great relaxation times involved make this method difficult to use at high pressures (i.e., for high densities).

The swing separator does not have these drawbacks, but when working at high pressures, there are technological problems with the construction and the operation of the pump, which has to push and pull the gas as a whole through the assembly.

Another method for the experimental determination of the thermal diffusion factor α_T is gas separation process analysis in a thermal diffusion column [7]. The TDC method seems to be the most universal one with respect to the working temperature and pressure ranges [15]. An ideal TDC with flat-parallel geometry is shown schematically in Fig. 1. The gravitational field and the difference between temperature T_2 and temperature T_1 of the hot and cold wall, respectively, create convective flows L and G through the column, leading to a considerable multiplication of the elementary TD effect expressed by the transverse diffusion mass flow τ along the height of the column. According to Vasaru et al. [23],

$$\tau = Hx(1-x) - K\,\partial x/\partial z - K'_d\,\partial^2 x/\partial z^2 + K_t\,\partial x/\partial t \tag{7}$$

where H, K, K'_d, and K_t are transport coefficients, reflecting the influence of the diffusion, hydrodynamic, and thermal processes on the formation of the concentration field; $(\partial x/\partial t)$ denotes the time derivative.

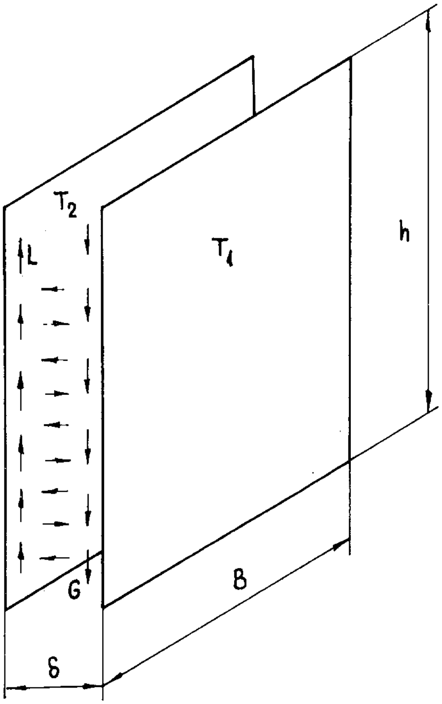

Fig. 1. Schematic drawing of a thermal diffusion column with flat-parallel geometry.

In the case of the stationary or quasi-stationary process, $\partial x/\partial t = 0$ and the term $K_t\, \partial x/\partial t$ should be omitted [23]. Saxena and Raman showed [24] that neglecting the third term in Eq. (7), i.e., assuming that $(K'_d\, \partial^2 x/\partial z^2) \approx 0$, leads to inaccuracy in the determination of the flow rate τ which does not exceed 1%, so that eq. (7) would be reduced to the Furry and Jones relation [13]:

$$\tau = Hx(1-x) - K\, \partial x/\partial z \tag{7a}$$

Integrating Eq. (7a) in the static case gives

$$\ln Q = (H/K)h \tag{8}$$

where h is the geometrical height of the column.

The quantity Q is defined as the degree of separation for the TDC. It gives the interval in which the concentration of each component can vary along the height of the column. By definition,

$$Q = x(1-x_0)/[x_0(1-x)]$$

where x_0 is the initial and x is the final concentration of whichever gas component. If the TDC is considered as a single separation element, $Q = q$.

The coefficients H and K can be interpreted as components of mass flow and depend on the geometry of the column. As shown in Ref. 13 for flat geometry,

$$H = (\alpha_T\, g\rho^2\, \delta^3\, \Delta T^2 B)/(6!\, \eta \bar{T}^2) \tag{9}$$

$$K = K_c + K_d + K_p \tag{10}$$

$$K_c = (\rho^3 g^2\, \delta^7\, \Delta T^2 B)/(9!\, \eta^2 \bar{T}^2 D) \tag{11}$$

$$K_d = \rho\, D \delta B \tag{12}$$

Here g is earth's gravitational acceleration, η is the viscosity of the initial gas mixture, D is the diffusion coefficient, B is the width (average perimeter) of the column, δ is the distance between the hot and the cold wall of the column (see Fig. 1),

$$\Delta T = T_2 - T_1$$

and

$$\bar{T} = [T_1 T_2/(T_1 + T_2)] \ln(T_2/T_1)$$

is the average temperature at which the values of the parameters depending on T are given. It is generally assumed that in the case of large ΔT, it is better to use the mean logarithmic than the simple mean value of T [25].

