

MEASUREMENT OF THE MUTUAL DIFFUSION
COEFFICIENTS OF A NONIDEAL GAS MIXTURE
OF HELIUM AND CARBON DIOXIDE

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We consider a method for the calculation of the mutual diffusion coefficient of nonideal gases. A formula is presented for the barometric dependence of the helium-carbon dioxide system.

Recent investigations have shown that the diffusion process in nonideal gas mixtures is complicated. In the case of mutual diffusion in a closed diffusion device, one observes an increase of pressure and inequality of molar concentrations of the components diffusing in the opposite directions [1, 2]. These features of the diffusion process in real gases make it difficult to find the mutual diffusion coefficients and must be taken into account in the derivation of the theoretical formulas.

We consider the mutual diffusion in a two-vessel device. In this method [3], two vessels with gases under investigation (the temperature and initial pressures are equal) are connected by a long capillary. The diffusion coefficient is inferred from the change of the concentration of one of the components during the diffusion time.

As is known [3], a theoretical formula has been obtained for the equimolar diffusion of two gases diffusing in opposite directions. Without corrections, this formula cannot be applied in the study of real gases since, because of different compressibilities of the individual components, the molar densities in the vessels are not identical and the number of molecules, which cross the transverse cross section of the capillary from opposite sides will be different. The difference of molar concentrations of the diffusing components can be considerable. Ivakin et al. [4] assume that, in a closed diffusion device, an additional flow of the total number of particles takes place together with the usual concentration diffusion flow. Also possible is a hydrodynamic flow of the mixture which is due to the asymmetric change of pressure in the diffusion vessels. To take this flow into account, Bondarenko and Golubev [5] have proposed that the theoretical formulas be supplemented by a correction for "counterdiffusion" in obtaining the mutual diffusion coefficient.

We assume that the correct description of mutual diffusion of real gases in closed devices necessitates the study of volume flows and, consequently, the use of volume concentrations, since in these devices, the mean-volume reference system (Fick system [6]) is realized.

Devices which are often used in experiments to analyze gas mixtures (interferometers, mass spectrometers, etc.) make it possible to determine molar concentrations. Therefore, the calculation of mutual diffusion coefficients in nonideal gases involves the conversion of volume concentrations into molar. This can be done by using the condition of constant partial volumes of the components during the diffusion. An analogous assumption was used in [7] to study the mutual diffusion of liquid vapors in compressed gases.

We consider the mutual diffusion of nonideal gases in a two-vessel device, when the vessels are filled by pure gases prior to diffusion. The volume concentration of the first component will be expressed in terms of the molar concentration:

$$c_{v1}^i = \frac{V_1^i}{V^i} = \frac{N_1^i v_1}{V^i} = \frac{c_{n1}^i N^i v_1}{V^i} \quad (1)$$

The volume of the vessel will be expressed as the sum of volumes of both components in the vessel:

$$V^i = N_1^i v_1 + N_2^i v_2 = c_{n1}^i N^i v_1 + c_{n2}^i N^i v_2 \quad (2)$$

Using Eqs. (1) and (2) and expressing v_1 and v_2 in terms of compressibilities of the individual components, we obtain a relationship between the volume and molar concentrations:

$$c_{v1}^i = \frac{c_{n1}^i z_1}{c_{n1}^i z_1 + c_{n2}^i z_2} \quad (3)$$

TABLE 1. Comparison of Mutual Diffusion Coefficients Calculated with and without Taking into Account the Realistic Properties of the Gas Mixture

$\frac{z_1}{z_2}$	1	1,1	1,2	1,3	1,5	2	3	4
$\frac{D_{12}^{id} - D_{12}}{D_{12}}, \%$	0	0,3	1,0	2,1	5,2	15,5	41	70

TABLE 2. Mutual Diffusion Coefficients of the Helium–Carbon Dioxide System at Increased Pressures

$P, \text{ MPa}$	$c_{n1}^{II} \cdot 10^3$	$\frac{c_{n1}^{II}}{c_{n2}^I}$	$\frac{c_{v1}^{II}}{c_{v2}^I}$	$D_{12} \cdot 10^8, \text{ m}^2 \cdot \text{sec}^{-1}$	$D_{12}^{calc} \cdot 10^8, \text{ m}^2 \cdot \text{sec}^{-1}$	$\frac{D_{12} - D_{12}^{calc}}{D_{12}}, \%$
$T = 273,2 \text{ K}$						
1,0	239	1,18	1,06	501	505	+0,8
1,5	236	1,26	1,05	327	325	-0,6
2,0	243	1,34	1,03	234	231	-1,3
2,5	261	1,51	1,06	180	177	-1,7
2,8	261	1,57	1,04	156	152	-2,6
3,0	270	1,66	1,05	142	138	-2,9
3,2	293	1,74	1,06	129	126	-2,4
3,4	359	1,78	1,06	117	115	+1,7
3,46	308	1,87	1,06	114	111	-2,7
3,48	324	1,84	1,04	113	111	-1,8
$T = 303,2 \text{ K}$						
1,0	204	1,13	1,05	614	616	+0,3
2,0	221	1,25	1,04	298	292	-2,1
3,0	232	1,36	1,02	186	183	-1,6
4,0	245	1,57	1,03	128	128	0,0
5,0	265	1,88	1,05	92,8	92,3	-0,3
6,0	296	2,37	1,05	67,3	67,7	+0,6
6,5	335	2,82	1,07	56,5	56,6	+0,2
6,8	374	3,14	1,04	50,6	49,1	-3,1
7,0	405	3,58	1,03	44,6	43,2	-3,2
$T = 323,2 \text{ K}$						
1,0	204	1,10	1,03	685	689	+0,6
2,0	215	1,17	1,02	335	336	-0,3
3,0	219	1,28	1,01	207	212	+2,4
4,0	236	1,43	1,03	149	153	+2,6
5,0	253	1,60	1,04	113	116	+2,6
6,0	280	1,93	1,11	88,2	88,7	+0,6
7,0	219	2,23	1,10	52,0	52,8	+1,5

