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DIFFUSION IN GAS MIXTURES CONTAINING THE COMPONENTS OF THE SYNTHESIS OF AMMONIA

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The diffusional process in certain multicomponent gas mixtures that contain the components of the synthesis of ammonia is investigated experimentally as a function of pressure. The effective coefficients of diffusion and the matrices of the coefficients of multicomponent diffusion are determined. The dependence of the coefficients on the pressure is shown. A comparison of the experimental and calculated data shows their good agreement.

At present, it is no longer possible to develop and calculate a complex mass-exchange process restricting oneself to the knowledge of only diffusion coefficients of binary mixtures. However, in the reference literature, monographs, and isolated publications, the issues of multicomponent mass transfer have been given a very incomplete coverage. This is due to the significant difficulties that occur both theoretically and experimentally. Some particular problems [1–3] can be solved analytically, but in most cases use has to be made of various approximate methods [4–8]. Unlike binary systems, multicomponent mass transfer can be accompanied by different effects [4–12] that make its calculation in technological schemes difficult (see, for example, [13]).

According to a rigorous kinetic theory, the isothermal diffusion in an n-component gas mixture is described by the Stefan–Maxwell equation [14]

$$\nabla x_i = \sum_{j=1}^{n} \frac{1}{D_{ij}} \left(c_i \mathbf{J}_j - c_j \mathbf{J}_i \right), \quad i = 1, 2, 3, \ldots, n, \quad i \neq j, \tag{1}$$

where x_i is the mole concentration of the component i in the mixture, $c_i = x_i/x$ is the mole fraction of the component i for the mole concentration of the mixture x, $\mathbf{J}_i$ is the density of the diffusion flux of the component i, and D_{ij} is the coefficient of mutual diffusion of the pair of gases i and j.

In the case of equimolar diffusion, $\sum_{i=1}^{n} \mathbf{J}_i = 0$ and $\sum_{i=1}^{n} \nabla x_i = 0$ and Eq. (1) for independent fluxes and gradients is transformed to the form [14, 15]

$$\mathbf{J}_i = - \sum_{j=1}^{n-1} D_{ij}^{*} \nabla x_j, \quad i = 1, 2, 3, \ldots, (n-1). \tag{2}$$

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The diffusion coefficients D_{ii}^{*} and D_{ij}^{*} form the matrix of coefficients of multicomponent diffusion (in the literature these coefficients are sometimes referred to as practical; see, for example, [16]).

In describing diffusion in multicomponent gas mixtures, use is often made of effective diffusion coefficients [4–8], which are introduced similarly to the coefficient of binary diffusion by the first Fick law

$$\mathbf{J}_i = -D_i^{\mathrm{ef}} \nabla x_i\,, \quad i = 1, 2, 3, \ldots, (n-1)\,, \tag{3}$$

where D_i^{ef} is the effective diffusion coefficient that characterizes the rate of diffusion of the component i into the mixture of the other gases.

Thus, the density of the flux of any component in the mixture is determined by its effective diffusion coefficient and only by its gradient of concentration. The effective diffusion coefficient is a complex quantity that changes in a diffusing mixture from point to point; therefore, for practical application use is made of integral (averaged over the entire diffusion layer) effective diffusion coefficients [8, 17]. The effective diffusion coefficients can be measured by the same experimental methods as the binary diffusion coefficients [8], since the effective diffusion coefficient was introduced similarly to the mutual diffusion coefficient by the first Fick law.

In this work, we give results of an investigation of mass transfer in four- and five-component gas mixtures containing the components of the synthesis of ammonia: hydrogen, nitrogen, methane, ammonia, and argon. As far as we know, there are practically no similar works in the literature; therefore, the study of mass-exchange processes in mixtures used for the synthesis of ammonia is of a certain significance for the production of this product.

The experiments were conducted at different pressures (from 0.484 to 1.073 MPa) and $T = 298$ K with four- and five-component mixtures in which the gas concentrations were close to the compositions of blow-through mixtures at the inlet and outlet of the column of ammonia synthesis. As a result of these investigations, the coefficients of mutual diffusion of gas pairs incorporated into the mixture [18, 19] and the effective coefficients of the components' diffusion were measured, and in addition, the matrices of the coefficients of multicomponent diffusion for independent fluxes and gradients (in a four-component system, for hydrogen, nitrogen, and ammonia and in a five-component one, for hydrogen, nitrogen, ammonia, and methane) were calculated [19, 20]. The calculations of the matrices of the coefficients of multicomponent diffusion were done for equilibrium values of the components' concentrations.

