Journal of Engineering Physics and Thermophysics, Vol. 77, No. 2, 2004

THERMODIFFUSION IN A HYDROGEN–NITROGEN GAS SYSTEM

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UDC 533.15

Characteristics of thermodiffusion molecular mass transfer of a binary "frozen" hydrogen–nitrogen gas mixture are predicted by the method of entropy similarity. Calculations are made within a wide range of variation of temperatures and concentrations at normal pressure.

The effect of thermal diffusion in gases strongly depends on the nature of forces of interaction between molecules. Consequently, values of thermodiffusion constants and thermodiffusion relations, being a complex function of temperatures, concentrations, and masses of molecules [1], can be used for determination of force parameters of intermolecular interactions and, thus, calculation of other coefficients of transfer (viscosity, thermal conductivity, and mutual diffusion) [1] without resorting to complex, labor-consuming, and expensive experiments. In [2–4] it is shown where the characteristics of thermodiffusion molecular transfer of binary gas mixtures are used.

In molecular-kinetic diffusion in the two-flask installation designed by Chapman and Dootson [5], a steady state is reached upon termination of the process of separation of a mixture having a certain constant composition; concentrations of the mixture in the flasks of the device take different fixed values. Certain values of entropies correspond to temperatures of the "cold" and "hot" flasks of the device and concentrations of mixture attained in them. Thus, mass transfer in a connecting capillary tube (thermodiffusion cell) under steady-state conditions is kept due to the difference of potentials at its ends, i.e., due to the difference of absolute molar entropies. Consequently, a thermodiffusion cell of the Chapman–Dootson two-volume device can be considered as a physical model in generalization of experimental data on thermodiffusion separation.

Processing of the results on thermal diffusion of binary gas systems given in [6–11] allowed one to obtain a similarity equation:

$$\frac{\Delta\lambda}{\Delta\lambda_{\Delta S}} = A\,\frac{S_1 - S_2}{R}\,. \tag{1}$$

The scale thermodiffusion separation $\Delta\lambda_{\Delta S}$ was determined in variation of molar entropies at the boundaries of the scale cell [4.1896 kJ/(kmole·K) = 1 kcal/(kmole·K)] reckoned from a constant value of S_1. The latter was taken proceeding from the available experimental data [12–15] with account for conveniency of calculations.

The essence of the generalization method was considered in [7, 10], where it was shown that for most binary mixtures studied the values of $\Delta\lambda_{\Delta S}$ are constant for the mixture of the given composition at any temperature of the "cold" and "hot" flasks of the device.

Absolute molar entropies of mixtures were determined by the relations

$$S_1 = n'_{20}S'_{20} + n'_{10}S'_{10}\,, \quad S_2 = n_{20}S_{20} + n_{10}S_{10}\,, \tag{2}$$

and thermodiffusion characteristics were found from the formulas [1]

$$\Delta\lambda = k_{\mathrm{th}}\ln(T_1/T_2)\,, \quad \alpha_{\mathrm{th}} = \frac{k_{\mathrm{th}}}{n_{10}n_{20}}\,, \quad \ln q = \alpha_{\mathrm{th}}\ln(T_1/T_2)\,, \quad D_{\mathrm{th}} = Dk_{\mathrm{th}}\,, \tag{3}$$

Kazan’ State Technological University, 68 K. Marx Str., Kazan’, 420015, Russia. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 77, No. 2, pp. 148–152, March–April, 2004. Original article submitted August 12, 2003.

