PREDICTING THE THERMAL-DIFFUSION CHACTERISTICS OF A HYDROGEN–OXYGEN BINARY GAS MIXTURE BY THE SIMILARITY METHOD

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Separation coefficients, thermal-diffusion separations, thermal-diffusion ratios, and thermal-diffusion constants are calculated for a hydrogen–oxygen binary gas mixture over a wide range of variations of temperatures and concentrations under rarefaction conditions.

The properties of thermal-diffusion mass transfer in gases are used in calculations and for optimization of isotope separation [1] and mass exchange processes [2], for evaluation of the parameters of intermolecular interactions [3, 4] and physical equilibrium constants [5], and in other cases [6].

Based on an entropy generalization of numerous experimental data on thermal diffusion in binary gas mixtures under rarefaction conditions, the following similarity equation has been obtained [7]:

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

A method for evaluation of $\Delta\lambda_{\Delta s}$, S_1, and S_2 is also presented in [7].

Using Eq. (1) and the well-known relationships for estimating thermal-diffusion intensity

$$\Delta\lambda = n'_{20} - n_{20}, \quad \Delta\lambda = k_T \ln \frac{T_1}{T_2}; \tag{2}$$

$$\alpha_T = k_T / n_{10} n_{20}, \quad \ln q = \alpha_T \ln \frac{T_1}{T_2}, \tag{3}$$

the following algorithm for predicting the properties of thermal-diffusion transfer for gas-phase binary systems has been found [8]:

$$\Delta\lambda = \frac{\Delta\lambda_{\Delta s}\,[n'_{20}\,(S'_{20} - S_{20}) + (1 - n'_{20})\,(S'_{10} - S_{10})]}{1 + \Delta\lambda_{\Delta s}\,(S_{10} - S_{20})}, \tag{4}$$

$$\alpha_T = \frac{k_T}{(n'_{20} - \Delta\lambda)\,(1 - n'_{20} + \Delta\lambda)}. \tag{5}$$

Calculations were carried out within the limits of the governing similarity criterion $(S_1 - S_2)/R$ from 7.92 (found upon generalization of experimental data) and lower for a wide range of variations of temperatures and compositions of the hydrogen–oxygen mixture. The preponderance of values of the characteristics of thermal-diffusion transfer were obtained for regions of parameters of state that have not been studied experimentally. This can be substantiated by the fact that Eq. (1), as has been shown in [7], is not restricted by ranges of parameters of state available for predicting the properties of thermal-diffusion mass transfer in binary gas systems. In

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TABLE 1. Calculated Values of Characteristics of Thermal-Diffusion Mass Transfer in Hydrogen−Oxygen Systems [*]

