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PERTURBATION SOLUTION OF THE DIFFUSION EQUATION IN THE CASE OF MUTUAL NON-STATIONARY ISOCHORIC AND ISOTHERMAL DIFFUSION OF TWO REAL GASES†

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Abstract—The diffusion equation for the mutual non-stationary isochoric and isothermal concentration diffusion of two real gases is solved by perturbation calculus. In view of corresponding experiments with a Loschmidt diffusion apparatus, pressure and temperature gradients are assumed to be negligible. The concentration dependence of the diffusion coefficient D according to gas kinetic theory, the pressure change during gas mixing, gas sorption by the seals of the diffusion apparatus and the corresponding stream velocities produced are taken into account as small perturbations in a physically reasonable manner. The results show that the complete concentration dependence of D may be determined by only one or two non-stationary diffusion experiments with pure gases, which is the great advantage of this method over all previously used methods.

NOMENCLATURE

$a(x_1)$,	function in $\Delta(x_1)$ of kinetic gas theory;
a_0, a_1, a_2, a_3,	mass ratio expressions in $\Delta(x_1)$ of kinetic gas theory;
a_x,	$(2x+1)\pi/L$, $x \equiv n, r = 0, 1, \ldots$;
A,	series coefficients in Section 3.4;
A,	abbreviation in Section 4;
A_{12}^*,	ratio of collision integrals;
$A_{r,n}$,	series expressions;
$b(x_1)$,	function in $\Delta(x_1)$ of kinetic gas theory;
b_x,	$2x\pi/L$, $x \equiv n, m = 1, 2, \ldots$;
B,	series coefficients in Section 3.4;
B,	$\Delta p_K(t)K_0/2$ in Section 4;
B_{11}, B_{22}, B_{12},	second virial coefficients;
B_m,	second virial coefficient of mixture, $\beta_3+\beta_2 x_1+\beta_1 x_1^2$;
c,	molar density;
c_1, c_2, c_3,	fitting coefficients of estimated $\Delta(x_1)$;
c_D,	$D_1(c_2+2c_1 x_1^m)$;
c_w,	$(p_0 D/RT)(\beta_2+2\beta_1 x_1^m)$;
C, C_i,	constants, $i = 0, 1, 2, 3, 4$;
C_{12}^*,	ratio of collision integrals;
C_n^u, C_n^g,	coefficients of perturbation calculus;
D,	binary mutual diffusion coefficient, $D_{12} = D_{21}$;
D_0,	nD_1;
D_1, D_2,	first and second kinetic gas theory approximation of D;
E,	series coefficients;
$f^{(i)}$,	perturbation functions, $i = 0, 1, 2, 3, 4$;
f_x,	$\exp(-a_x^2 Dt)/a_x$;
F,	series coefficients;
$F(z, t)$,	perturbation term of the diffusion equation $F_D+F_w+F_K$;
F_D, F_w, F_K,	perturbation terms of the diffusion equation;
$F^{(i)}$,	perturbation functions, $i = 0, 1, 2, 3, 4$;
G,	series coefficients;
$g_n, g_n^{(0)}, g_n^{(1)}$,	(even) Fourier coefficients of $x_1(z, t)$;
G_n,	(even) Fourier coefficients of $F(z, t)$;
h_x,	$\exp(-a_x^2 Dt)$;
H,	series coefficients;
I,	series expression;
k,	Boltzmann constant;
k_1,	$K_1/n = K_1 v/N_A$;
k_1^*,	$(\mathrm{d}\ln p/\mathrm{d}t)_K$;
$K(t)$,	$(K_1/N_A)(\mathrm{d}p/\mathrm{d}t)_K$;
K_0,	$\{RT+p_0[B_m(x_1^m)+\beta_1(\Delta x)^2/8]\}^{-1}$;
K_1, K_2,	rates of formation of species 1, 2 in unit time and unit volume;
L,	length of diffusion cell;
m_{12},	reduced mass;
M,	ratio of molar masses, M_1/M_2;
n, n_1, n_2,	particle number densities;
N_A,	Avogadro constant;
p,	pressure;
p_0,	initial pressure;
P_1, P_2, P_{12},	expressions in $\Delta(x_1)$ of kinetic gas theory;
Q_1, Q_2, Q_{12},	expressions in $\Delta(x_1)$ of kinetic gas theory;
$\mathbf{r}$,	position vector;
r,	two-particle distance;
R,	molar gas constant;
S,	symbol for series expressions $\underset{0,r}{S}, \underset{n,r}{S^+}, \underset{n,r}{S^-}, S_{3n}, S_{4n})$;
t,	time;
T,	temperature;
T_{12},	reduced temperature, kT/ε_{12};
$u_n, u_n^{(0)}, u_n^{(1)}$,	(odd) Fourier coefficients of $x_1(z, t)$;
U_n,	(odd) Fourier coefficients of $F(z, t)$;
v, v_1, v_2,	molar volume;
v_1, v_2,	z-component of stream velocity (only in Section 2.2);

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V_u, V_o,	volumes of the two diffusion half-cells;
w,	z-component of average particle velocity;
W_1, W_2,	z-components of particle diffusion velocities;
x,	coordinate (in direction of optical axis, only used in Section 2.1);
x,	$B_m p/RT$;
x_0,	$B_m p_0/RT$;
x_1,	mole fraction of heavier gas component;
x_2,	mole fraction of lighter gas component, $1-x_1$;
x_1^{id},	solution of ideal-gas diffusion equation;
x_{1u}, x_{1o},	initial mole fractions;
x_1^m,	mean mole fraction, $(x_{1u}+x_{1o})/2$;
$x_1^{(1,2)}, x_1^{(1,3)}$,	perturbation contributions to x_1;
y,	coordinate (shearing direction of diffusion cell, only used in Section 2.1);
y,	$2(x_{1u}-x_{1o})/L$;
z,	coordinate (direction of diffusion);
z_A,	coordinate of the point of observation of diffusion.

Greek symbols

β_1,	$B_{11}+B_{22}-2B_{12}$;
β_2,	$2(B_{12}-B_{22})$;
β_3,	B_{22};
Δx,	$x_{1u}-x_{1o}$;
$\Delta, \Delta(x_1)$,	kinetic gas theory correction for the concentration dependence of D;
Δx_1,	perturbation contributions to x_1 (measured);
Δp,	$p-p_0$;
$\varepsilon, \varepsilon_{12}$,	potential well depth;
σ,	potential well distance parameter;
$\Sigma_2, \Sigma_3, \Sigma_4$,	series expressions;
τ,	reference time, $L^2/\pi^2 D$;
φ,	intermolecular pair potential;
$\Omega_{ij}^{(k,l)*}$,	reduced collision integrals of kinetic gas theory.

Subscripts

D,	denotes diffusion terms;
g,	denotes even-parity functions or constants;
K,	denotes sorption terms;
m,	denotes quantities of the gas mixture or molar quantities;
m,	denotes corresponding summation index;
M,	denotes mixing-volume terms;
n,	denotes corresponding summation index;
o,	denotes quantities of upper diffusion half-cell;
r,	denotes corresponding summation index;
u,	denotes quantities of lower diffusion half-cell;
w,	denotes average-particle-velocity terms;
1,	denotes quantities of heavier gas component;
2,	denotes quantities of lighter gas component.

1. INTRODUCTION

THIS paper supplements and improves the doctoral thesis of Jescheck [1]. The knowledge of accurate and reliable gas diffusion coefficients D is very important for the solution of many problems in technical and natural sciences. The Chapman–Enskog theory, for instance, shows [2–5] that, contrary to other transport coefficients of binary gaseous mixtures, reliable information about the mutual intermolecular interaction pair-potential $\varphi(1, 2)$ of chemically different atoms or molecules, 1 and 2, may successfully be extracted out of accurately measured binary gas diffusion coefficients D. For this purpose, the dependence of D on both the temperature and the concentration of the mixture must be investigated with great care. Diffusion experiments of this kind, which give D with permissible uncertainty of at most 1%, are scarce in the literature [6–9]. In addition, gas diffusion experiments are not simple to do, which is one reason why only a few laboratories have dealt with such investigations. Most workers in this field tend to neglect the concentration dependence of D as 'unimportant', although this effect is predicted by the Chapman–Enskog theory to be up to 13% in the limiting case of hard-sphere molecules.

The uncertainty of different methods for measuring gas diffusion coefficients has been investigated [7–9]. Among other things, our examinations [8, 9] have shown that the measured temperature dependence of D seems to be different according to whether the diffusion measurements are non-stationary, quasi-stationary or stationary. As another result we find that the absolute measurement of D in observing the non-stationary diffusion of two gases or gas mixtures in a Loschmidt shearing cell at a fixed point of observation z_A should be the most reliable measuring procedure. Thereby the density $\rho(t)$, and therefore the composition of the binary gas mixture, should be analysed continuously in time t at z_A with the aid of an optical interferometer to avoid disturbances of the diffusion experiment. Such a method has been developed and described [10, 11].

To investigate the concentration dependence of D at fixed temperature T with this method, the mutual diffusion of quasi-ideal gas mixtures of nearly the same composition was hitherto studied with few exceptions. The result of such experiments is only an arithmetic mean of D, which may be associated with the mean concentration of the mixture after diffusion. This procedure of measuring the concentration dependence of D was first applied by Lonius [12] in the case of gas diffusion and is the only method in literature till now. The advantage of this method is the fact that the ideal unperturbed non-stationary diffusion may be described by a simple diffusion equation, the well-known Fick's second law, which possesses known solutions for many initial and boundary conditions [13, 14]. Disadvantages of the Lonius method are the uncertainties caused by averaging D, the use of gas mixtures with possible errors in their production and composition (which gives an additional factor of 2 or more in the uncertainty of D [8, 9]), and the great number of very time-consuming independent diffusion experiments which must be carried out to get a reasonable dependence of D in the whole range of the mole fraction, $0 \leqslant x_1 \leqslant 1$, of the chemical species 1 (at least 10 experiments).

This procedure is, however, inefficient in comparison with our method. We have already mentioned [9] that the whole information of the concentration dependence of D should be embedded directly in the measuring signal (interferogram), since the composition of the gas mixture is measured at each time t at the fixed point of observation z_A. This great advantage is not inherent in any other known method for measuring gas diffusion coefficients and was obviously not recognized by other authors [15, 16] who have used the same experimental method.

Understanding this advantage suggests the investigation of the diffusion of two pure gases by observing the decrease of the mole fraction x_1 in one-half of the Loschmidt cell and simultaneously (or in another independent experiment with the same physical conditions) the increase of x_1 in the other half-cell. In this way the concentration dependence of D could be measured in the entire mole fraction range $0 \leqslant x_1 \leqslant 1$ of component 1 in only one or two diffusion experiments, a procedure which would considerably minimize the uncertainty of the measured D and the quantity of measurements necessary.

The only disadvantage of this method is the fact that the diffusion equation is more complicated than Fick's simple law, since the results on mixing two imperfect gases under the conditions of constant temperature and cell volume must be known at every time t. Therefore, simultaneously with the change of concentration at the point of observation z_A, the accompanying pressure change in the diffusion cell was measured. As well as this mixing volume effect, an additional pressure effect may occur due to gas sorption at the walls of the diffusion cell. This sorption pressure effect may be separated from the entirely measured pressure change $\Delta p(t)$ if the thermodynamics of mixing of the two gases is known. On the other hand, the thermodynamics of mixing may be determined by diffusion experiments if the sorption effect vanishes. Experiments of this kind should therefore give self-consistent information on the kinetics and thermodynamics of mixing two gases with previously unknown mixing conditions. This is another great advantage of our method.

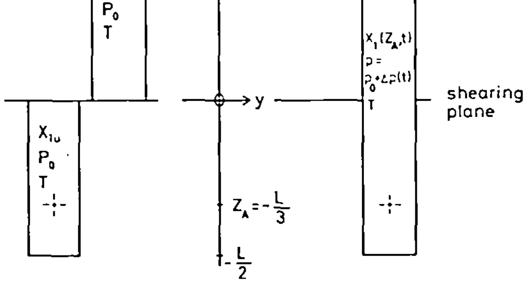
Ljunggren [15] was the first to introduce the pure mixing volume effect in the solution of the non-stationary diffusion equation in the case of two diffusing gas mixtures of nearly the same composition. Gavalas *et al.* [17] have used the corresponding pressure effect to determine binary diffusion coefficients D at elevated gas densities. Beside this mixing volume effect Gotoh *et al.* [16] have considered gas sorption by the seals at the ends and in the shearing plane of the Loschmidt diffusion cell, but their information about sorption was poor, since they only measured the static pressures at the beginning and at the end of an experiment. They have also considered the concentration dependence of D, but, as a result of a very complicated perturbation calculus with four free adjustable parameters, they obtained only one diffusion coefficient D, which was constant in the entire mole fraction range investigated, $0 \leqslant x_1 \leqslant 0.5$, and was associated with the mean mole fraction $x_1^m = 0.5$ in the diffusion cell with diffusing pure gases. In some cases, however, they noticed that calculated diffusion coefficients D of this kind are of little use in view of their estimated experimental uncertainties. In these cases they have repeated their measurements with two gas mixtures of adequate composition and obtained more reliable constant values of D (Section 3.3.3).