To conduct the experiments, use was made of a two-flask apparatus [21] with the volumes of the upper and lower flasks $V_{\mathrm{upp}} = V_{\mathrm{low}} = 76.9$ cm^3 and the diameter and length of the diffusion channel $d = 0.40$ cm and $L = 7.05$ cm, respectively. The numerical values of the instrument constant (the combination of the geometric parameters $\beta = L_{\mathrm{ef}} V_{\mathrm{upp}} V_{\mathrm{low}} / S(V_{\mathrm{upp}} + V_{\mathrm{low}})$, where S is the cross-sectional area of the diffusion channel; $L_{\mathrm{ef}} = L + 0.745d$), measured by the geometric parameters and by means of standardizing by a binary helium–argon system, coincided within the experimental error. The value of the instrument constant was taken to be equal to 2215 cm^2.

The design of the apparatus, which was made of stainless steel, and that of the supply service lines did not require substantial changes (individual parts capable of reacting with ammonia had been replaced).

The procedure for analyzing gas mixtures containing ammonia was developed as applied to a chromatograph with catharometric sensors. At the same time, it was taken into account that direct chromatographic determination of ammonia on columns with different polymeric sorbents does not yield satisfactory results due to the dependence of the zone's shape and the retention time on the size of the analyzed sample. Moreover, some authors [22] note the low sensitivity of the catharometer to ammonia. Therefore, we used the method of removing ammonia from the analyzed mixture before the latter reaches the chromatograph's separation column. Ammonia is usually removed from the gas mixture either by freezing, or dissolution in water, or absorption by a sorbent.

TABLE 1. Effective Coefficients of Diffusion of Hydrogen and Ammonia ($cm^2 \cdot sec^{-1}$) for the System 0.6126 H_2 + 0.1929 N_2 + 0.0458 NH_3 + 0.1487 CH_4 – 0.5148 H_2 + 0.1636 H_2 + 0.1546 NH_3 + 0.1670 CH_4 as Functions of Pressure. The Calculated Integral Values of the Coefficients Are Obtained for the Time of the Experiment, Except the Values for Pressures of 0.092 and 0.288 MPa Calculated for the Initial Concentration Distribution

Experimental data		Values calculated according to [23]	
$D^{ef}_{H_2}$	$D^{ef}_{NH_3}$	$D^{ef}_{H_2}$	$D^{ef}_{NH_3}$
$P = 0.092$ MPa			
–	–	0.8456	0.5014
$P = 0.288$ MPa			
–	–	0.2700	0.1600
$P = 0.484$ MPa			
0.163	0.0851	0.1604	0.0919
$P = 0.681$ MPa			
0.120	0.0613	0.1142	0.0662
$P = 0.877$ MPa			
0.0860	0.0465	0.0887	0.0517
$P = 1.073$ MPa			
0.0711	0.0386	0.0724	0.0421

TABLE 2. Matrices of the Coefficients of Multicomponent Diffusion of the System 0.6126 H_2 +0.1929 N_2 + 0.0458 NH_3 + 0.1487 CH_4 – 0.5148 H_2 + 0.1636 N_2 + 0.1546 NH_3 + 0.1670 CH_4 as Functions of Pressure

Matrix of the coefficient of multicomponent diffusion, $cm^2 \cdot sec^{-1}$	P, MPa					
	0.092	0.288	0.484	0.681	0.877	1.073
D^*_{11}	0.8352	0.2665	0.1586	0.1129	0.0876	0.0716
D^*_{12}	–0.0209	–0.0067	–0.0040	–0.0028	–0.0022	–0.0018
D^*_{13}	–0.0150	–0.0048	–0.0028	–0.0020	–0.0016	–0.0013
D^*_{21}	–0.1825	–0.0583	–0.0347	–0.0247	–0.0192	–0.0156
D^*_{22}	0.4175	0.1332	0.0793	0.0564	0.0438	0.0359
D^*_{23}	–0.0021	–0.0007	–0.0004	–0.0003	–0.0002	–0.0002
D^*_{31}	–0.1034	–0.0330	–0.0196	–0.0140	–0.0109	–0.0089
D^*_{32}	–0.0030	–0.0010	–0.0006	–0.0004	–0.0003	–0.0003
D^*_{33}	0.4076	0.1301	0.0774	0.0551	0.0428	0.0349

We used a combination of methods: absorption of ammonia by a sorbent (5A molecular sieves) and then by water with subsequent drying of the remaining gas mixture on silica gel.

After this procedure, the dried gas mixtures of hydrogen, nitrogen, methane, and argon were fed (with helium as a carrier gas) into a chromatographic column with 5A molecular sieves for subsequent analysis. Chromatographic peaks were processed on an I-02 integrator.

The concentration of ammonia was determined from the condition of material balance $\sum_{i=1}^{n} c_i = 1$ (here c_i is the mole fraction of the component i). We note that in measuring the mutual diffusion coefficients, binary gas mixtures containing ammonia were analyzed on an ITR-1 interferometer.