The coefficient K_p is introduced because of the nonideal geometry of the TDC and the nonuniform temperature field leading to a parasitic convection. For an ideal column $K_p = 0$.

Introducing the expressions for H and K from Eqs. (9)–(12) in Eq. (8) for an ideal TDC ($K_p = 0$), one obtains

$$\ln Q = \frac{\alpha_T \Delta T}{\bar{T}} \frac{h}{(\rho g \Delta T \delta^4/1008\eta D\bar{T}) + (360\eta D\bar{T}/\rho g \Delta T \delta^2)} \tag{13}$$

Equation (13) can be used for the determination of the thermal diffusion factor α_T from the experimental data of the TDC: the degree of separation Q is calculated from the compositions of the initial and final mixtures. T_1 and T_2 can be accurately determined during the experiment, but the averaging of the kinetic coefficients and the density of the gas mixture along the height of the column is quite difficult. The possible error resulting from the nonideal geometry of TDC and from neglecting K_p in Eq. (10) is considered below.

The difficulties in the method for determining α_T as proposed by Clusius and Hüber [26] and later developed by Saviron et al. [27, 28] are considerably overcome by the introduction of a "scaling" factor F_s in Eq. (13), keeping the exponential form of this equation,

$$\ln Q_{\max} = \alpha_T F_s \tag{14}$$

According to Clusius and Hüber [26], F_s is a temperature-dependent constant for a particular TDC but is independent of the initial concentration of the mixture, x_0. F_s is experimentally determined by calibrating TDC using a gas mixture of known α_T (e.g., determined by the two-bulb method). The thermal diffusion factor can be deduced from Eq. (14) for any other gas mixture if, in the same column, $Q_{\max}$ is reliably determined. The use of $Q_{\max}$ in Eq. (14) leads to the isobaric nature of F_s. As is well known from the general theory of FJO [12], Q strongly depends on the pressure, and $\ln Q(p)$ passes through a maximum. In this way the theory was experimentally confirmed [29, 30]; see also Ref. 15. By applying

$$\left[\frac{\partial(\ln Q)}{\partial p}\right]_{Q = Q_{\max}} = 0$$

$$F_s = F_s(R, r, \delta, h, T)$$

The temperature dependence of the isobaric scaling factor F_s was carefully examined by Acharyya et al. [31] and the method was further developed.

We would like to give some remarks concerning the isobaric nature of F_s, especially at elevated pressures and for nonisotopic mixtures (i.e., gases with considerably different masses).

If x_0, δ, h, T_1, and T_2 are invariable constants, practically in all cases p_{opt} at which $Q=Q_{\max}$ can be found. Generally for different x_0, p_{opt} would also be different. In the case of isotopic mixtures or mixtures of gases with similar physical properties, the dependence of p_{opt} on x_0 is weak and can be neglected if the changes in ρ and η are very small. Therefore the validity of the relation $\alpha_{\mathrm{T}}^{-1}(x_0)$ determined by use of the scaling factor F_s is restricted not only at $\bar{T}=\text{const}$, but also at $p\approx\text{const}$. In the separation of gases with very different physical properties, the value of p_{opt} actually depends on the initial concentration x_0, as can be seen in Fig. 2, where the shift of p_{opt} with the initial concentration x_0 of He–N_2 mixtures is shown. Such an effect has been previously observed by Saviron et al. [28] in He–Ar and Ne–Xe mixtures. In such a case this method would give $\alpha_{\mathrm{T}}^{-1}(x_0)$ for $\mathrm{p}\neq\text{const}$, which is unacceptable. The experimental determination of the thermal diffusion factor α_{T} using F_s does not give the relations $\alpha_{\mathrm{T}}(p)$ for $\bar{T}=\text{const}$ and $x_0=\text{const}$. In order to obtain these relations, several TDC with different δ must be employed. This is quite inconvenient and was not practical for use.