TABLE 1. Calculated Values of the Coefficients of Separation, Thermodiffusion Separation, and Thermodiffusion Ratios of the Binary Hydrogen–Nitrogen Gas System

T_1, K	T_2, K	q	$\Delta\lambda$, %	k_{th}
1	2	3	4	5
$n'_{20} = 0.9$, $\Delta\lambda_{\Delta S} = 0.0063$				
6000	1400	1.6721	7.38	0.0507
5000	1200	1.6443	7.03	0.0493
4000	1000	1.6093	6.58	0.0475
4000	500	1.8463	9.43	0.0454
6000	290	2.1400	13.91	0.0459
2000	290	1.7650	8.14	0.0422
1200	290	1.5482	5.83	0.0410
700	290	1.3563	3.58	0.0406
400	290	1.1460	1.30	0.0405
$n'_{20} = 0.8$, $\Delta\lambda_{\Delta S} = 0.0115$				
6000	1400	1.7725	12.58	0.0865
5000	1200	1.7357	12.00	0.0841
4000	1000	1.6898	11.27	0.0813
4000	500	1.9850	16.16	0.0777
6000	290	2.8001	23.82	0.0786
2000	290	1.7653	13.98	0.0724
1200	290	1.6150	10.00	0.0704
700	290	1.3738	6.13	0.0696
400	290	1.1452	2.24	0.0695
$n'_{20} = 0.7$, $\Delta\lambda_{\Delta S} = 0.0153$				
6000	1400	1.9005	15.97	0.1098
5000	1200	1.8508	15.25	0.1069
4000	1000	1.7893	14.37	0.1037
4000	500	2.2818	20.62	0.0992
6000	290	3.7500	30.34	0.1001
2000	290	2.0591	17.87	0.0925
1200	290	1.6872	12.78	0.0899
700	290	1.3905	7.82	0.0888
400	290	1.1398	2.86	0.0887
$n'_{20} = 0.6$, $\Delta\lambda_{\Delta S} = 0.0167$				
6000	1400	1.9758	17.11	0.1176
5000	1200	1.8819	16.40	0.1149
4000	1000	1.8451	15.48	0.1117
4000	500	2.4906	22.22	0.1069
6000	290	4.9300	32.66	0.1078
2000	290	2.1852	19.30	0.0999
1200	290	1.7109	13.79	0.0970
700	290	1.3780	8.43	0.0957
400	290	1.1301	3.08	0.0956
$n'_{20} = 0.5$, $\Delta\lambda_{\Delta S} = 0.0143$				
6000	1400	1.9421	15.09	0.1037
5000	1200	1.8565	14.48	0.1015
4000	1000	1.8250	13.70	0.0988
4000	500	2.5349	19.66	0.0946
6000	290	5.6328	28.84	0.0952
2000	290	2.2000	17.10	0.0886
1200	290	1.8502	12.21	0.0859
700	290	1.3564	7.45	0.0846
400	290	1.1154	2.72	0.0845
$n'_{20} = 0.4$, $\Delta\lambda_{\Delta S} = 0.0114$				
6000	1400	1.9081	12.47	0.0857
5000	1200	1.8559	11.99	0.0840
4000	1000	1.7872	11.36	0.0820
4000	500	2.5100	16.31	0.0785
6000	290	6.0001	23.87	0.0788

TABLE 1 Continued

1	2	3	4	5
2000	290	2.1802	14.20	0.0735
1200	290	1.6542	10.13	0.0713
700	290	1.3338	6.18	0.0701
400	290	1.1031	2.25	0.0699
$n'_{20} = 0.3,\ \Delta\lambda_{\Delta S} = 0.0086$				
6000	1400	1.8651	9.76	0.0670
5000	1200	1.7932	9.40	0.0659
4000	1000	1.7483	8.92	0.0644
4000	500	2.4920	12.80	0.0616
6000	290	6.5000	18.70	0.0617
2000	290	2.1531	11.16	0.0578
1200	290	1.6233	7.96	0.0560
700	290	1.3094	4.85	0.0551
400	290	1.0938	1.77	0.0550
$n'_{20} = 0.2,\ \Delta\lambda_{\Delta S} = 0.0057$				
6000	1400	1.8330	6.72	0.0462
5000	1200	1.7532	6.49	0.0455
4000	1000	1.7191	6.17	0.0445
4000	500	2.4498	8.85	0.0426
6000	290	7.4308	12.90	0.0426
2000	290	2.1250	7.72	0.0400
1200	290	1.5850	5.51	0.0388
700	290	1.2839	3.35	0.0380
400	290	1.0861	1.22	0.0379
$n'_{20} = 0.1,\ \Delta\lambda_{\Delta S} = 0.0030$				
6000	1400	1.8192	3.68	0.0253
5000	1200	1.7500	3.55	0.0249
4000	1000	1.6754	3.38	0.0244
4000	500	2.4399	4.85	0.0233
6000	290	8.0659	7.06	0.0233
2000	290	2.0951	4.24	0.0220
1200	290	1.5502	3.02	0.0213
700	290	1.2652	1.84	0.0209
400	290	1.0853	0.67	0.0208