$T_1 - T_2$, K	q	$\Delta\lambda$, %	k_T, %	q	$\Delta\lambda$, %	k_T, %
	$n'_{20} = 0.9;\ 35\cdot10^{-4}$			$n'_{20} = 0.8;\ 68\cdot10^{-4}$		
6000−1400	1.4155	4.25	2.92	1.4780	7.85	5.40
5000−1200	1.3972	4.04	2.83	1.4556	7.48	5.24
4000−1000	1.3747	3.78	2.73	1.4275	7.02	5.06
4000−500	1.5150	5.42	2.61	1.6145	10.08	4.85
6000−290	1.7191	8.00	2.64	1.9242	14.86	4.90
2000−290	1.4522	4.67	2.42	1.5296	8.70	4.50
1200−290	1.3351	3.34	2.35	1.3791	6.22	4.37
700−290	1.2134	2.05	2.33	1.2334	3.81	4.32
400−290	1.0813	0.75	2.32	1.0864	1.39	4.33
	$n'_{20} = 0.7;\ 94\cdot10^{-4}$			$n'_{20} = 0.6;\ 106\cdot10^{-4}$		
6000−1400	1.5450	10.48	7.20	1.5966	11.69	8.03
5000−1200	1.8127	10.00	7.01	1.5635	11.17	7.83
4000−1000	1.4826	9.40	6.78	1.5227	10.51	7.58
4000−500	1.7293	13.52	6.50	1.8434	15.13	7.28
6000−290	2.2181	19.91	6.57	2.5785	22.26	7.35
2000−290	1.2825	11.68	6.05	1.6905	13.08	6.77
1200−290	1.4233	8.35	5.87	1.4530	9.35	6.57
700−290	1.2506	5.10	5.78	1.2576	5.69	6.46
400−290	1.0899	1.87	5.80	1.0895	2.09	6.49
	$n'_{20} = 0.5;\ 106\cdot10^{-4}$			$n'_{20} = 0.4;\ 99\cdot10^{-4}$		
6000−1400	1.6474	11.83	8,14	1.7279	11.53	7.99
5000−1200	1.6090	11.32	7.94	1.6793	11.04	7.74
4000−1000	1.5610	10.67	7.70	1.6219	10.42	7.52
4000−500	1.9629	15.36	7.39	2.1567	15.98	7.69
6000−290	3.0889	22.56	7.47	4.1202	21.97	7.27
2000−290	1.7679	13.28	6.89	1.8868	12.96	6.73
1200−290	1.4807	9.48	6.68	1.5249	9.25	6.52
700−290	1.2621	5.76	6.55	1.2732	5.61	6.38
400−290	1.0887	2.12	6.62	1.0896	2.06	6.44
	$n'_{20} = 0.3;\ 85\cdot10^{-4}$			$n'_{20} = 0.2;\ 62\cdot10^{-4}$		
6000−1400	1.8556	10.11	6.96	2.0019	7.69	5.29
5000−1200	1.7914	9.69	6.79	1.9215	7.38	5.17
4000−1000	1.7180	9.15	6.60	1.8267	6.98	5.04
4000−500	2.4925	13.17	6.33	2.9600	10.03	4.82
6000−290	6.8551	19.27	6.38	15.6959	14.66	4.85
2000−290	2.0693	11.38	5.91	2.3231	8.67	4.50
1200−290	1.5933	8.12	5.72	1.6635	6.19	4.36
700−290	1.2927	4.91	5.59	1.3094	3.73	4.24
400−290	1.0924	1.81	5.66	1.0942	1.38	4.31
	$n'_{20} = 0.1;\ 33\cdot10^{-4}$					
6000−1400	2.1990	4.30	2.96			
5000−1200	2.0915	4.13	2.90			
4000−1000	2.5485	3.94	2.84			
4000−500	3.7333	5.62	2.70			
6000−290	83.8475	8.19	2.71			
2000−290	2.4051	4.85	2.52			
1200−290	1.9228	3.46	2.44			
700−290	1.3295	2.08	2.37			
400−290	1.3280	0.77	2.40			

[*] In the Table, composition values are followed by values of scaling separations.

TABLE 2. Comparison of Calculated and Experimental Values [9] of Thermal-Diffusion Constants for Hydrogen–Oxygen System

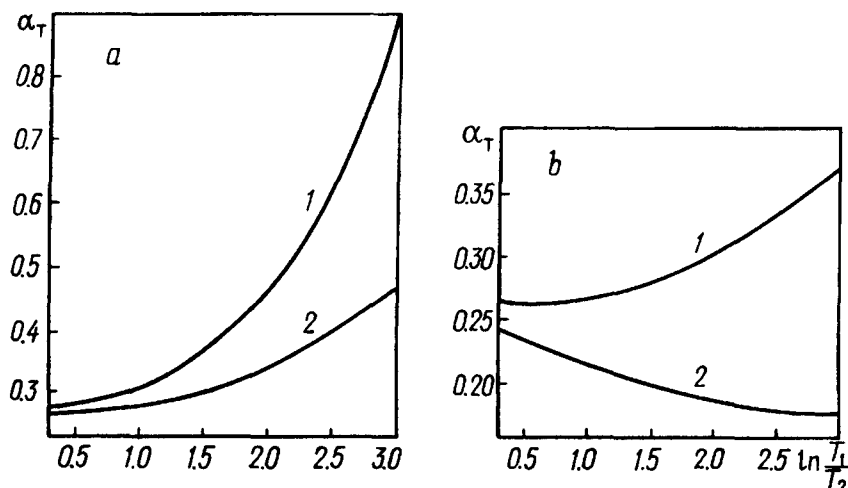| n'_{20}	$\alpha_T^e \cdot 10$	$\alpha_T^c \cdot 10$	$\varepsilon, \%$
0.2	2.80	2.76	−1.4
0.4	3.15	2.64	−16.2
0.6	3.60	2.68	−25.6
0.75	4.10	2.64	−35.6