The analysis of TDC was accomplished by Rozen [20] in the framework of the general theory of mass transfer. Essential for this theory is the concept of the transfer unit height (TUH), a quantity with a dimension of length (h_0), which can be physically interpreted as the effective height of the column at which an "elementary" part of the total concentration change for the chosen component takes place. By the introduction of TUH the mass transfer process is described discretely as consisting of N stages, so that

$$N=h/h_0 \tag{15}$$

In principle, the value of h_0 (or N) can be found from the main equation of the mass transfer theory, which in the most general case is

$$dM=j_{\perp}\,dF, \qquad j_{\perp}=k(y-y_p) \tag{16}$$

where M is the transfered mass through unit area for local deviations of the equilibrium concentration of the appropriate component in either of the two vertical flows (L or G)$(y-y_p)$, and k is the phenomenological coefficient of mass transfer.

In the case of laminar flow, regardless of the kind of process of

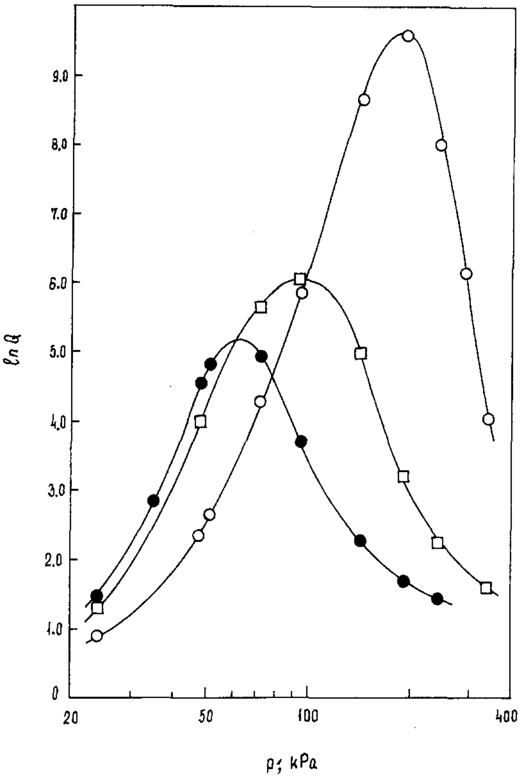

Fig. 2. Degree of separation Q in a thermal diffusion column as a function of pressure at $\bar{T} = 365$ K and initial concentration of the light component of the He–N_2 mixtures: (●) values of $\ln Q$ at $x_0 = 0.298$; (□) values of $\ln Q$ at $x_0 = 0.534$; (○) values of $\ln Q$ at $x_0 = 0.854$.

separation, including irreversible single phase processes such as thermal diffusion, the equation for transverse diffusion flow $j_\perp$ has the form

$$j_\perp = \rho D[-\partial x/\partial s + \varepsilon x(1-x)] \tag{17}$$

where x is the local concentration of the light component.

To simplify the equations the coefficient ε, defined as

$$\varepsilon = (q-1)/q \tag{18}$$

is introduced. Both coefficients (q and ε) are commonly used in the theory of gas separation in columns.

The local concentration x, as well as ε, depends on the coordinate s (or on the radius r in the case of cylindrical symmetry), and obviously in the case of thermodiffusion $\varepsilon = \alpha_T \, \partial \ln T/\partial s$ [see Eqs. (1) and (3)]. For cylindrical symmetry (i.e., two coaxial cylinders) instead of the linear approximation of Furry and Jones [13, 14], where the gradients in Eq. (1) are replaced by the averaged-over δ values of the concentrations x and y and velocity of the vertical flows σ, Rozen [20] derived exact solutions of the equations of convectional diffusion, by integrating Eq. (17) over the coordinate s in the approximation

$$s \ll r_1 < r_2$$

where r_1 and r_2 are the inner and outer radii of the cylindrical ring,

$$dx/dz = dy/dz = 0$$

i.e., there is no vertical diffusion and the velocity of the convectional flows is determined from the equation of continuity. In view of an exact solution for ε, the limitation of the elementary theory [14] $\varepsilon \ll 1$ can be overcome and thus one can work not only with isotopic mixtures, but also at large values of α_T and large gradients of T, i.e., in large intervals of temperatures, pressures, and concentrations. The full system of Rozen's equations is quite complicated and it is not the aim of this paper to review them, but some resulting equations are essential for our work.

For the transverse diffusion flow, in the approximation used by Furry and Jones, one obtains

$$j_\perp = (D\rho/\delta)[y - x + \varepsilon x(1-x)] \tag{19}$$

where x and y are the concentrations of the appropriate component in the two vertical flows.