TABLE 2. Calculated Values of the Coefficients of Thermal Diffusion ($D_{\text{th}}\cdot 10^6$, m^2/sec) of the Binary Hydrogen–Nitrogen Gas System

n'_{20}	T_{Br}, K				
	923.2	655.0	543.1	436.3	339.1
	$D\cdot 10^6$, m^2/sec				
	558	316	235	161	111
0.9	25.61	13.34	9.64	6.54	4.52
0.8	43.86	22.88	16.54	11.21	7.78
0.7	55.91	29.26	21.13	14.30	9.96
0.6	60.15	31.57	22.80	15.41	10.77
0.5	53.12	27.97	20.19	13.62	9.56
0.4	43.97	23.23	16.76	11.29	7.95
0.3	34.43	18.26	13.16	8.86	6.25
0.2	23.77	12.64	9.09	6.12	4.34
0.1	13.00	6.95	4.98	3.35	2.39

TABLE 3. Comparison of Experimental and Calculated Values of Thermodiffusion Separation of the Hydrogen–Nitrogen Gas System

n'_{20}	$\log (T_1/T_2)$	T_1	$\Delta\lambda^e$, %	$\Delta\lambda^c$, %	ε, %
0.2188	0.2		2.39*	1.99	–16.7
0.5000			3.84*	3.84	0
0.7100			3.46*	3.88	12.1
0.2188	0.4		4.80*	3.70	–22.9
0.5000			8.18*	7.60	–7.1
0.7100			7.35*	7.96	8.3
0.2188	0.6		7.32*	5.83	–20.4
0.5000			12.96*	11.80	–9.0
0.7100			11.75*	12.01	2.2
0.327		547	3.67**	3.77	2.7
		510	3.46**	3.25	–6.1
		479	3.03**	2.94	–3.0
		456	2.50**	2.72	8.8
		418	2.26**	2.15	–4.9
		379	1.71**	1.64	–4.1
		328	0.76**	0.77	1.3

*, by the data of [12]; **, by the data of [13] at T_2 = 284 K.

TABLE 4. Comparison of Experimental and Calculated Values of Thermodiffusion Constant of the Hydrogen–Nitrogen Gas System (T_{Br} = 318.6 K)

Parameters	n'_{20}						
	0.1	0.2	0.3	0.4	0.5	0.6	0.7
α^e_{th} [14]	0.232	0.255	0.280	0.308	0.338	0.368	0.402
α^c_{th}	0.245	0.249	0.273	0.301	0.334	0.400	0.418
ε, %	5.6	–2.4	–2.5	–2.3	–1.2	8.7	4.0

$$\Delta\lambda = n'_{20} - n_{20} \,. \tag{4}$$

It is known [1] that $n'_{10} = 1 - n'_{20} \approx 1 - n_2$, $n'_{20} \approx n_2$, since $V' >> V$; the relation $n'_{20} \approx n_2$ was taken into account in comparison of calculated and experimental data.