This paper will deal with the solution of the complete diffusion equation including the effects of the mixing volume, the concentration dependence of D, and sorption. These effects will be considered as small perturbations, which are superposed on the proper concentration diffusion effect. The perturbation calculus used is of higher order than the calculus of Gotoh *et al.* [16]. Throughout the paper numerical values are given for the gas pair $C(CH_3)_4$–Ar, one of the most imperfect binary systems investigated by us. Based on this work, further publications will deal with experimental results of corresponding diffusion experiments. In all cases the diffusion thermoeffect is completely negligible.

2. THE DIFFUSION EQUATION

2.1. *Experimental conditions*

Figure 1 shows schematically the diffusion shearing cell used. In Fig. 1(a) the apparatus is in the filling position, the two identical half-cells of length $L/2$ and rectangular cross-section are separated (gas-tight) from each other. In this position the two gases or gas mixtures are put into the evacuated half-cells up to the same initial pressure p_0 at the same temperature T. x_{1_u} and x_{1_o} are the initial mole fractions of the heavier



1a filling position 1b diffusion position

FIG. 1. Schematic representation of the Loschmidt diffusion cell used.

component 1 in the lower (x_{1_u}) and the upper (x_{1_o}) half-cell. Since $x_1+x_2 = 1$ and $D_{12} = D_{21} = D$ only the diffusion of this heavier component 1 need be considered. The gravitation of earth acts in the ($-z$)-direction. To avoid density convection of the gases, the condition $x_{1_u} > x_{1_o}$ should be fulfilled.

The gas-tightening of the two half-cells to each other and to the surroundings is achieved by using a thin film of silicon grease and two Viton O-rings, which are incorporated into the shearing plane of the half-cell with the two opposite optical windows at $|z_A| = L/3$. These construction features are important to the understanding of gas sorption phenomena (Section 3.3.3).

At time $t = 0$ the open sites of the two half-cells are connected by shearing the half-cell without windows pneumatically in the ($-y$)-direction over the half-cell with the windows. The corresponding diffusion arrangement of the apparatus is shown in Fig. 1(b). The change of the mole fraction $x_1(z_A, t)$ is continuously measured for times $t > 0$ at the point of observation z_A by means of a Michelson interferometer. The optical axis is directed in the x-direction perpendicular to the plane drawn, and the geometrical effective length of the light rays is l (twice the window distance of the diffusion cell in the case of a Michelson interferometer).

Immediately after connecting the two half-cells, the pressure p changes from the initial pressure p_0 to $p = p_0+\Delta p(t)$ due to the mixing volume and gas sorption effects, since the entire volume of the diffusion cell remains constant during an experiment. If the diffusion of two pure gases ($x_{1_u} = 1, x_{1_o} = 0$) is investigated with a diffusion cell as in Fig. 1, only the dependence $D(x_1)$ for the mole fraction range $x_{1_u} = 1 \geqslant x_1(-L/3, t) \geqslant x_1(-L/3, \infty) \approx 0.5$ can be observed. By inverting the entire diffusion cell, however, one gets from a second diffusion experiment with the same physical conditions a value of $D(x_1)$ for the mole fraction range $x_{1_o} = 0 \leqslant x_1(+L/3, t) \leqslant x_1(+L/3, \infty) \approx 0.5$. In this experiment the point of observation $z_A = +L/3$ is now in the upper half-cell, the arrangement used by Gotoh *et al.* [16].

2.2. *Some results of the kinetic theory of gases*

In deriving the complete diffusion equation in the next section, the validity of the Chapman–Enskog kinetic theory of gases is assumed. Moreover, the diffusion coefficient D will be determined only by pure concentration diffusion. Gradients in temperature and pressure in the gas mixture and external forces (e.g. gravitational forces) as driving forces for particle currents are assumed to be negligible. These conditions are fulfilled in our experiments within the uncertainty of the measurements [1, 10, 11].

Since in the diffusion experiments described, phenomena of friction or acceleration are negligible, the diffusion is reasonably examined by means of the frame of reference of the average particle velocity $\mathbf{w}(\mathbf{r}, t)$ [2–5]. In the case of Fig. 1, only the z-components of the velocities must be taken into account, which therefore are not marked explicitly in the following considerations. In the case of two diffusing species we have

$$w(z,t) = \left(\frac{1}{n}\right)(n_1v_1+n_2v_2) = x_1v_1+x_2v_2. \quad (2.1)$$

$n(z,t) = n_1(z,t)+n_2(z,t)$ is the particle number density of the mixture, $v_i(z,t)$ is the z-component of the molecular (mass average) or stream velocity, $x_i(z,t) = n_i/n$ the mole fraction and $n_i(z,t)$ the particle number density of the species $i = 1, 2$. The particle diffusion velocity $W_i(z,t)$ is therefore given by

$$W_i(z,t) = v_i(z,t)-w(z,t). \quad (2.2)$$

According to equations (2.1) and (2.2),

$$n_1W_1+n_2W_2 = 0. \quad (2.3)$$

The sum of the particle diffusion currents, n_iW_i, through a frame perpendicular to the stream direction z therefore vanishes if this frame of reference is moving with a velocity $w(z,t)$ within the gas mixture. By means of equation (2.2) the equation of continuity for each species i is given by [2, 3]

$$\frac{\partial n_i}{\partial t}+\frac{\partial}{\partial z}(n_iv_i) = \frac{\partial n_i}{\partial t}+\frac{\partial}{\partial z}[n_i(w+W_i)] = K_i. \quad (2.4)$$

K_i is the rate of formation of the chemical species i in unit time and unit volume. By summing equation (2.4) for both species and using equation (2.3) the following equation of continuity for the entire gas mixture is obtained:

$$\frac{\partial n}{\partial t}+\frac{\partial}{\partial z}(nw) = K_1+K_2. \quad (2.5)$$

Inserting $x_1 = n_1/n$ in equation (2.4) gives, with equation (2.5), the equation for the total change of x_1 in the w-reference system,

$$\begin{aligned}\left(\frac{\mathrm{d}x_1}{\mathrm{d}t}\right)_w &\equiv \frac{\partial x_1}{\partial t}+w\frac{\partial x_1}{\partial z}\\ &= -\frac{1}{n}\frac{\partial}{\partial z}(n_1W_1)\\ &\qquad +\frac{1}{n}[K_1-x_1(K_1+K_2)]. \quad (2.6)\end{aligned}$$

In this general diffusion equation, the total (substantial) derivative $(\mathrm{d}x_1/\mathrm{d}t)_w$ describes the change of x_1 with time t within a volume element, which is moving with velocity w in z-direction. Therefore $\partial x_1/\partial t$ is the change of x_1 with time t which will be observed at a fixed point of observation $z = z_A$ of the diffusion cell.

In the case of pure concentration diffusion the particle diffusion current n_1W_1 of species 1 in the z-direction is given by the following expression of the Chapman–Enskog theory [3, 4]:

$$n_1W_1 = -nD\frac{\partial x_1}{\partial z}. \quad (2.7)$$

The second gas kinetic approximation of D due to

Kihara [18, 5, 6] is given by

$$D_2 = D_1[1+\Delta(x_1)], \tag{2.8}$$

$$D_1 = \frac{D_0}{n}, \quad D_0 = \frac{3}{8}\frac{(kT/2\pi m_{12})^{1/2}}{\sigma_{12}^2\Omega_{12}^{(1,1)*}(T_{12}^*)}. \tag{2.9}$$

D_1 is the concentration-independent first approximation of D. $m_{12} = m_1 m_2/(m_1+m_2)$ is the reduced mass of the two species, k is the Boltzmann constant, and T is the thermodynamic temperature. $\Omega_{12}^{(1,1)*}$ is the reduced collision integral of diffusion, which depends on the reduced temperature $T_{12}^* = kT/\varepsilon_{12}$. The expressions (2.8) and (2.9) follow from the kinetic theory by the assumption that the intermolecular interaction of two molecules may be described by a spherosymmetrical two-parameter potential $\varphi(r) = \varepsilon f(r/\sigma)$, $\varphi(r \to \infty) = 0$. $f(r/\sigma)$ is the same universal function for all substances, r is the distance between the two particles, σ is a length parameter $[\varphi(r = \sigma) = 0]$, and ε an energy parameter (potential well depth). The indices 12 refer to a molecular impact of species 1 and 2.

Contrary to other transport coefficients, D_1 in equation (2.9) depends only on the pair-potential function $\varphi(1,2)$ of the chemically different species 1 and 2. This is the great importance of the first approximation D_1. The pair potentials $\varphi(1,1)$ and $\varphi(2,2)$ of chemically identical particles first appear in the second approximation D_2, which according to Mason [19] differs from the exact diffusion coefficient D in equation (2.7) by at most 1%. In most cases however this difference is much smaller. Therefore it seems reasonable to identify the second approximation D_2 according to equation (2.8) with the proper (measured) diffusion coefficient D. Kihara [18, 5, 6] has given the following expression for $\Delta(x_1)$ $[x_2 = 1-x_1]$:

$$\Delta(x_1) = \tfrac{1}{10}(6C_{12}^*-5)^2\frac{a(x_1)}{b(x_1)}, \tag{2.10}$$

$$a(x_1) = P_1x_1^2+P_2x_2^2+P_{12}x_1x_2,$$

$$b(x_1) = Q_1x_1^2+Q_2x_2^2+Q_{12}x_1x_2,$$

$$C_{12}^* = \Omega_{12}^{(1,2)*}/\Omega_{12}^{(1,1)*}.$$

The quantities P and Q with $P, Q \geqslant 0$ may be written in terms of the mass fraction $M = M_2/M_1$ of the molar masses of the two species in the following manner:

$$P_1 = a_1\frac{\sigma_{11}^2\Omega_{11}^{(2,2)*}}{\sigma_{12}^2\Omega_{12}^{(1,1)*}},$$

$$P_2 = a_2\frac{\sigma_{22}^2\Omega_{22}^{(2,2)*}}{\sigma_{12}^2\Omega_{12}^{(1,1)*}}, \tag{2.10a}$$

$$P_{12} = a_3+a_0A_{12}^*,$$

$$Q_1 = P_1(1+3M^2+\tfrac{8}{5}MA_{12}^*),$$

$$Q_2 = P_2\left[1+\frac{3}{M^2}+\frac{8}{5M}A_{12}^*\right],$$

$$Q_{12} = 4P_{12}-3a_3+\frac{16}{5}\left(\frac{2}{a_0}\right)^{1/2}\frac{P_1P_2}{a_1a_2},$$

$$a_0 = 8\frac{M}{(1+M)^2}, \quad a_1 = \frac{1}{M}\left(\frac{a_0}{1+M}\right)^{1/2},$$

$$a_2 = a_1M^2M^{1/2}, \quad a_3 = 15\left(\frac{1-M}{1+M}\right)^2,$$

$$A_{12}^* = \Omega_{12}^{(2,2)*}/\Omega_{12}^{(1,1)*}.$$

$\Omega^{(2,2)*}$ is the reduced collision integral for viscosity and heat conduction of gases. Expression (2.10) is symmetrical with respect to the indices 1 and 2. Therefore only the case $0 \leqslant M \leqslant 1$ need be discussed. It should be noted that, according to equations (2.8) and (2.9), $nD \approx nD_2 = D_0[1+\Delta(x_1)]$ only depends on z and t in the small correction term $\Delta(x_1[z,t])$. Therefore the particle diffusion current n_1W_1 is, according to equation (2.7), mainly proportional to the gradient $\partial x_1/\partial z$ of the mole fraction. These facts are used for the first time in this paper to derive expression (2.12) for the gradient $\partial D/\partial z$ and the general diffusion equation (2.13) in the following Section.