It was shown in Ref. 20 that if the mass transfer process is regarded as a second-order reaction,

$$[y - x + \varepsilon x(1-x)] = y - y_p \tag{20}$$

which means that the process in the thermal diffusion column is described by the phenomenological expression for mass transfer, Eq. (16), as

$$k = D\rho/\delta \tag{21}$$

There exists a simple relation between the coefficient with a dimension of length in the Rozen's equations and the kinetic coefficients of Furry and Jones [Eqs. (10)–(12)]:

$$K_c = h_c L; \qquad K_d = h_d L \tag{22}$$

where L is the hydrodynamical laminar vertical flow along the column

$$L=\frac{1}{2}\int_0^{2\delta} |\rho\sigma|\, ds \tag{23}$$

The coefficients h_c and h_d are taken for the appropriate components of h_0 (TUH) by analogy with Eq. (10).

In Ref. 20 it is consecutively shown that

$$h_0=h_c+h_d+h_p \tag{24}$$

$$h_c=(\rho g\,\Delta T\,\delta^4)/(1008\eta\, D\bar{T}) \tag{25}$$

$$h_d=(360\eta\, D\bar{T})/(\rho g\,\Delta T\,\delta^2) \tag{26}$$

h_p is part of h_0, analogous to K_p in Eq. (10).

From Eqs. (13), (15)–(17), and (19) it follows that

$$\ln Q=(\alpha_{\mathrm{T}}\,\Delta Th)/(2\bar{T}h_0)=(\alpha_{\mathrm{T}}\,\Delta TN)/(2\bar{T}) \tag{27}$$

Using Eq. (27), α_{T} can also be calculated from the experimental data of TDC. Equation (27) is clearly equivalent to Eq. (13).

In the present work a new method is proposed for the determination of α_{T} over large temperature and pressure ranges by a TDC. We should emphasize the important role of the concept of TUH in this method. The results of Rozen obtained in Ref. 20 by integration of the mass transfer equation are also essentially used. The method itself is considered in detail in Section 3.

3. NEW METHOD FOR EXPERIMENTAL DETERMINATION OF THE THERMAL DIFFUSION FACTOR FROM COLUMN MEASUREMENTS

Having in mind Eqs. (15) and (16), it is easy to show that the number of discrete steps of the thermodiffusion process (i.e., the number of TUH), in the mass transfer theory, can be calculated from

$$N=h/h_0=\int_{x_1}^{x_2}\frac{dx}{y-y_p} \tag{28}$$

When the TDC is used for determination of α_{T}, there is no gas production, or $y=x$ along the height of the column. The equilibrium curve for such a process should be described by the equation

$$y_p=\frac{(1-\varepsilon)x}{1-\varepsilon x} \tag{29}$$

and, respectively,

$$y - y_p = \frac{\varepsilon x(1-x)}{1-\varepsilon x} \tag{30}$$

The integration of Eq. (28) using Eq. (30) gives for N

$$N = (1/\varepsilon)\ln Q - \ln Q_{\mathrm{L}} \tag{31}$$

or

$$\ln Q = \varepsilon(N + \ln Q_{\mathrm{L}}) \tag{32}$$

The relation between the first kinetic coefficient H of Furry et al. deduced in Ref. 20 is analogous to Eq. (22)

$$H = \varepsilon L \tag{22a}$$

From Eqs. (32) and (22a), one gets

$$\ln(Q_H Q_L^{1-\varepsilon}) = \varepsilon N = (H/K)h \tag{33}$$

The quantities in Eq. (33) are as follows:

$$Q_H = x_{H1}/x_{H2} \tag{34}$$

$$Q_1 = x_{L1}/x_{L2} \tag{35}$$

$$H = (2\varepsilon\rho^2 g\,\delta^3\,\Delta TB)/(6!\,\eta\bar{T}) \tag{36}$$

where x_{L1} and x_{L2} are the concentrations of lighter gas at the top and bottom of the TDC respectively, and x_{H1} and x_{H2} are the concentrations of the heavier gas at the bottom and top of the TDC, respectively. α_{T} is implicitly included in Eq. (33) through ε.