It is seen from formula (3) that the volume concentration is equal to the molar concentration for ideal gases ($z_1 = z_2 = 1$). For a real gas, equal molar and volume concentrations will be observed when compressibilities of the components are equal. The expression for the mutual diffusion coefficient of real gases takes the form, using the two-vessel method and assuming that the volumes of the vessels are equal,

$$D_{12} = -\frac{VL}{2S\tau} \ln(c_{v1}^I - c_{v1}^{II}) \quad (4)$$

Formula (4) differs from the formula obtained in [3] by the fact that it contains volume concentrations instead of molar ones.

Table 1 shows the results of a comparison of the mutual diffusion coefficients calculated using the formula given in [2] and (4), for various ratios of compressibilities of the diffusing gases. The calculations were carried out for volume concentration equal to 0.2. It is seen from Table 1 that, when the ratio of compressibilities of the components exceeds 1.3, the difference of diffusion coefficients exceeds the error of the diffusion experiment. Thus, in the determination of the mutual diffusion coefficients of real gases by the two-vessel method when the compressibilities of the components differ considerably, it is necessary to use Eq. (4).

The apparatus, described in detail in [8] and based on the two-vessel method, was used to measure the mutual diffusion coefficient of the helium–carbon dioxide system at temperatures 273, 303, and 323°K and various pressures. The upper limit on the pressure in the experiments at 273 and 303°K was set by the phase transition in carbon dioxide. Before the diffusion experiment, the vessels were filled with pure gases, and at the end of the experiment, the molar concentration of the components was measured in each of the vessels using the interferometer ITR-1. The compressibilities of the components were calculated from the data of [9, 10]. In all experiments, we included the correction for the time

needed for reaching the quasi-steady state. The error in the determination of the mutual diffusion coefficients was 2-3%. The results of experiments are given in Table 2.

It is seen from Table 2 that the ratios of molar concentrations of the components diffusing in opposite directions are considerable. At the same time, the ratio of volume concentrations of the diffused components is observed to be constant in all experiments. A small deviation of this ratio from unity is due to different volumes of the vessels (in our two-vessel apparatus, $V^I = 1.05 V^{II}$). The results which are shown in column 4 of Table 2 confirm that the partial specific volumes of the components are independent of the concentration of the mixture. This verifies the assumptions used in the derivation of formula (4).

The mutual diffusion coefficients in the helium-carbon dioxide system at temperature 273.2°K and pressures up to 3.05 MPa are available from [2]. It should be noted that Ivakin et al. [2] used the two-vessel method for the determination of the mutual diffusion coefficient, and in obtaining the theoretical formula, they took into account the nonideal nature of the gas mixture. It can be shown that the theoretical formula in [2] leads to formula (4) of the present work. The results of our experiments and the data of [2] agree within the limits of experimental error.

A calculation of D_{12} using the Enskog-Torn theory [11], and a comparison of the result with the obtained experimental data showed that the Torn correction does not explain the pressure dependence of the diffusion coefficient of the system.

An analysis of the obtained experimental data (Table 2) made it possible to find an empirical formula for the description of barometric dependence of the mutual diffusion coefficient of the helium-carbon dioxide system:

$$D_{12}^{\text{calc}} = D_0 \frac{P_0}{P} z_1 z_2, \quad (5)$$

where $D_0 = 0.538 \times 10^{-4} \text{ m}^2 \text{ sec}^{-1}$, and $P_0 = 0.1 \text{ MPa}$.

The temperature dependence of the diffusion coefficient follows a power law with exponent $n = 1.683$. The values of D_0 and n were taken from [12] where the temperature dependences of the diffusion coefficient were generalized using a large volume of experimental data.

It is seen from Table 2 that the presented formula (5) describes well the barometric dependence of the mutual diffusion coefficient of the system under investigation.

NOTATION

c_v and c_n , volume and molar concentrations; V , volume of the vessel; N , number of moles; v , partial molar volume; z , compressibility; L and S , length and cross-sectional area of the capillary; τ , time; P , pressure; D_{12} , mutual diffusion coefficient; D_{12}^{id} , mutual diffusion coefficient calculated without taking into account the realistic properties of the mixture; and D_{12}^{calc} , mutual diffusion coefficient calculated using formula (5). The indices 1 and 2 refer to components in the gas mixture, and I and II to the vessel of the diffusion cell.

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