2.3. *The general diffusion equation*

By inserting equation (2.7) into equation (2.6) the following general diffusion equation can be obtained:

$$\frac{\partial x_1}{\partial t} = D\frac{\partial^2 x_1}{\partial z^2}+\frac{\partial D}{\partial z}\frac{\partial x_1}{\partial z}+D\frac{\partial \ln n}{\partial z}\frac{\partial x_1}{\partial z} -w\frac{\partial x_1}{\partial z}+\frac{1}{n}\Big[K_1-x_1(K_1+K_2)\Big]. \tag{2.11}$$

Ljunggren [15], Gotoh *et al.* [16] and Jescheck [1] have solved this equation assuming $K_1 = K_2 = 0$ and $\partial D/\partial z = 0$. According to the results, equations (2.8) and (2.9), of the kinetic theory of gases, however, for the gradient $\partial D/\partial z$ we have obtained the expression

$$\frac{\partial D}{\partial z} = -D\frac{\partial \ln n}{\partial z}+D_1\frac{\partial \Delta(x_1)}{\partial x_1}\frac{\partial x_1}{\partial z}. \tag{2.12}$$

Therefore by inserting equation (2.12) into equation (2.11), the general diffusion equation may be written in a form suitable for perturbation calculus as

$$\frac{\partial x_1}{\partial t} - D\frac{\partial^2 x_1}{\partial z^2} = F(z,t), \tag{2.13}$$

$$F(z,t) = F_D(z,t)+F_w(z,t)+F_K(z,t), \tag{2.14}$$

$$F_D(z,t) = D_1\frac{\partial \Delta(x_1)}{\partial x_1}\left(\frac{\partial x_1}{\partial z}\right)^2,$$

$$F_w(z,t) = -w\frac{\partial x_1}{\partial z}, \tag{2.15}$$

$$F_K(z,t) = \frac{1}{n}[K_1-x_1(K_1+K_2)].$$

$\partial x_1/\partial t$ describes the total change of x_1 with time t at a fixed position z of the diffusion cell and is therefore the quantity measured in our experiments. The main contribution is the term $D\partial^2x_1/\partial z^2$ on the LHS of equation (2.13), whereas the term $F(z,t)$ on the RHS may be considered to be a small perturbation term. This diffusion equation (2.13) will be solved in the next section by means of first order perturbation calculus for the following initial and boundary conditions, which are appropriate in the case of our diffusion experiments (Fig. 1):

$$\left.\begin{array}{ll} x_1(z,0) = x_{1_u}, & -\dfrac{L}{2} \leqslant z < 0 \\ x_1(z,0) = x_{1_o}, & 0 < z \leqslant +\dfrac{L}{2} \end{array}\right\} t = 0, \tag{2.16}$$

$$\left.\begin{array}{l} \left(\dfrac{\partial x_1}{\partial z}\right)_{z=\pm L/2} = 0 \\ w(\pm L/2, t) = 0 \end{array}\right\} t > 0. \tag{2.17}$$

3. SOLUTION OF THE GENERAL DIFFUSION EQUATION (2.13)

3.1. *Solution of Fick's second law*

In the case $F(z,t) = 0$, from equation (2.13), the well-known Fick's second law can be obtained,

$$\frac{\partial x_1}{\partial t} = D\frac{\partial^2 x_1}{\partial z^2}. \tag{3.1}$$

This 'ideal' unperturbed diffusion equation describes the non-stationary diffusion of quasi-ideal (perfect) gases or gas mixtures in the case of constant diffusion coefficient D. The general solution $x_1^{\mathrm{id}}(z,t)$ follows from equation (3.1), with the estimate $x_1(z,t) = f(z)g(t)$ on account of conditions (2.16), (2.17), as a Fourier series

$$x_1^{\mathrm{id}}(z,t) = x_1^{\mathrm{m}} - yF^{(0)}(z,t), \tag{3.2}$$

$$F^{(0)}(z,t) = \sum_{n=0}^{\infty} \frac{\exp(-a_n^2 Dt)}{a_n} \sin a_n z, \tag{3.3}$$

$$x_1^{\mathrm{m}} = (x_{1_u} + x_{1_o})/2, \quad y = 2\Delta x/L = 2(x_{1_u} - x_{1_o})/L, \quad a_n = (2n+1)\pi/L.$$

The solution (3.2) of Fick's second law, equation (3.1), is the main part of the desired mole fraction x_1 and was previously fully discussed in the case of a system of coordinates with the origin at $z = -L/2$ in Fig. 1 [9, 10].

The following expressions, which will be used in the next sections, result from equation (3.3):

$$\frac{\partial F^{(0)}}{\partial z} = \sum_{n=0}^{\infty} \exp(-a_n^2 Dt)\cos a_n z, \tag{3.4}$$

$$\left(\frac{\partial F^{(0)}}{\partial z}\right)^2 = \frac{1}{2}\underset{0,r}{S} + \sum_{n=1}^{\infty} \cos b_n z\left(\underset{n,r}{S^+} + \frac{1}{2}\underset{n,r}{S^-}\right) = \Sigma_2, \tag{3.5}$$

$$\begin{gathered} b_n = 2n\pi/L, \quad \underset{0,r}{S} = \sum_{r=0}^{\infty} \exp(-2a_r^2 Dt), \quad \underset{n,r}{S^+} = \sum_{r=0}^{\infty} \exp(-[a_r^2 + (a_r + b_n)^2]Dt, \\ \underset{n,r}{S^-} = \sum_{r=0}^{n-1} \exp(-[a_r^2 + (a_r - b_n)^2]Dt). \end{gathered} \tag{3.6}$$

Equations (3.5) and (3.6) follow from equation (3.4) by multiplying the series term by term and using the relation $2\cos\alpha\cos\beta = \cos(\alpha - \beta) + \cos(\alpha + \beta)$.

3.2. *Solution of the general diffusion equation* (2.13) *by perturbation calculus*

In the theory for solving partial differential equations, the method for solving equation (2.13) is known as the eigen- and boundary-condition problem [20]. The perturbation term $F(z,t)$ has to be developed for fixed time t in terms of the orthogonal eigen-functions $\sin a_n z$ and $\cos b_n z$

$$F(z,t) = \sum_{n=0}^{\infty} [U_n(t)\sin a_n z + G_n(t)\cos b_n z], \quad a_n = (2n+1)\pi/L, \quad b_n = 2n\pi/L. \tag{3.7}$$

A corresponding general estimate with the same coefficients a_n and b_n is attempted for the desired solution $x_1(z,t)$

$$x_1(z,t) = \sum_{n=0}^{\infty} [u_n(t)\sin a_n z + g_n(t)\cos b_n z]. \tag{3.8}$$

The Fourier coefficients $u_n(t)$ and $g_n(t)$ may be determined if the Fourier coefficients $U_n(t)$ and $G_n(t)$ of equation (3.7) are known. For this purpose equation (3.8) is inserted in the LHS of the diffusion equation (2.13), which is then equated with $F(z, t)$ in equation (3.7). Thereafter the two linearly independent expansions in the sine and cosine functions are separated. Comparison of coefficients yields the following system of ordinary inhomogeneous linear differential equations:

$$\frac{\mathrm{d}u_n(t)}{\mathrm{d}t} + Da_n^2 u_n(t) = U_n(t), \quad \frac{\mathrm{d}g_n(t)}{\mathrm{d}t} + Db_n^2 g_n(t) = G_n(t), \tag{3.9}$$

which have the general solutions:

$$u_n(t) = u_n^{(0)}(t) + u_n^{(1)}(t), \quad u_n^{(0)}(t) = C_n^{\mathrm{u}} \exp(-a_n^2 Dt), \quad u_n^{(1)}(t) = \exp(-a_n^2 Dt)\int_0^t U_n(t')\exp(a_n^2 Dt')\,\mathrm{d}t', \tag{3.10}$$

$$g_n(t) = g_n^{(0)}(t) + g_n^{(1)}(t), \quad g_n^{(0)}(t) = C_n^{\mathrm{g}} \exp(-b_n^2 Dt), \quad g_n^{(1)}(t) = \exp(-b_n^2 Dt)\int_0^t G_n(t')\exp(b_n^2 Dt')\,\mathrm{d}t'. \tag{3.11}$$

The coefficients C_n^{u} and C_n^{g} are available on inserting equations (3.10) and (3.11) into equation (3.8) and adapting this expression to the initial and boundary conditions (2.16) and (2.17),

$$C_0^{\mathrm{g}} = x_1^{\mathrm{m}}, \quad C_n^{\mathrm{g}} = 0 \quad (n > 0), \quad C_n^{\mathrm{u}} = -y/a_n \quad (n \geqslant 0). \tag{3.12}$$

Therefore on account of equations (3.2) and (3.3) the solution of equation (2.13) with conditions (2.16), (2.17) is given by

$$x_1(z, t) = x_1^{\mathrm{id}}(z, t) + x_1^{(1,2)}(z, t) + x_1^{(1,3)}(z, t), \tag{3.13}$$

$$x_1^{(1,2)}(z, t) = \sum_{n=0}^{\infty} g_n^{(1)}(t)\cos b_n z = x_1^{(1,2)}(-z, t), \tag{3.14}$$

$$x_1^{(1,3)}(z, t) = \sum_{n=0}^{\infty} u_n^{(1)}(t)\sin a_n z = -x_1^{(1,3)}(-z, t). \tag{3.15}$$

The main contribution to the (measured) mole fraction $x_1(z, t)$ in equation (3.13) is the mole fraction $x_1^{\mathrm{id}}(z, t)$, according to equation (3.2), for 'ideal' diffusion. The correction terms $x_1^{(1,2)}$ and $x_1^{(1,3)}$ are due to the perturbation term $F(z, t)$ of equation (2.14). They may be determined according to equations (3.14) and (3.15) if the Fourier coefficients $g_n^{(1)}$ and $u_n^{(1)}$ are calculated by means of equations (3.10) and (3.11). To do this the Fourier coefficients $U_n(t)$ and $G_n(t)$ of the estimate (3.7) must first be determined by inserting into the LHS of equation (3.7) physically reasonable expressions for F_{D}, F_{w} and F_{K}. Then these single perturbation terms may be evaluated explicitly if $x_1(z, t)$ is replaced everywhere by the first approximation $x_1^{\mathrm{id}}(z, t)$ according to equation (3.2), which is of course the main term in the perturbation solution (3.13). In the same approximation $\partial x_1/\partial t$ may be replaced by the RHS $D\partial^2 x_1/\partial z^2$ of Fick's second law (3.1), a term simply integrated if one assumes that D is (only for this purpose) independent of position z.

3.3. *Estimates of n, $\partial\Delta/\partial x_1$, K_1, K_2 and w*

3.3.1. *Estimate of n.* If one assumes local thermal equilibrium in the gas mixture the following second approximation for the molar volume v of the mixture is obtained:

$$v = \frac{1}{c} = \frac{N_{\mathrm{A}}}{n} = \frac{RT}{p}(1+x), \quad x = \frac{p}{RT}B_{\mathrm{m}}(x_1, T), \tag{3.16}$$

$$\begin{aligned} B_{\mathrm{m}} &= B_{11}x_1^2 + B_{22}x_2^2 + 2B_{12}x_1x_2 = \beta_3 + \beta_2 x_1 + \beta_1 x_1^2, \\ \beta_3 &= B_{22}, \quad \beta_2 = 2(B_{12} - B_{22}), \quad \beta_1 = B_{11} + B_{22} - 2B_{12}. \end{aligned} \tag{3.17}$$

n is the desired particle number density, c is the molar density, N_{A} is Avogadro's constant, and R is the molar gas constant. T is the thermodynamic temperature, p the pressure and B_{m} the second virial coefficient of the gas mixture. The virial coefficients B_{11}, B_{22} of the pure components and the mixing virial coefficient B_{12} depend in each case on the intermolecular interaction pair-potential $\varphi(1,1)$, $\varphi(2,2)$ or $\varphi(1,2)$ and in other respects only on temperature T. In the case of the relatively strong imperfect gas mixture $C(CH_3)_4(1)$–Ar(2) at $T = 332$ K and $p = 1$ bar we have for example: $B_{11} = -747.4\ \mathrm{cm^3\,mol^{-1}}$, $B_{22} = -9.8\ \mathrm{cm^3\,mol^{-1}}$, $B_{12} = -65.7\ \mathrm{cm^3\,mol^{-1}}$.

Since $x_1 = x_1(z, t)$ equation (3.16) describes the dependence of v, c and n on position z and time t in the diffusing gas mixture. Thereby $p = p(t)$ is nearly independent of position z, since pressure changes propagate with the velocity of sound through the gas mixture. By equation (3.16) one gets immediately

$$\ln c = \ln p(t)/RT - \ln(1+x), \quad \ln(1+x) = x - x^2/2 + x^3/3 \mp \cdots = \sum_{l=1}^{\infty}(-1)^{l-1}\frac{x^l}{l}, \quad (-1 < x \leqslant +1). \tag{3.18}$$

In the case of an equimolar mixture of $C(CH_3)_4$–Ar at $p = 1$ bar, $T = 332$ K we have $x = -0.008$. Therefore the series expansion of $\ln(1+x)$ may be truncated after the first term, as has been done before [15]. Moreover x may be replaced by x_0 if p in x is replaced by the constant initial pressure $p_0 = p(0)$, since in the corresponding isochoric diffusion experiments $|(p(t)-p_0)/p_0| < 0.01$. Then instead of equation (3.18) the following approximation of $\ln c$ is obtained:

$$\ln c = \ln p(t)/RT - x_0(z,t), \quad x_0(z,t) = \frac{p_0}{RT}[\beta_3+\beta_2 x_1(z,t)+\beta_1 x_1^2(z,t)]. \tag{3.19}$$

With respect to the above given experimental conditions, the difference in $\ln c$, calculated with equation (3.18) or (3.19), is only 0.1%. In other cases the correct formula (3.18) with $p(t)$ may be used, or the approximation (3.19) may be expanded to any extent in powers of x_0, whichever is desirable.