TABLE 3. Effective Coefficients of Diffusion for Hydrogen, Ammonia, and Argon ($cm^2 \cdot sec^{-1}$) for the System 0.6037 H_2 + 0.1908 N_2 + 0.1256 CH_4 + 0.0345 NH_3 + 0.0454 Ar – 0.4614 H_2 + 0.1697 N_2 + 0.1397 CH_4 + 0.1591 NH_3 + 0.0701 Ar as Functions of Pressure. The Calculated Integral Values of the Coefficients Are Obtained for the Time of the Experiment, Except the Values for Pressures of 0.092 and 0.288 MPa Calculated for the Initial Concentration Distribution

Experimental data			Value calculated according to [23]		
$D^{ef}_{H_2}$	$D^{ef}_{NH_3}$	D^{ef}_{Ar}	$D^{ef}_{H_2}$	$D^{ef}_{NH_3}$	D^{ef}_{Ar}
P = 0.092 MPa					
–	–	–	0.8604	0.5041	0.7473
P = 0.288 MPa					
–	–	–	0.2746	0.1609	0.2385
P = 0.484 MPa					
0.168	0.0964	0.140	0.1634	0.0916	0.1367
P = 0.681 MPa					
0.112	0.0668	0.0988	0.1160	0.0660	0.0984
P = 0.877 MPa					
0.0891	0.0514	0.0784	0.0903	0.0519	0.0773
P = 1.073 MPa					
0.0746	0.0430	0.0640	0.0738	0.0423	0.0631

TABLE 4. Matrices of the Coefficients of Multicomponent Diffusion of the System 0.6037 H_2 + 0.1908 N_2 + 0.1256 CH_4 + 0.0345 NH_3 + 0.0454 Ar – 0.4614 H_2 + 0.1697 N_2 + 0.1397 CH_4 + 0.1591 NH_3 + 0.0701 Ar as Functions of Pressure

Matrix of the coefficient of multicomponent diffusion, $cm^2 \cdot sec^{-1}$	P, MPa					
	0.092	0.288	0.484	0.681	0.877	1.073
D^*_{11}	0.8767	0.2798	0.1665	0.1185	0.0920	0.0752
D^*_{12}	0.0116	0.0037	0.0022	0.0016	0.0012	0.0010
D^*_{13}	0.0308	0.0098	0.0059	0.0042	0.0032	0.0026
D^*_{14}	0.0171	0.0054	0.0032	0.0023	0.0018	0.0015
D^*_{21}	–0.1915	–0.0611	–0.0364	–0.0259	–0.0201	–0.0164
D^*_{22}	0.3886	0.1240	0.0739	0.0525	0.0408	0.0333
D^*_{23}	–0.0114	–0.0036	–0.0022	–0.0015	–0.0012	–0.0010
D^*_{24}	–0.0135	–0.0043	–0.0026	–0.0018	–0.0014	–0.0012
D^*_{31}	–0.1334	–0.0426	–0.0253	–0.0180	–0.0140	–0.0114
D^*_{32}	–0.0056	–0.0018	–0.0011	–0.0008	–0.0006	–0.0005
D^*_{33}	0.3736	0.1192	0.0709	0.0505	0.0392	0.0320
D^*_{34}	–0.0033	–0.0011	–0.0006	–0.0004	–0.0003	–0.0003
D^*_{41}	–0.1018	–0.0325	–0.0193	–0.0138	–0.0107	–0.0087
D^*_{42}	–0.0072	–0.0023	–0.0014	–0.0010	–0.0008	–0.0006
D^*_{43}	–0.0044	–0.0014	–0.0008	–0.0006	–0.0005	–0.0004
D^*_{44}	0.3871	0.1236	0.0735	0.0523	0.0406	0.0332

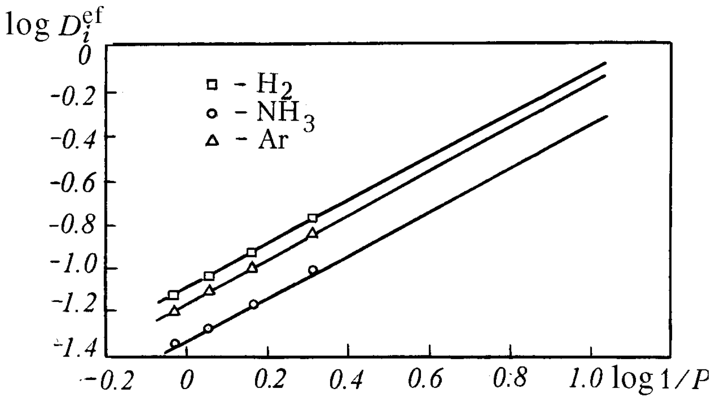

Fig. 1. Baric (pressure) dependence of the effective coefficients of diffusion of hydrogen, ammonia, and argon of the system 0.6037 H_2 + 0.1908 N_2 + 0.1256 CH_4 + 0.0345 NH_3 + 0.0454 Ar – 0.4614 H_2 + 0.1697 N_2 + 0.1397 CH_4 + 0.1591 NH_3 + 0.0701 Ar that indicates the applicability of the ideal gas laws to the investigated range of pressures. Points, experimental data; continuous curves, values calculated according to [23].