For $\varepsilon \ll 1$ the obvious approximation for Eq. (30) is

$$y - y_p \approx \varepsilon x(1-x) \tag{37}$$

The integration of Eq. (28) using Eq. (37) gives

$$N = 1/\varepsilon \ln Q \tag{38}$$

from which the equation of Furry et al. (8) is easily derived.

An important new aspect in the theory is the exponential factor $(1-\varepsilon)$ in the left-hand side of Eq. (22). The further derived relations are more complicated, but the method for determination of α_{T} is not restricted to isotopic mixtures and low pressures.

From Eq. (33), using Eqs. (6) and (18), for α_{T} follows an equation different from those cited above:

$$\alpha_{\mathrm{T}} = \ln\left(\frac{N + \ln Q_L}{N - \ln Q_H}\right)\bigg/\ln(T_2/T_1) \tag{39}$$

This relation can be used for more precise experimental determination of α_{T} than by Eq. (27). It is applicable, on the other hand, to gas mixtures practically of all kinds.

Strictly speaking, the above-derived equation [Eq. (39)] is valid for an ideal column ($K_p = 0$ or $h_p = 0$). It is convenient to describe the deviations from an ideal TDC introducing a new coefficient in the following way:

$$k_p = K/(K_c + K_d) \tag{40}$$

Having in mind the two sets of relations, Eqs. (9)–(12) and Eqs. (24)–(26), it can be shown that

$$k_p = h_0/(h_c + h_d) = h_0/h_0^* \tag{41}$$

In Eq. (41) h_0^* denotes the TUH for an ideal column. From Eqs. (15) and (41), it follows that

$$N^* = h_0/h_0^* = k_p N \tag{42}$$

From Eqs. (41), (42), and (39), one obtains

$$\alpha_{\mathrm{T}} = \ln\left(\frac{N^*/k_p + \ln Q_L}{N^*/k_p - \ln Q_H}\right)\bigg/\ln(T_2/T_1) \tag{43}$$

The condition for an ideal column ($K_p = 0$) is equivalent to $k_p = 1$ in Eq. (40), i.e.

$$\alpha_{\mathrm{T}}^* = \ln\left(\frac{N^* + \ln Q_L}{N^* - \ln Q_H}\right)\bigg/\ln(T_2/T_1) \tag{44}$$

Using Eq. (5), one obtains

$$k_s = \alpha_{\mathrm{T}}/\alpha_{\mathrm{T}}^* = \ln q/\ln q^* \tag{45}$$

For the thermodiffusion process, in all practical cases $q < 2$. Therefore, with an error less than 3% it is sufficient to hold only the first term of the power-series expansion of $\ln q$. In that case, employing Eq. (39), one obtains

$$\ln q = 2(q - 1)/(q + 1) = 2\ln Q/[2N + \ln(Q_L/Q_H)] \tag{46}$$

$$\ln q^* = 2(q^* - 1)/(q^* + 1) = 2\ln Q/[2N^* + \ln(Q_L/Q_H)] \tag{47}$$

Substituting the values of $\ln q$ and $\ln q^*$ from Eqs. (46) and (47) in Eq. (45) and using Eq. (42) for k_s, one obtains

$$k_s = k_p \frac{1 + (1/2N^*)\ln(Q_L/Q_H)}{1 + (k_p/2N^*)\ln(Q_L/Q_H)} \tag{48}$$

As so far as $k_p \geqslant 1$, it is obvious that

$$\frac{1 + (1/2N^*)\ln(Q_L/Q_H)}{1 + (k_p/2N^*)\ln(Q_L/Q_H)} \leqslant 1.0$$

and subsequently,

$$k_p \geqslant k_s \geqslant 1.0$$

On the other hand, it can be shown that

$$(1/2N^*)\ln(Q_L/Q_H) \ll 1.0$$

so that in the first approximation, $k_s \simeq k_p$.

In such a case,

$$\ln q = k_s \ln q^* = k_p \ln q^*, \qquad \alpha_\mathrm{T} = k_s \alpha_\mathrm{T}^* = k_p \alpha_\mathrm{T}^*$$

The real value of α_T can be determined from Eq. (39) if k_p (or k_s) is known. If not, only the ideal value α_T^* is calculated. Its values are always lower than the real one (α_T).