3.3.2. *Estimate of* $\partial\Delta/\partial x_1$. According to the kinetic theory equation (2.10), $\partial\Delta/\partial x_1$ may be calculated exactly. The resulting expression

$$\frac{\partial\Delta}{\partial x_1} = \Lambda(x_1)\left[\frac{\mathrm{d}\ln a(x_1)}{\mathrm{d}x_1} - \frac{\mathrm{d}\ln b(x_1)}{\mathrm{d}x_1}\right]$$

is however too complicated for perturbation calculus. Since on the other side $\Delta(x_1)$ may, with respect to the experimental uncertainty, be well approximated by a polynomial of second order, the following estimate seems reasonable for perturbation calculus:

$$\Delta(x_1) = c_3 + c_2 x_1 + c_1 x_1^2, \quad \frac{\partial\Delta}{\partial x_1} = c_2 + 2c_1 x_1. \tag{3.20}$$

If one sets $c_3 = 0$, the diffusion coefficient $D(0)$ may be identified with the first approximation D_1 of the Chapman–Enskog theory according to equation (2.9). This is, however, not true in all cases, but is an approximation often used [5].

3.3.3. *Estimate of* K_1 *and* K_2. According to equation (2.4), K_1 and K_2 are the rates of formation of chemical species 1 and 2 in unit time and unit volume of the gas mixture, which has to be considered as a single phase system. For this system the equations of continuity (2.4) and (2.5) are valid. Strictly speaking $K_i \neq 0$ therefore means that chemical reactions are occurring in the mixture [3,5]. On the other side, sorption phenomena should be considered in a thermodynamically strict sense regarding the mixture as a system open to additional phases which act as particle sinks or sources. This concept was firstly used by Gotoh *et al.* [16], who considered gas sorption at the ends and in the shearing plane of their Loschmidt diffusion cell by introducing two additional phases and adequate equations of continuity. However, on account of their lack of information about the equilibrium gas distribution between the three phases before diffusion, of the source strength and the sorption mechanism, the corresponding free parameters, for instance distribution coefficients and desorption constants, are misleadingly adjusted so that $D \equiv D(x_1 = 0.5)$ comes out to be independent of concentration in most experiments for the mole fraction range investigated, $0 \leqslant x_1 \leqslant 0.5$ (Section 1).

In our diffusion experiments with neopentane $C(CH_3)_4$, sorption of this gas by the silicon grease in the shearing plane $z = 0$ of our diffusion cell was observed too. These observations were confirmed by additional independent isochoric sorption experiments with pure neopentane and other gases, which have shown no measurable sorption by the V_2A-walls of our diffusion cell at $p = 1$ bar. On account of the large volume of the diffusion cell (about 700 cm^3), the local fixed particle source or sink in the shearing plane was so weak that the total particle number density, $n = n_1 + n_2$, of equation (2.6) was only slightly changed until the proper diffusion current $n_1 W_1$ in (2.7) had died away. This change of n was experimentally observed by means of continuous pressure measurements, which give us more information about the gas sorption kinetics than Gotoh *et al.* [16] had. Therefore, in contrast to their concept, our intention is to treat gas sorption like chemical reactions, and to determine rates of formation K_i of sorption with the aid of the pressure measurements. Since sorption of the other diffusing gas components like Ar or CH_4 was not observed we assume in the following sections $|K_1| \gg |K_2|$ or $K_2 = 0$. On the other hand, sorption is always small even in the case of neopentane as mentioned above. Therefore, we assume for simplicity that $K_1(z,t)/n(z,t) = k_1(t)$ is only time dependent, which is in accordance with our intention to determine this property by means of $p(t)$-measurements. To summarize we make the following assumptions:

$$K_1/n = K_1 v/N_A = k_1(t), \quad K_2 = 0. \tag{3.21}$$

3.3.4. *Estimate of* w *and pressure change during isochoric diffusion.* w may be determined by means of the equation of continuity (2.5) for the gas mixture. Replacing n in this equation by the molar density $c = n/N_A$ and dividing by $c \neq 0$ the following inhomogeneous linear differential equation in w is obtained:

$$w\frac{\partial \ln c}{\partial z} + \frac{\partial w}{\partial z} = -\frac{\partial \ln c}{\partial t} + \frac{1}{c}\frac{K_1+K_2}{N_A}. \tag{3.22}$$

The general solutions of equation (3.22) for the lower (−) and upper (+) half-cell are

$$w_{\pm} = \exp\left(-\int_{\pm L/2}^{z} \frac{\partial \ln c}{\partial z'}\,\mathrm{d}z'\right)\left[C-\int_{\pm L/2}^{z}\left(\frac{\partial \ln c}{\partial t}-\frac{1}{c}\frac{K_1+K_2}{N_A}\right)\exp\left(+\int_{\pm L/2}^{z'}\frac{\partial \ln c}{\partial z''}\,\mathrm{d}z''\right)\mathrm{d}z'\right]. \tag{3.23}$$

It is necessary that $C = 0$ since $w(\pm L/2, t) = 0$ according to the boundary conditions (2.17). Moreover according to equations (3.19) and (3.17), for all z in $0 \leqslant |z| \leqslant L/2$ and $t \geqslant 0$,

$$\left|\int_{\pm L/2}^{z}\frac{\partial \ln c}{\partial z'}\,\mathrm{d}z'\right| \leqslant \frac{p_0}{RT}|B_{11}-B_{22}|. \tag{3.24}$$

In the case of the imperfect gas mixture C(CH$_3$)$_4$–Ar of Section 3.3.1, the RHS of equation (3.24) has the value 0.027. In the case of the observing positions used, $z_A = \pm L/3$, the LHS of equation (3.24) is however smaller than 0.002. Therefore the exponential expressions in equation (3.23) are about 1.0 [$\exp(\pm 0.002) = 1 \pm 0.002$]. With these conditions and equations (3.19) and (3.17), $w_{\pm}$ in equation (3.23) may be approximated by

$$\begin{aligned} w_{\pm}(z,t) &= \int_{\pm L/2}^{z}\left(\frac{\partial \ln v}{\partial t}+v\frac{K_1+K_2}{N_A}\right)\mathrm{d}z' \\ &= -\int_{\pm L/2}^{z}\frac{\mathrm{d}\ln p}{\mathrm{d}t}\,\mathrm{d}z'+\frac{p_0}{RT}\int_{\pm L/2}^{z}(\beta_2+2\beta_1x_1)\frac{\partial x_1}{\partial t}\,\mathrm{d}z'+\frac{1}{N_A}\int_{\pm L/2}^{z}v(K_1+K_2)\,\mathrm{d}z'. \end{aligned} \tag{3.25}$$

Since $w_-(0,t)-w_+(0,t) = 0$ the pressure change during diffusion in the entire diffusion cell $-L/2 \leqslant z \leqslant +L/2$ follows from equation (3.25) as

$$\begin{aligned} &\frac{\mathrm{d}\ln p}{\mathrm{d}t} = \left(\frac{\mathrm{d}\ln p}{\mathrm{d}t}\right)_M + \left(\frac{\mathrm{d}\ln p}{\mathrm{d}t}\right)_K, \quad \left(\frac{\mathrm{d}\ln p}{\mathrm{d}t}\right)_M = \frac{p_0}{RT}\frac{1}{L}\int_{-L/2}^{+L/2}(\beta_2+2\beta_1x_1)\frac{\partial x_1}{\partial t}\,\mathrm{d}z', \\ &\left(\frac{\mathrm{d}\ln p}{\mathrm{d}t}\right)_K = \frac{1}{N_A}\frac{1}{L}\int_{-L/2}^{+L/2}v(K_1+K_2)\,\mathrm{d}z'. \end{aligned} \tag{3.26}$$

The first contribution (subscript M) describes the pressure change due to the pure mixing volume effect at constant particle number whereas the second contribution (subscript K) follows from particle number changes by, for example, gas sorption at the walls of the diffusion cell or chemical reactions in the gas mixture. After inserting equation (3.26) into equation (3.25) one gets

$$\begin{aligned} &w_{\pm}(z,t) = w_{M\pm}(z,t)+w_{K\pm}(z,t), \quad w_{M\pm}(z,t) = \int_{\pm L/2}^{z}\left[\frac{p_0}{RT}(\beta_2+2\beta_1x_1)\frac{\partial x_1}{\partial t}-\left(\frac{\mathrm{d}\ln p}{\mathrm{d}t}\right)_M\right]\mathrm{d}z', \\ &w_{K\pm}(z,t) = \int_{\pm L/2}^{z}\left[v\frac{K_1+K_2}{N_A}-\left(\frac{\mathrm{d}\ln p}{\mathrm{d}t}\right)_K\right]\mathrm{d}z'. \end{aligned} \tag{3.27}$$

$w_M(z,t)$ is the mean particle velocity due to the mixing volume effect and $w_K(z,t)$ the mean particle velocity due to particle number changes. Inserting the estimates (3.21) for K_1, K_2 into equations (3.26) and (3.27) gives

$$\left(\frac{\mathrm{d}\ln p}{\mathrm{d}t}\right)_K = k_1(t), \quad w_K(z,t) = w_{K\pm}(z,t) = 0. \tag{3.28}$$

This simple and physically reasonable result is of great importance for the evaluation of diffusion experiments.

Equations (3.26) and (3.27) may be explicitly evaluated by using the approximate relations $x_1 = x_1^{\mathrm{id}}$ according to equation (3.2) and $\partial x_1/\partial t$ according to equation (3.1) and obeying the conditions (2.17). If D is assumed to be independent of position z only for the purpose of simple integration, the result is

$$\begin{aligned} &\int_{\pm L/2}^{z}(\beta_2+2\beta_1x_1)\frac{\partial x_1}{\partial t}\,\mathrm{d}z' = D\left[(\beta_2+2\beta_1x_1)\frac{\partial x_1}{\partial z}-2\beta_1\int_{\pm L/2}^{z}\left(\frac{\partial x_1}{\partial z'}\right)^2\mathrm{d}z'\right], \\ &\int_{\pm L/2}^{z}\left(\frac{\partial x_1}{\partial z'}\right)^2\mathrm{d}z' = y^2\left[\left(z\mp\frac{L}{2}\right)\frac{1}{2}\underset{0,r}{S}+I\right], \quad I = \sum_{n=1}^{\infty}\left[\underset{n,r}{S^+}(t)+\frac{1}{2}\underset{n,r}{S^-}(t)\right]\frac{\sin b_nz}{b_n}. \end{aligned} \tag{3.29}$$

The last two expressions result by using equation (3.5). Therefore, in this approximation, according to equations (3.26) and (3.27),

$$\begin{aligned} &\left(\frac{\mathrm{d}\ln p}{\mathrm{d}t}\right)_M = -\frac{p_0D}{RT}\beta_1y^2\underset{0,r}{S}(t), \\ &w_{M\pm}(z,t) = -\frac{p_0D}{RT}\left[(\beta_2+2\beta_1x_1^{\mathrm{m}})y\frac{\partial F^{(0)}}{\partial z}-2\beta_1y^2\left(F^{(0)}\frac{\partial F^{(0)}}{\partial z}-I\right)\right] = w_M(z,t). \end{aligned} \tag{3.30}$$

Integration of equations (3.26), (3.28) and (3.30) with respect to time t gives

$$\ln\frac{p}{p_0} = \ln\frac{p_K}{p_0} + \ln\frac{p_M}{p_0}, \quad p = \frac{p_K p_M}{p_0}. \tag{3.31}$$

$p(t) = p_0 + \Delta p(t)$ is the measured pressure during the diffusion experiment. Therefore equation (3.31) may be written in the following manner:

$$\begin{gathered}\ln\left(1+\frac{\Delta p}{p_0}\right) = \ln\left(1+\frac{\Delta p_K}{p_0}\right) + \ln\left(1+\frac{\Delta p_M}{p_0}\right), \quad \ln\left(1+\frac{\Delta p_K}{p_0}\right) = \int_0^t k_1(t')\,\mathrm{d}t' \approx \frac{\Delta p_K}{p_0}, \\ \ln\left(1+\frac{\Delta p_M}{p_0}\right) = -\frac{D p_0 \beta_1}{RT} y^2 F^{(1)}(t) \approx \frac{\Delta p_M}{p_0}, \quad \Delta p \approx \Delta p_K + \Delta p_M,\end{gathered} \tag{3.32}$$

$$F^{(1)}(t) = \int_0^t \underset{0,r}{S}(t')\,\mathrm{d}t' = \sum_{r=0}^{\infty} \frac{1-\exp(-2a_r^2 Dt)}{2a_r^2 D}. \tag{3.33}$$

The approximative relations in equations (3.32) are valid only if the corresponding relative pressure changes $\Delta p/p_0$ are small enough, which was the case in our diffusion experiments.