Based on the experimental data, we found mutual diffusion coefficients of binary gas mixtures with ammonia—hydrogen–ammonia, nitrogen–ammonia, and methane–ammonia — and the effective diffusion coefficients of hydrogen and ammonia in the four-component system 0.6126 $H_2(1)$ + 0.1929 $N_2(2)$ + 0.0458 $NH_3(3)$ + 0.1487 $CH_4(4)$ – 0.5148 $H_2(1)$ + 0.1636 $N_2(2)$ + 0.1546 $NH_3(3)$ + 0.1670 $CH_4(4)$ and the effective diffusion coefficients of hydrogen, ammonia, and argon in the five-component system 0.6037 $H_2(1)$ + 0.1908 $N_2(2)$ + 0.1256 $CH_4(3)$ + 0.0345 $NH_3(4)$ + 0.0454 Ar(5) – 0.4614 $H_2(1)$ + 0.1697 $N_2(2)$ + 0.1397 $CH_4(3)$ + 0.1591 $NH_3(4)$ + 0.0701 Ar(5) (the concentrations of the components are given in mole fractions) at different pressures. The effective diffusion coefficients of nitrogen and methane in the first system and of nitrogen and methane in the second one were not determined because of the small value of the differences of their concentrations. In the experiments, the concentrations of these gases, because of the manifestation of the Toor effects [9], were close to the equilibrium value, which led to a large error of the experimental data.

For theoretical calculation of the effective diffusion coefficients and the matrices of the coefficients of multicomponent diffusion, the procedure of [23] was used. The values of the coefficient of mutual diffusion used in the calculations were either measured on the same installation [18] or taken from [24]. Their numerical values for T = 298.0 K and P = 0.101 MPa were as follows: $D_{H_2-N_2}$ = 0.80; D_{H_2-Ar} = 0.85; $D_{H_2-CH_4}$ = 0.73; $D_{N_2-CH_4}$ = 0.220; D_{N_2-Ar} = 0.211; D_{Ar-CH_4} = 0.211; $D_{H_2-NH_3}$ = 0.78; $D_{N_2-NH_3}$ = 0.230; $D_{CH_4-NH_3}$ = 0.212; D_{Ar-NH_3} = 0.209; $cm^2 \cdot sec^{-1}$. The error of the experimental data is from 4 to 9%. The reproducibility of the measurements is no worse than 4%. The obtained data are presented in Tables 1–4.

We reckoned it expedient to consider in more detail the physical side of the above results of the experiment and calculation reflected in the tables on diffusion coefficients [19, 20], supplementing them with new data.

The main conclusion is that the diffusion fluxes of the components calculated using the matrix of the coefficients of multicomponent diffusion and the effective diffusion coefficient are identical. This is obvious because both calculation methods are based on the same Stefan–Maxwell equation, but at the same time there is more difficulty in using the matrix of the coefficients of multicomponent diffusion (9 coefficients in the first case and 16 in the second one) as compared to 4 and 5 values of the effective diffusion coefficient. The use of the effective diffusion coefficient, which acts as a characteristic of the total mass transfer of the component, makes it possible not only to give a physically substantiated picture of the diffusional process in multicomponent gas mixtures but also to do the required quantitative calculations.

Thus, in diffusing complex gas mixtures, if the mass transfer of a component is not related to the manifestation of the Toor effects [9], its effective diffusion coefficient can be considered to be a constant quantity with a high accuracy in the Fick law with significant changes in the concentrations. Sometimes, in conducting *estimative* calculations of the diffusion fluxes of the components using the matrix of the coefficients of multicomponent diffusion, one can restrict oneself only to the main elements of the matrix (D^*_{ii}).

As follows from the data obtained, in the pressure intervals where the investigations were conducted, gas mixtures can be considered to be ideal with an error no higher than the experimental error. This is indicated by the experimental dependence of the effective diffusion coefficient on pressure for all components, i.e., $D_i^{\mathrm{ef}} \sim 1/P$, which is known [3] to be inherent in the coefficient of mutual diffusion of the binary systems of ideal gases. As an example confirming this dependence, Fig. 1 shows the data for the effective diffusion coefficient of hydrogen, ammonia, and argon in a five-component mixture.

If the conditions of the problem require that the density of the components' diffusion fluxes be determined, the effective diffusion coefficient of the corresponding component and its concentration gradient are substituted into the first Fick law. The actually calculated integral values of the effective diffusion coefficient correspond to the equilibrium concentration (the arithmetic mean) of the system's components.

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