The quantities q, $\Delta\lambda$, α_{th}, k_{th}, and D_{th} are calculated by (1)–(4) within the limits of the determining similarity criterion $(S_1 - S_2)/R$ from 0 to 9.80 (found in generalization in [6–11]) for wide ranges of variation of arbitrarily chosen temperatures and compositions of the hydrogen–nitrogen mixture. An example of calculation is given in [10]. The characteristics of thermodiffusion molecular mass transfer for the ranges of parameters for which experimental data are absent were obtained for the first time. Prediction of characteristics of thermodiffusion molecular mass transfer of the hydrogen–nitrogen mixture turned out to be possible, since Eq. (1), as was shown in [7–11], is not limited by the ranges of variation of the parameters of state. In calculations by (1)–(4), the hydrogen–nitrogen mixture was taken to be "frozen." The ranges of variation of the parameters of state, at which calculations were made, are the following: n'_{20} — from 0.1 to 0.9, T_1 — from 6000 to 4000 K, and T_2 — from 1400 to 290 K. The error of generalization which was estimated in [6, 8–11] is ±(3–4)%.

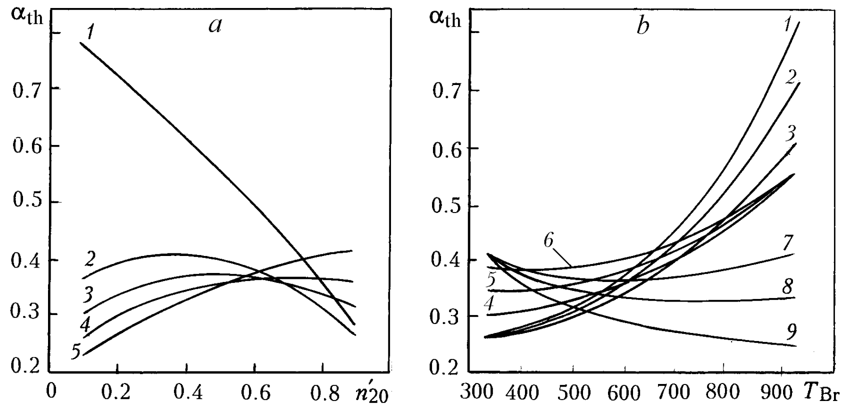

Fig. 1. Dependences of thermodiffusion constants on concentrations of hydrogen in the "hot" flask of the thermodiffusion device after separation at fixed temperatures (a) [1) T_1 = 6000 K; 2) 2000; 3) 1200; 4) 700; 5) 400; T_2 = 290 K] and on mean Brown temperatures at fixed compositions of hydrogen (b) [1) n'_{20} = 0.1; 2) 0.2; 3) 0.3; 4) 0.4; 5) 0.5; 6) 0.6; 7) 0.7; 8) 0.8; 9) 0.9].

Tables 1–4 and Fig. 1 give the results of the calculations. Table 2, moreover, presents values of the coefficients of mutual diffusion interpolated by the data of [16]. In Tables 3 and 4, the data on comparison of experimental and calculated data are given. The following quantities were used in comparison of experimental and calculated thermodiffusion relations of the hydrogen–nitrogen gas system: $n'_{20} = 0.500$, $\log (T_1/T_2) = 0.173$, $k^{\rm e}_{\rm th} = 0.0346$ [14], $k^{\rm c}_{\rm th} = 0.0345$, and $\varepsilon = 1\%$.

Thermodiffusion constants of the mixture studied were determined in [14] experimentally at a pressure of 125 mm Hg and a mean Brown temperature [1]:

$$T_{\rm Br} = \frac{T_1 T_2}{T_1 - T_2} \ln \frac{T_1}{T_2}\,.$$

In the present paper, generalization [6–11] and, thus, prediction of the characteristics of molecular thermodiffusion mass transfer were made at values of absolute molar entropies related to normal pressure. It is known that for simple binary gas systems, thermodiffusion constants do not depend on pressure from atmospheric and below [1]. Therefore, experimental data of [14] (see Table 4) are compared with calculated ones. It is seen from this table that the thermodiffusion constant $\alpha_{\rm th}$ increases with an increase of n'_{20} at $T_{\rm Br}$ = 318.6 K. This is in correspondence with the results of the present calculations.