According to equations (3.32) the contribution Δp_M to the total measured pressure change Δp may be calculated if β_1 is known. This calculation may iteratively be corrected by inserting $p(t)$ instead of p_0 in the factor $Dp_0\beta_1/RT$, a correction only effective for large t values [1]. If Δp_M and Δp are known, the contribution $\Delta p_K = \Delta p - \Delta p_M$ due to sorption may be determined. Differentiation of $\Delta p_K/p_0$ with respect to time t then gives the velocity law $k_1(t)$ for gas sorption according to equation (3.21). On the other hand the coefficient β_1, and therefore the mixing virial coefficient B_{12}, may be determined in the limit $t \to \infty$ if $\Delta p_K = 0$ and if the viral coefficients B_{11}, B_{22} of the pure gases are known [$F^{(1)}(t \to \infty) = \pi^2/16D$, see Sections 1 and 4]. In this sense, self-consistent diffusion measurements are possible.

3.4. *Evaluation of the perturbation terms*

To evaluate the perturbation terms F_D, F_w and F_K of equation (2.15), the approximations $x_1 = x_1^{id}$ and $\partial x_1/\partial t = D\partial^2 x_1/\partial z^2$ are used in the same manner as in Section 3.3.4. With the above estimates of $\partial\Delta/\partial x_1$, w, K_1/n and K_2/n, it can be shown that

$$\begin{gathered}F_D = D_1\frac{\partial\Delta}{\partial x_1}\left(\frac{\partial x_1}{\partial z}\right)^2 = c_D y^2\Sigma_2 - 2D_1c_1y^3\Sigma_3, \quad F_w = -w_M\frac{\partial x_1}{\partial z} = -c_w y^2\Sigma_2 + \frac{2\beta_1 p_0 D}{RT}y^3(\Sigma_3-\Sigma_4) = F_{wM}, \\ F_K = \frac{1}{n}[K_1 - x_1(K_1+K_2)] = k_1(t)[1-x_1] = k_1(t)[1-x_1^m + yF^{(0)}],\end{gathered} \tag{3.34}$$

$$c_D = D_1(c_2+2c_1x_1^m), \quad c_w = \frac{p_0 D}{RT}(\beta_2+2\beta_1 x_1^m), \quad \Sigma_2 = \left(\frac{\partial F^{(0)}}{\partial z}\right)^2, \quad \Sigma_3 = F^{(0)}\Sigma_2, \quad \Sigma_4 = \frac{\partial F^{(0)}}{\partial z}I. \tag{3.35}$$

Σ_2 is given by equation (3.5). Using $2\sin\alpha\cos\beta = \sin(\alpha-\beta)+\sin(\alpha+\beta)$ and equation (3.3), by multiplying the corresponding series term by term and rearranging one obtains

$$\begin{gathered}\Sigma_3 = \sum_{n=0}^{\infty} S_{3n}(t)\sin a_n z, \\ S_{3n}(t) = \frac{1}{2}\left\{\frac{\exp(-a_n^2 Dt)}{a_n}\underset{0,r}{S} + \sum_{m=1}^{\infty}\left[\underset{m,r}{S^+} + \frac{1}{2}\underset{m,r}{S^-}\right]\left[\frac{\exp(-[a_n-b_m]^2Dt)}{a_n-b_m} + \frac{\exp(-[a_n+b_m]^2Dt)}{a_n+b_m}\right]\right\},\end{gathered} \tag{3.36}$$

$$\begin{gathered}\Sigma_4 = \sum_{n=0}^{\infty} S_{4n}(t)\sin a_n z, \\ S_{4n}(t) = \frac{1}{2}\sum_{m=1}^{\infty}\left[\underset{m,r}{S^+} + \frac{1}{2}\underset{m,r}{S^-}\right][\exp(-[a_n-b_m]^2Dt) - \exp(-[a_n+b_m]^2Dt)]\left(\frac{1}{b_m}\right).\end{gathered} \tag{3.37}$$

Therefore the coefficients $U_n(t)$ and $G_n(t)$ of the Fourier series (3.7) are, in this approximation, given by

$$G_0(t) = k_1(t)[1-x_1^m] + (c_D - c_w)\frac{y^2}{2}\underset{0,r}{S}(t), \tag{3.38}$$

$$G_n(t) = (c_D - c_w)y^2\left[\underset{n,r}{S^+} + \frac{1}{2}\underset{n,r}{S^-}\right], \quad (n \geqslant 1), \tag{3.39}$$

$$U_n(t) = yk_1(t)\frac{\exp(-a_n^2Dt)}{a_n} - 2c_1D_1y^3S_{3n}(t) + \frac{2\beta_1p_0D}{RT}y^3[S_{3n}(t) - S_{4n}(t)], \quad (n \geqslant 0). \tag{3.40}$$

Finally these expressions may be used to calculate the desired coefficients $u_n^{(1)}(t)$ and $g_n^{(1)}(t)$ according to equations (3.10) and (3.11), respectively, and the desired correction terms $x_1^{(1,2)}(z,t)$, $x_1^{(1,3)}(z,t)$ of the mole fraction $x_1(z,t)$ according to equations (3.14) and (3.15)

$$\begin{gathered} x_1^{(1,2)}(z,t) = g_0^{(1)}(t) + (c_D - c_w)y^2F^{(2)}(z,t), \quad g_0^{(1)}(t) = [1 - x_1^m]\frac{\Delta p_K}{p_0} + (c_D - c_w)\frac{y^2}{2}F^{(1)}(t), \\ F^{(2)}(z,t) = \sum_{n=1}^{\infty} \exp(-b_n^2\,Dt)S(A,B)\cos b_nz, \end{gathered} \tag{3.41}$$

$$\begin{gathered} x_1^{(1,3)}(z,t) = yF^{(0)}(z,t)\left[\frac{\Delta p_K}{p_0} - c_1D_1y^2F^{(1)}(t) - \frac{\Delta p_M}{p_0}\right] - y^3\left\{c_1D_1F^{(3)}(z,t) - \frac{p_0\beta_1D}{RT}[F^{(3)}(z,t) - F^{(4)}(z,t)]\right\}, \\ F^{(3)}(z,t) = \sum_{n=0}^{\infty} \exp(-a_n^2Dt)\sum_{m=1}^{\infty}\left[\frac{S(E,F)}{a_n - b_m} + \frac{S(G,H)}{a_n + b_m}\right]\sin a_nz, \\ F^{(4)}(z,t) = \sum_{n=0}^{\infty} \exp(-a_n^2Dt)\sum_{m=1}^{\infty}\frac{1}{b_m}[S(E,F) - S(G,H)]\sin a_nz. \end{gathered} \tag{3.42}$$

$F^{(1)}(t)$ is given by equation (3.33). The following abbreviations are used:

$$S(X,Y) \equiv \sum_{r=0}^{\infty}\frac{1 - \exp(-Xt)}{X} + \frac{1}{2}\sum_{r=0}^{n-1}\frac{1 - \exp(-Yt)}{Y}, \tag{3.43}$$

$$\begin{aligned} A &= 2Da_r(a_r + b_n), & B &= 2Da_r(a_r - b_n), \\ E &= 2D[a_r(a_r + b_m) + b_m(b_m - a_n)], & F &= 2D[a_r(a_r - b_m) + b_m(b_m - a_n)], \\ G &= 2D[a_r(a_r + b_m) + b_m(b_m + a_n)], & H &= 2D[a_r(a_r - b_m) + b_m(b_m + a_n)]. \end{aligned}$$

In Fig. 2 the reduced functions

$$\begin{gathered} f^{(0)} = \left(\frac{\pi}{L}\right)F^{(0)}(z,t), \quad f^{(1)} = \left(\frac{1}{\tau}\right)F^{(1)}(t), \quad f^{(2)} = \left(\frac{1}{\tau}\right)F^{(2)}(z,t), \\ f^{(3)} = \left(\frac{\pi}{L\tau}\right)F^{(3)}(z,t), \quad f^{(4)} = \left(\frac{\pi}{L\tau}\right)F^{(4)}(z,t), \quad \tau = L^2/\pi^2D, \end{gathered} \tag{3.44}$$

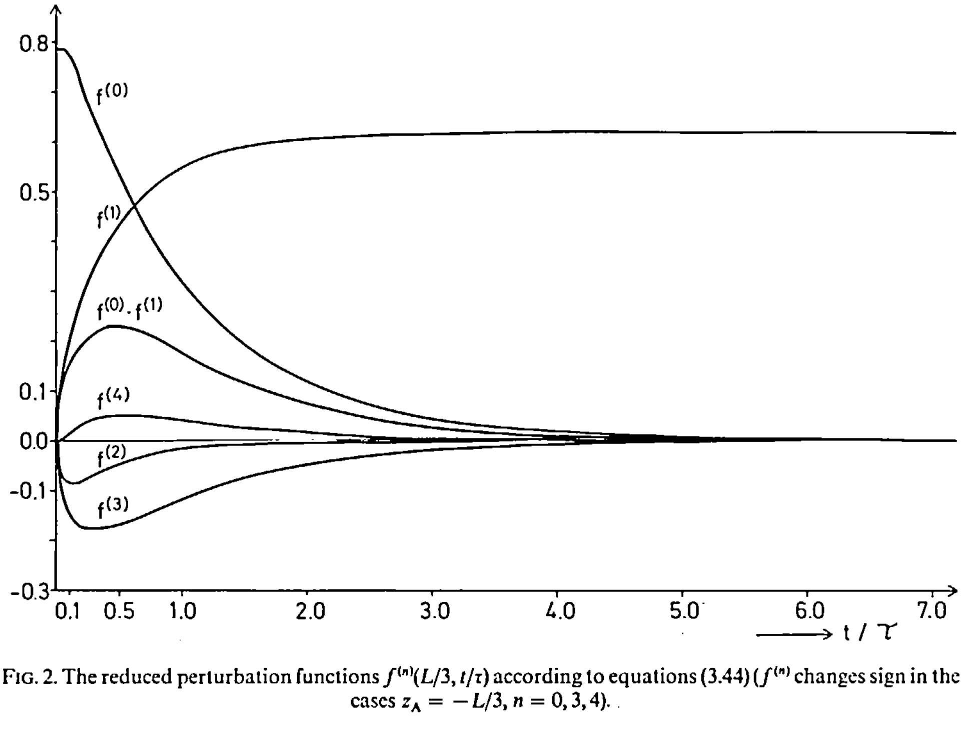


FIG. 2. The reduced perturbation functions $f^{(n)}(L/3, t/\tau)$ according to equations (3.44) ($f^{(n)}$ changes sign in the cases $z_A = -L/3$, $n = 0, 3, 4$).