Fig. 1. Dependences of the thermal-diffusion constant on the temperature ratio: a: 1) $n'_{20} = 0.2$; 2) 0.4; b: 1) $n'_{20} = 0.5$; 2) 0.9.
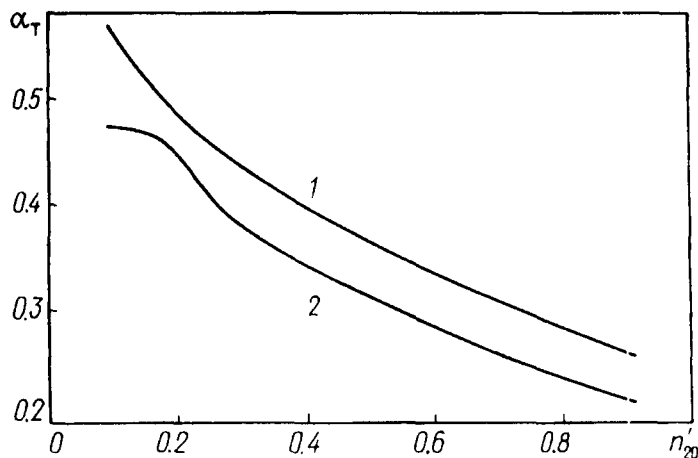

Fig. 2. Dependences of the thermal-diffusion constant on the composition of the mixture of "light" molecules in the "hot" reservoir of the device after separation at fixed temperatures T_1 and T_2: 1) T_1-T_2 = 6000–1400 K; 2) 2000–290 K.

calculations by formulas (2)-(5), the hydrogen—oxygen mixture was considered to be "frozen." The following intervals of the parameters were chosen for calculations: n_{20} = 0−1.0 and T_1-T_2 = 6000−290 K.

Table 1 and Figs. 1 and 2 present results of the calculations.

Figure 1 presents $\alpha_T = \varphi(\ln T_1/T_2)$ in the temperature range T_1 = 6000−400 K and for fixed T_2 = 290 K for various compositions of the hydrogen—oxygen mixture. Figure 2 presents $\alpha_T = \varphi(n_{20})$ for fixed T_1 and T_2.

The calculation results lie, as a rule, within the error bounds of the available experimental data. Comparison of calculated and experimental values of the thermal-diffusion constant are presented as an example

in Table 2. Experimental and calculated α_T values are marked by indices e and c respectively; ε stands for the deviation of calculated values from experimental data.

The data were compared at the average Brown temperature of 318.6 K, which corresponds to the experiments [9]. As has been pointed out in [7], generalizations were carried out for ratios of molar entropies to the normal pressure. It is well known that, within the framework of theoretical assumptions, the effect of thermal diffusion is pressure-independent [10]. This has been substantiated experimentally for a series of binary gas systems at pressures from about atmospheric and lower [3, 11, 12]. Therefore, experimental data on the thermal-diffusion constant obtained at a pressure of 123 mm Hg [9] are compared with the calculated values.

NOTATION

A, dimensionless constant; k_T, thermal-diffusion ratio; n_{10} and n_{20}, molar compositions of "heavy" and "light" molecules at temperature T_2; n'_{20}, molar composition of "light" molecules at temperature T_1; q, separation coefficient; R, gas constant; S_1 and S_2, absolute molar values of mixture entropies at temperatures T_1 and T_2, respectively; S'_{10} and S_{10}, absolute molar values of entropies of the "heavy" component at T_1 and T_2, respectively; S'_{20} and S_{20}, absolute molar values of entropies of the "light" component at T_1 and T_2, respectively; T_1 and T_2, absolute temperatures at boundaries of the system under consideration, i.e., temperatures of the "hot" and "cold" reservoirs of the thermodiffusion device; α_T, thermal-diffusion constant; $\Delta\lambda$, thermal-diffusion separation; $\Delta\lambda_{\Delta s}$, scaled thermal-diffusion separation.

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