It follows from Fig. 1a that at T_1 = 6000 K, T_2 = 290 K and with an increase of n'_{20} the thermodiffusion constant $\alpha_{\rm th}$ decreases within the entire range of variation of concentrations (curve 6) and at T_1 = 2000 K, T_2 = 290 K, and n'_{20} = 0.4 it reaches a maximum (curve 5). It is characteristic that within the entire range of variation of concentrations the thermodiffusion constant $\alpha_{\rm th}$ at T_1 = 6000 K is higher than in the case when T_1 = 2000 K, which corresponds to the physical essence of the process of thermodiffusion. It follows from Fig. 1a that at T_1 = 400 K, T_2 = 290 K (curve 2) and as n'_{20} increases, the thermodiffusion constant $\alpha_{\rm th}$ increases within the entire range of variation of concentrations, i.e., the dependence $\alpha_{\rm th}(n'_{20})$ has a qualitatively different form compared to the same dependence at a larger temperature difference T_1 = 6000 K, T_2 = 290 K (curve 6). The dependences $\alpha_{\rm th}(n'_{20})$ at both T_1 = 700 K, T_2 = 290 K (curve 1) and T_1 = 1200 K, T_2 = 290 K (curve 3) reach maximum values of the thermodiffusion constants $\alpha_{\rm th}$ at n'_{20} equal to 0.7 and 0.5, respectively. In this figure, maximum values of the thermodiffusion constants $\alpha_{\rm th}$ of the dependences $\alpha_{\rm th}(n'_{20})$ (curves 2–4) are in qualitative agreement with the classical dependences of thermodiffusion separation $\Delta\lambda$ on the mixture composition. It follows from Fig. 1b that within the range of concentrations n'_{20} = 0.7–0.9 (curves 7–9) and n'_{20} = 0.1–0.3 (curves 1–3) the dependences $\alpha_{\rm th}(T_{\rm Br})$ have almost the same qualitative character; however, at n'_{20} = 0.4–0.6 (curves 4–6) the dependences $\alpha_{\rm th}(T_{\rm Br})$ have another form. This variation corresponds to the dependences $\Delta\lambda(n'_{20})$ when thermodiffusion separations reach maximum values at concentrations n'_{20} = 0.4–0.6.

NOTATION

A, dimensionless constant; D and D_{th}, coefficients of mutual and thermal diffusion, m^2/sec; k_{th}, thermodiffusion ratio, mole fractions; n_2, concentration of hydrogen in the thermodiffusion device before the process of separation, mole fractions; n_{10} and n_{20}, concentration of nitrogen and hydrogen, respectively, in the "cold" flask of the thermodiffusion device in the equilibrium state, mole fractions; n'_{10} and n'_{20}, concentration of nitrogen and hydrogen, respectively, in the "hot" flask of the thermodiffusion device in the equilibrium state, mole fractions; q, coefficient of separation; R, universal gas constant, kJ/(kmole·K); S_1 and S_2, absolute molar entropies of the mixture in the equilibrium state in the "cold" and "hot" flasks of the thermodiffusion device, kJ/(kmole·K); S'_{10} and S'_{20}, absolute molar entropies of nitrogen and hydrogen in the "hot" flask of the thermodiffusion device in the equilibrium state, kJ/(kmole·K); S_{10} and S_{20}, absolute molar entropies of nitrogen and hydrogen in the "cold" flask of the thermodiffusion device in the equilibrium state, kJ/(kmole·K); T_1 and T_2, absolute temperatures of the "hot" and "cold" flasks of the thermodiffusion device, i.e., absolute temperatures at the boundaries of the system under consideration, K; T_{Br}, absolute mean Brown temperature, K; V' and V, volumes of the "hot" and "cold" flasks of the thermodiffusion device, m^3; α_{th}, thermodiffusion constant; $\Delta\lambda$, thermodiffusion separation, mole fractions, % — in tables; $\Delta\lambda_{\Delta S}$, scale thermodiffusion separation, mole fractions; ε, deviation of calculated values from experimental ones, %. Indices: th, thermal; e, experiment; c, calculation.

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