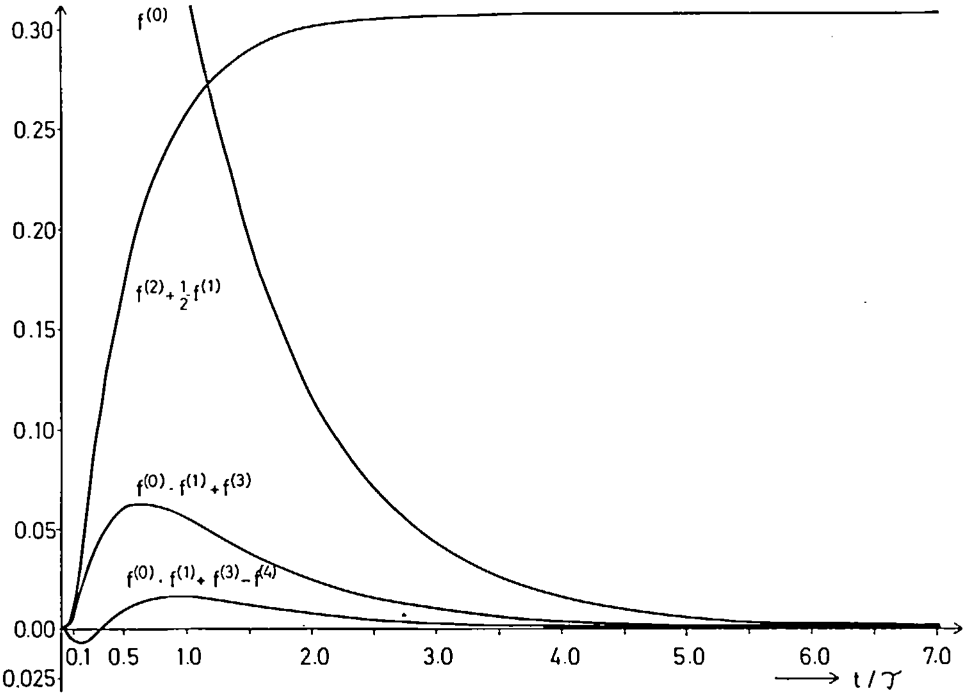


FIG. 3. Combinations of the reduced perturbation functions $f^{(n)}(L/3, t/\tau)$ which are used in equations (4.1)–(4.4) ($f^{(n)}$ changes sign in the cases $z_A = -L/3$, $n = 0, 3, 4$).

are drawn versus the reduced time $t/\tau = \pi^2 Dt/L^2$ in the case of the measuring position $z = z_A = +L/3$. In the case $z_A = -L/3$ the parity of the sine and cosine functions has to be noticed according to equations (3.14) and (3.15). The reduced functions (3.44) need only be calculated and tabulated once for all diffusion measurements at the same positions z_A and $-z_A$, since this calculation is very time-consuming. In Fig. 3, combinations of these functions are shown which are important in equations (4.1)–(4.4).

4. DISCUSSION

The general diffusion equation (2.13) was solved with first order perturbation calculus. The main contribution to the mole fraction $x_1(z, t)$, which is identical with the mole fraction measured in our diffusion experiments, is the solution $x_1^{id}(z, t)$ of Fick's second law (3.1). The correction terms $x_1^{(1,2)}(z, t)$ and $x_1^{(1,3)}(z, t)$, which are explicitly given by equations (3.41) and (3.42), are determined with the following assumptions:

(1) The gas mixture is only weakly real.
(2) The diffusion coefficient D is independent on position z only in deriving equations (3.29) and (3.30).
(3) The velocity law $k_1(t)$ for gas sorption is only time-dependent, i.e. $w_K = 0$.
(4) $x_1(z, t)$ may be replaced everywhere by $x_1^{id}(z, t)$ in calculating the perturbation term $F(z, t)$ in first order.

The same assumptions were made by other authors [1, 15, 16]. Nevertheless, the results of this paper differ considerably from the results of these previous papers. The main reason for this is the fact that the perturbation terms F_D and F_K according to equations (3.34) are used in this paper for the first time. Moreover the term $D(\partial \ln n/\partial z)(\partial x_1/\partial z)$ of equation (2.11) was cancelled in the exact diffusion equation (2.13) but not in the diffusion equations used by the other authors [1, 15, 16]. This means that the expressions of c_w and Σ_3 in equation (3.34) for the perturbation term F_W are only one-half of the corresponding expressions used in the earlier works. Σ_4, however, is unaltered. In the resulting equations (3.38)–(3.42) the expressions of c_w, $S_{3n}(t)$ in the square bracket on the RHS of equation (3.40), $-\Delta p_M/p_0$ and $(p_0\beta_1 D/RT)F^{(3)}$ in equation (3.42) are just only one-half of the previous corresponding expressions.

To understand the following discussion somewhat better it seems reasonable to rewrite equation (3.13) for the measured mole fraction $x_1(z_A, t)$ in three terms according to the three effects which cause them,

$$x_1(z_A, t) = x_{1D} + \Delta x_{1w} + \Delta x_{1K}, \tag{4.1}$$

$$x_{1D}(z_A, t) = x_1^{id} + \Delta x_{1D} = x_1^{m} - \left(\frac{2}{\pi}\right)\Delta x f^{(0)} + \Delta x_{1D}, \tag{4.2}$$

$$\Delta x_{1\mathrm{D}}(z_{\mathrm{A}},t)=\left(\frac{c_{\mathrm{D}}}{D}\right)\left(\frac{2}{\pi}\right)^2(\Delta x)^2[f^{(2)}+\tfrac{1}{2}f^{(1)}]-\left(\frac{c_1D_1}{D}\right)\left(\frac{2}{\pi}\right)^3(\Delta x)^3[f^{(0)}f^{(1)}+f^{(3)}],$$

$$\Delta x_{1\mathrm{w}}(z_{\mathrm{A}},t)=-\left(\frac{c_{\mathrm{w}}}{D}\right)\left(\frac{2}{\pi}\right)^2(\Delta x)^2[f^{(2)}+\tfrac{1}{2}f^{(1)}]+\frac{p_0\beta_1}{RT}\left(\frac{2}{\pi}\right)^3(\Delta x)^3[f^{(0)}f^{(1)}+f^{(3)}-f^{(4)}]=\Delta x_{1\mathrm{wM}},\tag{4.3}$$

$$\Delta x_{1\mathrm{K}}(z_{\mathrm{A}},t)=[1-x_1^{\mathrm{id}}]\frac{\Delta p_{\mathrm{K}}}{p_0}=\left[1-x_1^{\mathrm{m}}+\left(\frac{2}{\pi}\right)\Delta x f^{(0)}\right]\frac{\Delta p_{\mathrm{K}}}{p_0}.\tag{4.4}$$

Equation (4.1) may be considered as a power series in $\Delta x = x_{1\mathrm{u}}-x_{1\mathrm{o}}$. Omitting the term $D(\partial\ \ln n/\partial z)(\partial x_1/\partial z)$ in the diffusion equation (2.13) has the consequence that the expressions of c_{w} and $[f^{(0)}f^{(1)}+f^{(3)}]$ in equation (4.3) for $\Delta x_{1\mathrm{w}}(z_{\mathrm{A}},t)$ are only one-half of the corresponding older expressions [1, 15, 16] as just mentioned. In remembering this Jescheck was the first to derive the complete expression of $\Delta x_{1\mathrm{w}}$ corresponding to equation (4.3) and use this correction term in evaluating diffusion experiments with pure gases [1]. Gotoh *et al.* [16] have investigated the diffusion of pure real gases too, but they omitted the corresponding term in $(\Delta x)^3$ in equation (4.3) completely. They used, however, the corresponding term in $(\Delta x)^2$, whereas Ljunggren [15] used the pure time-dependent term $-c_{\mathrm{w}}2(\Delta x)^2f^{(1)}/D\pi^2$ in equation (4.3) twice to evaluate his diffusion experiments with diffusing gas mixtures of $\Delta x = 0.1$. Gas sorption was considered only by Gotoh *et al.* [16] and Jescheck [1], but both times in a more empirical manner and not as consistent as equation (4.4). The concentration dependence of D was not considered like equation (4.2), which is a result of the perturbation calculus described above.

Since all $f^{(n)}$-functions vanish in the limit $t\to\infty$, except $f^{(1)}(t)$ which gives $f^{(1)}(\infty)=\pi^2/16=0.616850$, the following limit of $x_1(z_{\mathrm{A}},t)$ results from equation (4.1):

$$\lim_{t\to\infty}x_1(z_{\mathrm{A}},t)=x_1^{\mathrm{m}}-\frac{c_{\mathrm{w}}-c_{\mathrm{D}}}{8D}(\Delta x)^2+[1-x_1^{\mathrm{m}}]\left(\frac{\Delta p_{\mathrm{K}}}{p_0}\right)_\infty.\tag{4.5}$$

The kinetic expressions (4.1)-(4.5) show that the concentration dependence of the diffusion coefficient D is incorporated in the measured mole fraction $x_1(z_{\mathrm{A}},t)$, as in the statement given previously (Section 1).

It is very interesting to compare the kinetic result (4.5) for the thermodynamical equilibrium state of the gas mixture after diffusion with the limit $x_1(\infty)$, which is given by pure thermodynamical considerations. According to the approximation (3.16) for the molar volume v the mole fraction $x_1(\infty)$ after diffusion is, in the case $\Delta p_{\mathrm{K}}=0$, given by

$$x_1(\infty)=\frac{n_{1\mathrm{u}}+n_{1\mathrm{o}}}{(n_{1\mathrm{u}}+n_{2\mathrm{u}})+(n_{1\mathrm{o}}+n_{2\mathrm{o}})}=\frac{V_{\mathrm{u}}/v_{1\mathrm{u}}+V_{\mathrm{o}}/v_{1\mathrm{o}}}{V_{\mathrm{u}}/v_{\mathrm{mu}}+V_0/v_{\mathrm{mo}}}.\tag{4.6}$$

V_{u} and V_{o} are the volumes of the two half-cells and are equal in the diffusion apparatus. $v_{1\mathrm{u}}=RT/p_{1\mathrm{u}}+B_{11}$ s the molar volume of gas 1 after adding it to the evacuated volume V_{u} up to a pressure $p_{1\mathrm{u}}$. Thereafter, gas 2 s added up to a pressure $p_0=p(0)$, which according to equation (3.17), corresponds to the molar volume $v_{\mathrm{mu}}(x_{1\mathrm{u}})=RT/p_0+B_{22}+\beta_2x_{1\mathrm{u}}+\beta_1x_{1\mathrm{u}}^2$ of the binary gas mixture with mole fraction $x_{1\mathrm{u}}=v_{\mathrm{mu}}/v_{1\mathrm{u}}$ of gas 1 before diffusion. If the corresponding meanings are given to $v_{1\mathrm{o}}$, v_{mo} and $x_{1\mathrm{o}}$ one gets with $V_{\mathrm{u}}=V_{\mathrm{o}}$ after some algebraic manipulations

$$x_1(\infty)=x_1^{\mathrm{m}}-\frac{1}{2}\frac{v_{\mathrm{mu}}-v_{\mathrm{mo}}}{2v_{\mathrm{mu}}+v_{\mathrm{mo}}}\Delta x=x_1^{\mathrm{m}}-\frac{1}{4}\frac{c_{\mathrm{w}}/D}{1+A}(\Delta x)^2,\tag{4.7}$$

$$A=\frac{p_0}{RT}[B_{22}+\beta_2x_1^{\mathrm{m}}+\beta_1(2x_1^{\mathrm{m}2}-x_{1\mathrm{u}}x_{1\mathrm{o}})].\tag{4.8}$$

Equating equations (4.7) and (4.5), in the case $\Delta p_{\mathrm{K}}=0$, gives

$$\frac{c_{\mathrm{D}}}{D}=-\left(\frac{c_{\mathrm{w}}}{D}\right)\left(\frac{1-A}{1+A}\right).\tag{4.9}$$

This equation (4.9) connects the kinetic variable c_{D}/D with the thermostatic variables c_{w}/D and A and may be discussed in the case $x_{1\mathrm{u}}=1$, $x_{1\mathrm{o}}=0$, which are our experimental conditions. Using the virial coefficients of Section 3.3.1, for the system $C(CH_3)_4$–Ar at $p = 1$ bar, $T = 332$ K, gives

$$\begin{aligned}&c_{\mathrm{w}}/D=(B_{11}-B_{22})p_0/RT=-0.0267,\quad A=(B_{11}+B_{22})p_0/2RT=-0.0137,\\&x_1(\infty)=\tfrac{1}{2}-\tfrac{1}{4}\left(\frac{c_{\mathrm{w}}/D}{1+A}\right)=0.50677,\quad \frac{c_{\mathrm{D}}}{D}=\frac{c_2+c_1}{1+\Delta(x_1^{\mathrm{m}})}=-\frac{c_{\mathrm{w}}}{D}\left(\frac{1-A}{1+A}\right)=0.0275.\end{aligned}\tag{4.10}$$

This value of c_{D}/D seems reasonable since $c_2+c_1=D(1)-D(0)$ is the difference of the diffusion coefficients in the limiting cases $x_1=1$ and $x_1=0$, and is therefore of the order of 3%. On the other hand, we have $c_{\mathrm{w}}/D=c_{\mathrm{D}}/D=0$

only if $p_0 = 0$ (vacuum conditions), $T \to \infty$ [perfect gas mixture with $B_{11}(T \to \infty) = B_{22}(T \to \infty) = 0$] or $B_{11}(T) = B_{22}(T)$, which means self-diffusion (interdiffusing gases with identical particles and therefore identical interaction pair-potentials). These conditions seem very reasonable too, although the dependence of c_D/D on p_0/RT like equations (4.9) and (4.10) is not inherent in the Chapman-Enskog kinetic theory of gases as was shown in Section 2.2. This is, however, not surprising since equations (4.9) and (4.10) are obtained by connecting the result, equation (4.5), of kinetic perturbation calculus with the result, equation (4.7), of the conservation of mass in a diffusion experiment.