According to Vasaru et al. [23] and Sørensen et al. [32], the coefficient K_p is up to 20% of the sum $(K_c + K_d)$, i.e., $k_p = 1.0 - 1.2$. So calculating α_T from Eq. (39) with $k_p = 1.0$, the error should be less than 20%. In order to lower the influence of the experimental error itself, it is convenient to work in relative units. It seems reasonable to accept that for two experiments in the same TDC at different temperatures and pressures,

$$k_p'/k_p'' \approx 1.0$$

Then with the same error a relative coefficient might be introduced

$$\bar{\alpha}_{T_i} = \alpha_{\mathrm{T}_i}/\alpha_{\mathrm{T}_0} = \alpha_{\mathrm{T}_i}^*/\alpha_{\mathrm{T}_0}^* \tag{49}$$

where α_{T_i} and $\alpha_{\mathrm{T}_i}^*$ are the values of α_T and α_T^* derived from the particular experiment and α_{T_0} and $\alpha_{\mathrm{T}_0}^*$ are the values of α_T and α_T^* under conditions accepted as a reference point.

Laranjeira [33] has shown that for given temperatures T_1 and T_2 and pressure p,

$$\alpha_\mathrm{T}^{-1} = b - mx_0 + ax_0(1 - x_0)/(x_0 + c) \tag{50}$$

where x_0 is the initial concentration and a, b, c, and m are characteristic constants of the gas mixture.

In relative units Eq. (50) should be

$$\bar{\alpha}_{\mathrm{T}}^{-1} = \bar{b} - \bar{m}x_0 + \bar{a}x_0(1 - x_0)/(x_0 + c) \tag{51}$$

where

$$\begin{aligned} \bar{m} &= m\alpha_{\mathrm{T}_0} \\ \bar{b} &= b\alpha_{\mathrm{T}_0} \\ \bar{a} &= a\alpha_{\mathrm{T}_0} \end{aligned} \tag{52}$$

Usually the nonlinear term in Eq. (50) is negligible [33], so that with sufficient accuracy,

$$\alpha_{\mathrm{T}}^{-1} = b - mx_0 \tag{53}$$

$$\bar{\alpha}_{\mathrm{T}}^{-1} = \bar{b} - \bar{m}x_0 \tag{54}$$

The relations (53) and (54) are equations of straight lines with a negative slope. They intercept the abscissa (see Fig. 3), but the interception point is at $x_0 > 1$, i.e., outside the interval of interest $(0 \leqslant x_0 \leqslant 1.0)$.

For a given gas mixture $\bar{\alpha}_{\mathrm{T}}$ can be calculated either from the exact equation (51) or from its linearized form, given by Eq. (54). If reliable data

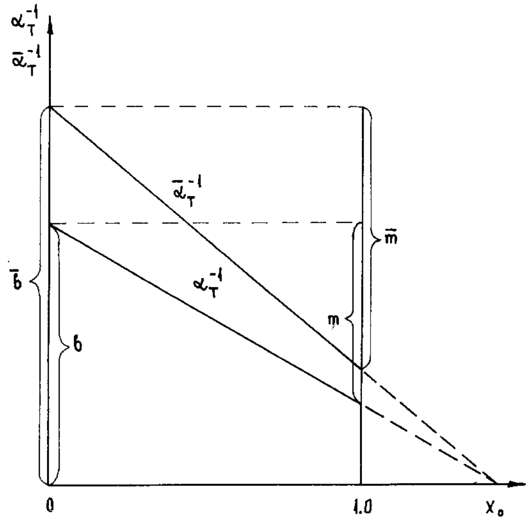

Fig. 3. Thermal diffusion factor α_{T}^{-1} and $\bar{\alpha}_{\mathrm{T}}^{-1}$ vs initial concentration of the light component x_0.

for α_{T_0} for the mixture under consideration exist, the coefficients b, m, and a can be determined experimentally, using the relations (52). Knowing the coefficients in Eq. (51) or in (54), one can transform them into the form (50) or (53) by employing the relations in Eqs. (52). The data for α_{T_0} could be obtained in the swing separator as well as by the two-bulb method. When interpreting the experimental data one has to keep in mind that the coefficients in Eq. (51) or (54) are derived using the values for

$$\bar{\alpha}_{T_i} = \alpha^*_{T_i}/\alpha^*_{T_0}$$

which are experimentally determined.