Some additional points should be mentioned at this stage. Firstly the mixing virial coefficient B_{12} does not appear in equation (4.10), which is of great importance for the evaluation of diffusion experiments with gas mixtures of unknown B_{12}. Secondly, the case $c_D/D = 0$ may also occur if $A = 1$ in equations (4.9) and (4.10), which in the case $p_0 = 1$ bar means $RT_0 = (B_{11}+B_{22})/2$ and $c_w/D = 2(B_{11}-B_{22})/(B_{11}+B_{22})$. By comparing this result with the second Kihara approximation (2.10) this definite temperature T_0 may correspond to $C_{12}^*(T_0^*) = 5/6$, in which case $T_0^* = kT_0/\varepsilon_{12}$ is of the order of 1.0 for many interaction pair-potentials [3].

To demonstrate the magnitudes of the correction terms in equations (4.1)–(4.4), we finally give numerical values for the same conditions as in equations (4.10),

$$\begin{aligned} x_1(z_A, t) &= x_{1D}+\Delta x_{1w}+\Delta x_{1K}, \quad x_{1D}(z_A, t) = 0.50000-0.63662f^{(0)}+\Delta x_{1D}, \\ \Delta x_{1D}(z_A, t) &= 0.01113\,[f^{(2)}+\tfrac{1}{2}f^{(1)}]+0.00774\,[f^{(0)}f^{(1)}+f^{(3)}], \\ \Delta x_{1w}(z_A, t) &= 0.01083\,[f^{(2)}+\tfrac{1}{2}f^{(1)}]-0.00585\,[f^{(0)}f^{(1)}+f^{(3)}-f^{(4)}], \\ \Delta x_{1K}(z_A, t) &= [0.50000+0.63662f^{(0)}]\frac{\Delta p_K}{p_0}, \quad \frac{\Delta p_K}{p_0} \leqslant \left(\frac{\Delta p_K}{p_0}\right)_\infty \approx \frac{7}{760} = 0.009. \end{aligned} \tag{4.11}$$

Some remarks concerning gas sorption will conclude this discussion.

(1) The last expression in equation (4.11) for $\Delta x_{1K}(z_A, t)$, and therefore equation (4.4), obviously hold only for the lower half-cell $z_A < 0$, because $f^{(0)}$ is not symmetrical with respect to the sorption source (sink) in the plane $z = 0$. Since this asymmetry with regard to adsorption ($\Delta p_K/p_0 < 0$) and desorption ($\Delta p_K/p_0 > 0$) seems to be physically unreasonable, we assume that $x_2^{id} = 1-x_1^{id}$ in equation (4.4) has to be replaced by x_1^{id} for the upper half-cell $z_A > 0$

$$\Delta x_{1K}(z_A < 0, t) = \frac{\Delta p_K}{p_0} x_2^{id}(z_A < 0, t), \quad \Delta x_{1K}(z_A > 0, t) = \frac{\Delta p_K}{p_0} x_1^{id}(z_A > 0, t). \tag{4.12}$$

(2) The simple results $\Delta x_{1w} = \Delta x_{1wM}$ in equation (4.3) as well as Δx_{1K} in equations (4.4) and (4.12) are mainly determined by the simplified estimates (3.21) of $K_1 v/N_A$ and K_2 for gas sorption. However using the approximation (3.16) of $v(z, t)$ the following more general estimates may be used:

$$\frac{K_1 v}{N_A} = \frac{K_1(t)}{N_A}\left[\frac{RT}{p} + B_m(x_1^{id})\right] = k_1(z, t), \quad K_2 = 0, \quad B_m(x_1^{id}) = \beta_3+\beta_2 x_1^{id}+\beta_1 x_1^{id\,2}. \tag{4.13}$$

$K_1 = K_1(t)$ seems to be reasonable, because the sorption source or sink is only weak and limited to $z = 0$, as it was in Section 3.3.2 too. Using equation (4.13) for perturbation calculus has some important consequences. According to equation (3.26) the first equation in equations (3.28) is now given by

$$\left(\frac{\mathrm{d}\ln p}{\mathrm{d}t}\right)_K = \left(\frac{K_1(t)}{N_A}\right)\left[\frac{RT}{p}+B_m(x_1^m)+\frac{\beta_1 y^2}{2}A_{r,0}\right] = k_1^*(t), \tag{4.14}$$

and the second equation by

$$w_K(z, t) = w_{K\pm}(z, t) = \left(\frac{K_1(t)}{N_A}\right)\left[y(\beta_2+2\beta_1 x_1^m)\sum_{n=0}^{\infty}\frac{f_n}{a_n}\cos a_n z+\beta_1 y^2\sum_{n=1}^{\infty}\left(\frac{A_{r,n}}{b_n}\right)\sin b_n z\right]. \tag{4.15}$$

The last equation fulfills the boundary conditions (2.17) and goes to zero in the limit $t \to \infty$. The following abbreviations are used:

$$\begin{aligned} &h_x(t) = \exp(-a_x^2 Dt), \quad f_x(t) = h_x(t)/a_x, \quad a_x = (2x+1)\pi/L, \\ &A_{r,0}(t) = \sum_{r=0}^{\infty} f_r^2, \quad A_{r,n\geqslant 1}(t) = \sum_{r=0}^{\infty} f_r f_{r+n}-\tfrac{1}{2}\sum_{r=0}^{n-1} f_r f_{n-1-r}. \end{aligned} \tag{4.16}$$

On account of equations (4.12)–(4.15) the perturbation terms F_K and $F_w = F_{wM}$ in equation (3.34), the last due only to the mixing volume effect, have to be modified in the following manner:

$$F_w = F_{wM}+F_{wK}, \quad F_{wK} = -w_K\frac{\partial x_1^{id}}{\partial z}, \tag{4.17}$$

$$F_K = \begin{cases} F_{K-} = k_1(z < 0, t)x_2^{id}(z < 0, t), \\ F_{K+} = k_1(z > 0, t)x_1^{id}(z > 0, t). \end{cases} \tag{4.18}$$

Using the expression (3.2) for x_1^{id} and some trigonometric and algebraic manipulations, F_K may be written as a Fourier series according to equation (3.7) as follows:

$$\begin{aligned} F_K &= \left(\frac{K_1(t)}{N_A}\right)\left[C_0 + C_1F^{(0)} + C_2F^{(0)2} + C_3F^{(0)3}\right] = \sum_{n=0}^{\infty} [U_{nK}(t)\sin a_nz + G_{nK}(t)\cos b_nz], \\ G_{0K}(t) &= \left(\frac{K_1(t)}{N_A}\right)\left[C_0 + \frac{C_2}{2}A_{r,0}(t)\right], \quad G_{nK}(t) = \left(\frac{K_1(t)}{N_A}\right)C_2A_{r,n}(t), \quad (n \geqslant 1), \\ U_{nK}(t) &= \left(\frac{K_1(t)}{N_A}\right)\left\{f_n\left(C_1 + \frac{C_3}{2}A_{r,0}\right) + \frac{C_3}{2}\sum_{k=1}^{\infty} A_{r,k}[f_{k+n} + f_{n-k}]\right\}, \quad (n \geqslant 0). \end{aligned} \tag{4.19}$$

According to equation (4.18) the coefficients C_0, C_1, C_2, C_3 in equation (4.19) are given either by the minus ($-$) or plus ($+$)-set of coefficients (4.20)

$$\begin{aligned} C_{0-} &= \left[\frac{RT}{p} + B_m(x_1^m)\right][1 - x_1^m], & C_{0+} &= \left[\frac{RT}{p} + B_m(x_1^m)\right]x_1^m, \\ C_{1-} &= y\left\{\left[\frac{RT}{p} + B_m(x_1^m)\right] - [\beta_2 + 2\beta_1x_1^m][1 - x_1^m]\right\}, & C_{1+} &= -y\left\{\left[\frac{RT}{p} + B_m(x_1^m)\right] + [\beta_2 + 2\beta_1x_1^m]x_1^m\right\}, \\ C_{2-} &= y^2\{\beta_1 - \beta_2 - 3\beta_1x_1^m\}, & C_{2+} &= y^2\{\beta_2 + 3\beta_1x_1^m\}, \\ C_{3-} &= y^3\beta_1, & C_{3+} &= -y^3\beta_1. \end{aligned} \tag{4.20}$$

In the same manner the perturbation term F_{wK} may be written as

$$\begin{aligned} F_{wK} &= \sum_{n=0}^{\infty} \{U_{nwK}(t)\sin a_nz + G_{nwK}(t)\cos b_nz\}, \\ G_{0wK}(t) &= \left(\frac{K_1(t)}{N_A}\right)C_4A_{r,0}, \quad G_{nwK}(t) = \left(\frac{K_1(t)}{N_A}\right)C_4\left[\sum_{r=0}^{\infty}\left(\frac{f_r}{a_r}h_{r+n} + \frac{f_{r+n}}{a_{r+n}}h_r\right) + \sum_{r=0}^{n-1}\frac{f_r}{a_r}h_{n-1-r}\right], \\ U_{nwK}(t) &= \left(\frac{K_1(t)}{N_A}\right)\left(\frac{C_{3-}}{2}\right)\sum_{k=1}^{\infty}\frac{A_{r,k}}{b_k}[h_{k-1-n} - h_{k+n}], \quad C_4 = y^2(\beta_2 + 2\beta_1x_1^m)/2. \end{aligned} \tag{4.21}$$

In order to calculate by equations (3.10) and (3.11) the corresponding desired coefficients $u_n^{(1)}(t)$ and $g_n^{(1)}(t)$ for the mole fraction changes Δx_{1K} due to F_K and Δx_{1wK} due to F_{wK} the Fourier coefficients of equations (4.19) and (4.21) have to be integrated with respect to time t. For this purpose $K_1(t)$ must be known, which seems to be the main problem. However the following approximation is evident. On account of equation (4.14) we have

$$\frac{K_1(t)}{N_A} = K(t)\left(\frac{dp}{dt}\right)_K, \quad K(t) = \{RT + p[B_m(x_1^m) + \beta_1y^2A_{r,0}/2]\}^{-1}. \tag{4.22}$$

$K(t)$ may be calculated exactly for each gas mixture and time t according to its definition. However since $(\Delta x)^2/4 \geqslant y^2A_{r,0}/2 \geqslant 0$ for $0 \leqslant t < \infty$, we may, by the same arguments as in Section 3.3.1, in realistic cases assume $K(t)$ to be nearly a constant mean value K_0, which leads to the further approximation:

$$\frac{K_1(t)}{N_A} = K_0\left(\frac{dp}{dt}\right)_K, \quad K_0 = \{RT + p_0[B_m(x_1^m) + \beta_1(\Delta x)^2/8]\}^{-1}. \tag{4.23}$$

For example in the case of the diffusion of pure $C(CH_3)_4$ in pure Ar one gets for the conditions given in Section 3.3.1 ($T = 332$ K, $p_0 = 1$ atm, $x_1^m = 0.5$, $(\Delta x)^2 = 1$: $K(0) = 3.772 \times 10^{-5}$, $K(\infty) = 3.701 \times 10^{-5}$, $K_0 = 3.712 \times 10^{-5}$ (units: mol cm^{-3} atm^{-1}).

The pressure change from $p_0 = 1$ atm to e.g. $p_0 = 0.99$ atm in equation (4.23) corresponds in this case to a change of 3×10^{-9} mol cm^{-3} atm^{-1} in K_0 and is therefore negligible.

Using the simple equation (4.23) for integration with respect to time t has the following great advantage. If $f(t)$ is some arbitrary function of time t one obtains by partial integration and the use of the mean-value theorem of integral calculus with equation (4.23)

$$\frac{1}{N_A}\int_0^t K_1(t')f(t')\,dt' = K_0\{[p_K(t) - \bar{p}_K(\bar{t})]f(t) + [\bar{p}_K(\bar{t}) - p_K(0)]f(0)\}. \tag{4.24}$$

$\bar{p}_K(\bar{t})$ is a mean value of $p_K(t)$ in the time interval $0 \leqslant t' \leqslant t$. If for simplicity the arithmetic mean $\bar{p}_K = [p_K(t) + p_K(0)]/2$ is chosen as an approximation one gets the very simple relation (4.25), which is used in all further calculations,

$$\frac{1}{N_A}\int_0^t K_1(t')f(t')\,dt' = \frac{\Delta p_K(t)}{p_0}\left(\frac{K_0 p_0}{2}\right)[f(t)+f(0)], \qquad (4.25)$$

$$\Delta p_K(t) = p_K(t) - p_K(0).$$

Δp_K is the pressure change due to gas sorption effects, which may be determined experimentally as described in Section 3.3.4. Now it is possible to calculate the mole fraction changes Δx_{1K} and Δx_{1wK}. The following results and the abbreviation B are used:

$$A_{r,0}(0) = L^2/8, \quad A_{r,n\geq 1}(0) = 0, \quad \sum_{r=0}^{\infty}\left[\frac{1}{a_r^2}+\frac{1}{a_{r+n}^2}\right] = \left(\frac{L^2}{\pi^2}\right)\left[\frac{\pi^2}{4} - \sum_{r=0}^{n-1}\frac{1}{(2r+1)^2}\right], \quad B = \frac{\Delta p_K(t)}{p_0}\left(\frac{K_0 p_0}{2}\right). \qquad (4.26)$$

Equation (4.19) gives

$$\Delta x_{1K} = \sum_{n=0}^{\infty}[u_{nK}^{(1)}(t)\sin a_n z + g_{nK}^{(1)}(t)\cos b_n z], \quad g_{0K}^{(1)}(t) = B[2C_0 + C_2(A_{r,0}+L^2/8)/2],$$

$$g_{nK}^{(1)}(t) = BC_2 A_{r,n}, \quad (n \geq 1), \quad u_{nK}^{(1)}(t) = B\{[2C_1 + C_3(A_{r,0}+L^2/8)/2]f_n + (C_3/2)\sum_{k=1}^{\infty} A_{r,k}[f_{k+n}+f_{n-k}]\}, \qquad (4.27)$$

with the coefficients C_i given by equations (4.20). Equation (4.21) gives

$$\Delta x_{1wK} = \sum_{n=0}^{\infty}[u_{nwK}^{(1)}(t)\sin a_n z + g_{nwK}^{(1)}(t)\cos b_n z], \quad g_{0wK}^{(1)}(t) = BC_4(A_{r,0}+L^2/8),$$

$$g_{nwK}^{(1)}(t) = BC_4\left\{\sum_{r=0}^{\infty} h_r h_{r+n}\left[\frac{1}{a_r^2}+\frac{1}{a_{r+n}^2}\right] + \sum_{r=0}^{n-1}\frac{h_r h_{n-1-r}}{a_r^2} + \frac{L^2}{4}\exp(-b_n^2 Dt)\right\}, \qquad (4.28)$$

$$u_{nwK}^{(1)}(t) = B\frac{C_3}{2}\sum_{k=1}^{\infty}\frac{A_{r,k}}{b_k}[h_{k-1-n} - h_{k+n}].$$

By analogy with equations (4.3) and (4.4), the correction terms (4.27) and (4.28) may be written as

$$\Delta x_{1K} = \left(\frac{\Delta p_K}{p_0}\right)\left(\frac{K_0 p_0}{2}\right)\left\{2C_0 + 2C_1\left(\frac{L}{\pi}\right)f^{(0)} + \left(\frac{C_2}{2}\right)\left(\frac{L}{\pi}\right)^2[f_{g0K}+2f_{gnK}] + \left(\frac{C_3}{2}\right)\left(\frac{L}{\pi}\right)^3[f_{unK}^{(1)}+f_{unK}^{(2)}]\right\}, \qquad (4.29)$$

with the coefficients C_i given by the expressions (4.20), and

$$\Delta x_{1wK} = \left(\frac{\Delta p_K}{p_0}\right)\left(\frac{K_0 p_0}{2}\right)\left\{C_4\left(\frac{L}{\pi}\right)^2[f_{g0K}+f_{gnwK}] + \left(\frac{C_3}{2}\right)\left(\frac{L}{\pi}\right)^3 f_{unwK}\right\}. \qquad (4.30)$$

The characteristic functions of these relations are given by

$$f_{g0K} = \left(\frac{\pi}{L}\right)^2\left(A_{r,0}+\frac{L^2}{8}\right), \quad f_{gnK} = \left(\frac{\pi}{L}\right)^2\sum_{n=1}^{\infty} A_{r,n}\cos b_n z,$$

$$f_{unK}^{(1)} = f_{g0K}f^{(0)} = \left(\frac{\pi}{L}\right)^3\left(A_{r,0}+\frac{L^2}{8}\right)\sum_{n=0}^{\infty} f_n \sin a_n z, \quad f_{unK}^{(2)} = \left(\frac{\pi}{L}\right)^3\sum_{n=0}^{\infty}\left\{\sum_{k=1}^{\infty} A_{r,k}(f_{k+n}+f_{n-k})\right\}\sin a_n z,$$

$$f_{gnwK} = \left(\frac{\pi}{L}\right)^2\sum_{n=1}^{\infty}\left\{\sum_{r=0}^{\infty} h_r h_{r+n}\left[\frac{1}{a_r^2}+\frac{1}{a_{r+n}^2}\right] + \sum_{r=0}^{n-1}\frac{h_r h_{n-1-r}}{a_r^2} + \left(\frac{L^2}{4}\right)exp(-b_n^2 Dt)\right\}\cos b_n z, \qquad (4.31)$$

$$f_{unwK} = \left(\frac{\pi}{L}\right)^3\sum_{n=0}^{\infty}\left\{\sum_{k=1}^{\infty}\frac{A_{r,k}}{b_k}[h_{k-1-n} - h_{k+n}]\right\}\sin a_n z.$$

$f^{(0)}$ is given by equation (3.44). In Fig. 4, the functions (4.31) are shown only for the measuring position $z_A = -L/3$ as functions of the reduced time t/τ. In the case $z = +L/3$ the parity of the sine and cosine functions have to be taken into account.

In this sorption model equation (4.4) has to be replaced by equation (4.29), and equation (4.30) must be added to equation (4.3). Finally numerical values are given for the same conditions as in equations (4.10) and (4.11)

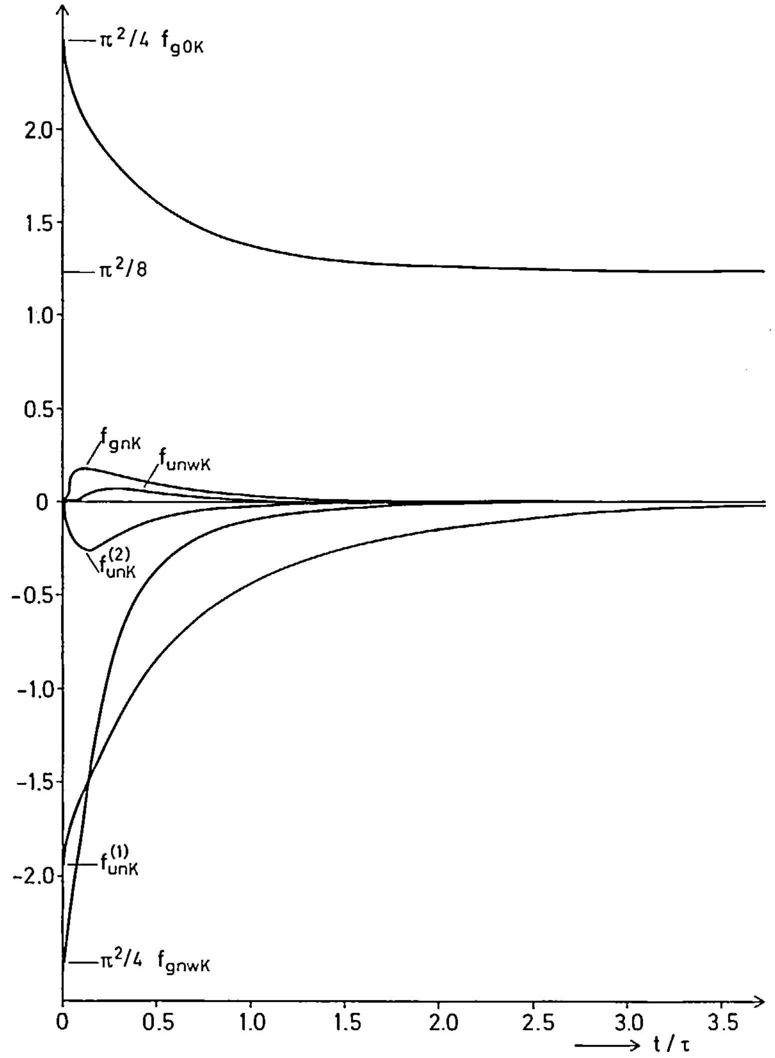


FIG. 4. The characteristic functions (4.31) as functions of the reduced time t/τ for $z_A = -L/3$.

$$\Delta x_{1wK}(z_A, t) = \left(\frac{\Delta p_K}{p_0}\right)\{-2.7741\times 10^{-3}[f_{g0K}+f_{gnwK}]-1.4984\times 10^{-3}f_{unwK}\},$$

$$\Delta x_{1K}(z_A < 0, t) = \left(\frac{\Delta p_K}{p_0}\right)\{0.50150+0.64725f^{(0)}+1.5973\times 10^{-3}[f_{g0K}+2f_{gnK}]-1.4984\times 10^{-3}[f_{unK}^{(1)}+f_{unK}^{(2)}]\},$$

$$\Delta x_{1K}(z_A > 0, t) = \left(\frac{\Delta p_K}{p_0}\right)\{0.50150-0.62982f^{(0)}-3.9510\times 10^{-3}[f_{g0K}+2f_{gnK}]+1.4984\times 10^{-3}[f_{unK}^{(1)}+f_{unK}^{(2)}]\}. \tag{4.32}$$

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SOLUTION DE PERTURBATION DE L'EQUATION DE DIFFUSION DANS LE CAS DE LA DIFFUSION MUTUELLE NON STATIONNAIRE DE DEUX GAZ REELS ISOCHORES ET ISOTHERMES

Résumé—L'équation de diffusion non stationnaire pour deux gaz réels isochores et isothermes est résolue par la méthode de perturbation. En vue d'expériences avec l'appareil de Loschmidt, les gradients de pression et de température sont supposés négligeables. Sont considérés comme des petites perturbations physiques: la dépendance du coefficient de diffusion D vis-à-vis de la concentration selon la théorie cinétique des gaz, le changement de pression pendant le mélange de gaz, la sorption des gaz par les cellules de l'appareil et les vitesses des écoulements correspondants. Les résultats montrent que la complète dépendance de D vis-à-vis de la concentration peut être déterminée par une seule ou deux expériences de diffusion non stationnaire avec deux gaz purs, ce qui est le grand avantage de cette méthode sur toutes les autres.

LÖSUNG DER DIFFUSIONSGLEICHUNG FÜR DEN FALL DER GEGENSEITIGEN NICHTSTATIONÄREN ISOCHOREN UND ISOTHERMEN DIFFUSION ZWEIER REALER GASE DURCH STÖRUNGSRECHNUNG

Zusammenfassung—Die Diffusionsgleichung für die gegenseitige nichtstationäre isochor-isotherme Konzentrationsdiffusion zweier realer Gase wird durch Störungsrechnung gelöst. Im Hinblick auf entsprechende Experimente in einer Loschmidt-Diffusionsapparatur werden Gradienten im Druck und in der Temperatur als vernachlässigbar klein angenommen. Die Konzentrationsabhängigkeit des Diffusionskoeffizienten D entsprechend der kinetischen Gastheorie, die Druckänderung während der Gasdurchmischung, Gassorption durch die Dichtungen der Diffusionsapparatur und die entsprechenden erzeugten Strömungsgeschwindigkeiten werden als kleine Störungen in einer physikalisch sinnvollen Weise berücksichtigt. Die Ergebnisse zeigen, daß die vollständige Konzentrationsabhängigkeit von D durch nur ein bis zwei nichtstationäre Diffusionsexperimente mit reinen Gasen bestimmt werden kann. Dies ist der große Vorteil der beschriebenen Methode gegenüber allen früher benutzten Methoden.

РЕШЕНИЕ МЕТОДОМ ВОЗМУЩЕНИЙ УРАВНЕНИЯ ДИФФУЗИИ ДЛЯ ВЗАИМНОЙ НЕСТАЦИОНАРНОЙ ИЗОХОРИЧЕСКОЙ И ИЗОТЕРМИЧЕСКОЙ ДИФФУЗИИ ДВУХ РЕАЛЬНЫХ ГАЗОВ

Аннотация — Методом возмущений решено уравнение диффузии для взаимной нестационарной изохорической и изотермической концентрационной диффузии двух реальных газов. С учетом условий, при которых проводятся конкретные эксперименты на диффузионном аппарате Лошмидта, сделано предположение, что градиенты давления и температуры пренебрежимо малы. Концентрационная зависимость коэффициента диффузии D в соответствии с кинетической теорией газов, изменение давления при смешивании газов, сорбция газа уплотнениями диффузионного аппарата и скорости потока газа учитывались на основе физических соображений как малые возмущения. Результаты показывают, что полную концентрационную зависимость коэффициента D можно определить только из одного или двух экспериментов по нестационарной диффузии чистых газов, что является важным преимуществом использованного метода.