By using Eq. (13) instead of Eq. (39), the error in assessing α_T can be obtained. If we set

$$n = \ln Q_H / \ln Q_L \tag{55}$$

expression (33) may be presented as

$$\ln Q = k_n \varepsilon N \tag{56}$$

where

$$k_n = 1/[1 - \varepsilon/(n+1)] \tag{57}$$

When $Q_L \to 1$, the coefficient n tends to ∞ and, respectively, $k_n \to 1$. As a result, Eq. (56) becomes equivalent to Eq. (8) or (38). If, however, $Q_H \to 1$, then $n \to 0$ and, correspondingly, $k_n \to 1/(1-\varepsilon) = q$. Consequently Eq. (56) becomes

$$\ln Q = q\varepsilon N \tag{58}$$

From Eq. (58) it follows that

$$\varepsilon = \ln Q/qN \tag{59}$$

and from Eq. (38),

$$\varepsilon = \ln Q/N \tag{60}$$

Evidently, Eq. (60) will give, in this case, larger values for ε (hence α_T) compared to those of Eq. (59). The corresponding error will be

$$\Delta\varepsilon/\varepsilon = (q-1) \cdot 100\% \tag{61}$$

This, in fact, is the maximum possible error. As an illustration one can consider the following example.

At $T_2/T_1 = 1.8$ (which can be easily obtained in practice) and $\alpha_T = 0.4$, which is normal for mixtures with a large value of $\Delta M/(M_1 + M_2)$ (cf., e.g., Ref. 34), we have

$$q = (T_2/T_1)^{\alpha_T} = 1.25$$

If we replace this value of q in Eq. (61), we obtain a maximum error of 25% for such a gas mixture.

The above considerations are also illustrated in Fig. 4 by the behavior of $\alpha_T(x_0)$ at $\bar{T} = \text{const}$ and $p = \text{const}$. The solid line gives the values of α_T^{-1} valculated from our experimental data on He–N_2 using Eq. (39). The dashed line corresponds to the α_T^{-1} values as calculated from the same experimental results using the FJO equation (13). Results, shown in Fig. 4, are obtained at $p = 48$ kPa, which is quite different from p_{opt} for all He–N_2 mixtures investigated by us (see Fig. 2). At p_{opt} there is a maximum gradient of concentrations along the column, i.e., an essential difference of the physical properties of the mixture. For gas mixtures consisting of com-

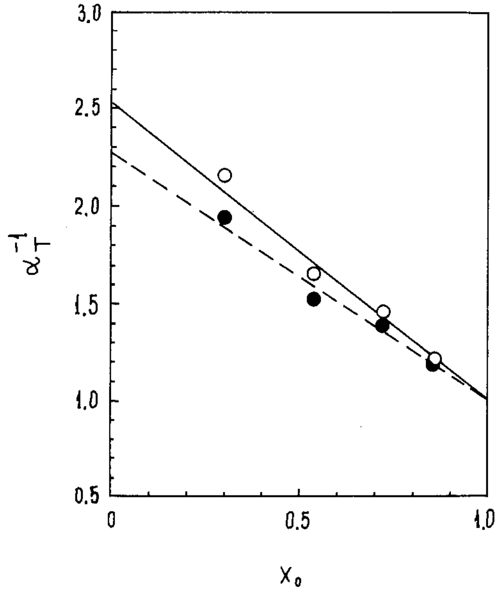

Fig. 4. Experimental data for the thermal diffusion factor α_T^{-1} vs initial helium concentration x_0 for He–N_2 mixture at the average temperature $\bar{T} = 365$ K and pressure $p = 48$ kPa. (○) Values of α_T^{-1} calculated by the method proposed in the present work; (●) values of α_T^{-1} calculated by the FJO method [12].

ponents with considerably different molecular masses a significant error in determining the thermal diffusion factor α_T may be introduced. For that reason the value $p = 48$ kPa was chosen.

The experimental setup used for obtaining the results, presented in Figs. 2 and 4, is described in detail in Ref. 35.

4. CONCLUSIONS

The proposed method makes it possible to get reliable experimental results for the thermal diffusion factor over large temperature and pressure ranges, for arbitrary concentrations and physical properties of the gas mixtures. This method can also be used in other types of experiments, e.g., for the determination of optimal conditions of the separation process in a thermal diffusion column.

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