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AN AUTOMATED SETUP FOR INVESTIGATION OF THE THERMAL DIFFUSION AND MUTUAL DIFFUSION OF GAS MIXTURES

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We present a block diagram of a setup for determining the thermal-diffusion factor and the coefficient of mutual diffusion of gas mixtures. The procedure of the experiment is described. Experimental results on the temperature and concentration dependence of α_t and D_{12} for He–Ar and Ar–CO mixtures are given.

The main source of information on the majority of the properties of substances is experiment. Execution of an experiment is usually an expensive process, and in this connection an increase in the efficiency of experimental determination is very timely and can be achieved by automating investigations and expanding the functional possibilities of measuring instruments.

Below we present a description of an automated setup for measuring thermodiffusion and diffusion characteristics of gas mixtures.

The basis behind the phenomenon of thermodiffusion is that superposition of a temperature gradient on an initially homogeneous mixture of gases leads to deterioration of homogeneity, i.e., to partial separation of the mixture into components. The concentration gradient arising, in turn, causes ordinary diffusion, which tends to eliminate this gradient. As a result, the system reaches a state where the effects of separation and mixing are mutually balanced out. In this case, a gas in a hot region is usually enriched with a light component [1] and in a cold region with a heavy component. The time of separation of a mixture under the influence of a temperature gradient depends on the coefficient of diffusion, whereas the magnitude of separation is characterized by the thermodiffusion factor.

Composition of the Setup and Purpose of Its Units. A block diagram of the setup is shown in Fig. 1. It includes a two-cylinder apparatus (blocks 1, 2, 3, 7, 8), systems for thermostating the upper and lower cylinders (blocks 13, 14), a measuring system (blocks 9-11), a computer (12), a commutation block (4, 5, 6), a system for preparing working mixtures (15), and a vacuum system (16).

A schematic diagram of the two-cylinder thermodiffusion apparatus is presented in Fig. 2. Upper cylinder 1 of the apparatus consists of two metal vessels (outer and inner). Lower cylinder 2 is made in the form of a massive block with two cells (a measuring cell V_1 and a comparison one V_c). The cells are fitted with measuring elements 10 connected to bridge 9. Cylinders 1 and 2 are connected by tube 3, whose upper and lower ends are covered by solenoid valves 4 and 5.

The vessel V_1 has outlet tube 12 for evacuating the apparatus and filling it with gas. The main geometric dimensions of the apparatus are: the volume of the upper vessel (cylinder) V_2 is 329.8 cm^3; the volume of the lower vessel (the measuring cell) V_1 is 2.35 cm^3, the length of the connecting tube L is 13.8 cm; its inner diameter and volume are equal to 0.38 cm and 1.6 cm^3, respectively.

System of Thermostating. To maintain the prescribed temperature in cylinders 1 and 2 of the apparatus two independent thermostating systems were used.

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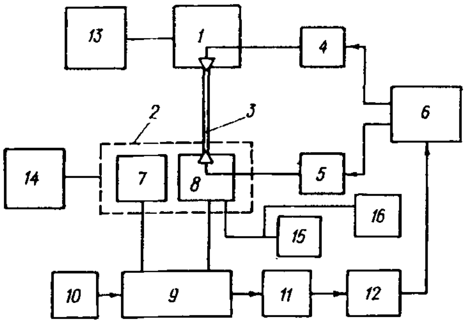


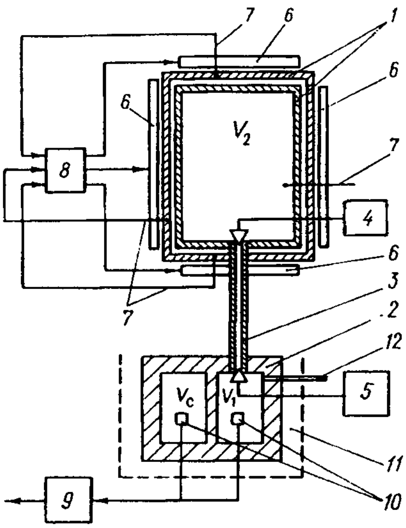


Fig. 1. Block diagram of the setup for determining thermodiffusion separation: 1) upper cylinder, 2) katharometer, 3) connecting tube, 4 and 5) electromagnets of commutation block 6 connected to the valves of the upper and lower cylinders, 7 and 8) comparision and measuring cells of the katharometer, 9) bridge connected to power-supply block 10 and digital voltmeter 11; 12) computer, 13 and 14) thermostating blocks for the upper and lower cylinders, 15) system for preparation of gas mixtures, 16) vacuum system.

Fig. 2. Block diagram of the two-cylinder apparatus: 1 and 2) upper and lower cylinders, 3) connecting tube, 4 and 5) solenoid valves, 6) heaters, 7) thermocouples, 8) electronic block, 9) bridge, 10) resistance thermometers, 11) thermostat, 12) outlet tube.

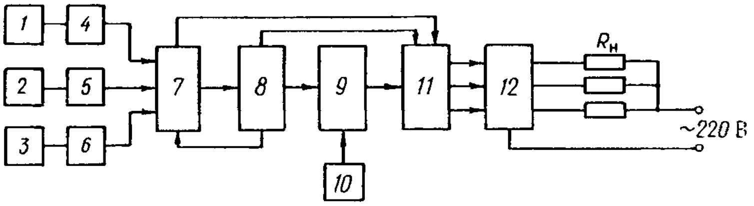
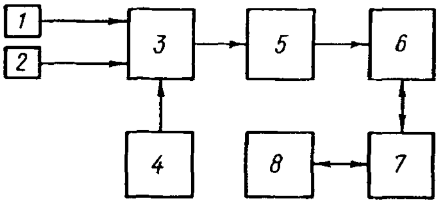


Fig. 3. Block diagram of the thermostat.

Cylinder 2 was maintained nearly at room temperature by means of a U-10-type liquid ultrathermostat. An additional heater installed on a contact thermometer following the scheme given in [2] and the use of an electronic relay instead of a mercury one in the thermostat made it possible to maintain the temperature within 0.05°C. The temperature of the lower cylinder was determined from the readings of a Chromel-Copel thermocouple located on its outer surface. The emf of the thermocouple was measured by an F30 digital voltmeter.

Thermostating of the upper cylinder was done by means of a Nichrome heater (Fig. 2). To stabilize the temperature and eliminate its gradient inside the cylinder, heating elements 6 with separate thermocouples 7 were positioned on all the surfaces of the outer vessel. A block diagram of the thermostat is given in Fig. 3. It contains three main units: a three-channel inlet (thermocouples 1-3 and amplifiers 4-6), a measuring channel (commutator 7, digital voltmeter 8, comparator 9, adjusting block 10, distributor of channels 11), and a load switch (R_{load}) 12. In the process of operation the channels at the inlet and outlet are commutated synchronously by a signal from the digital voltmeter. The emf of the thermocouple, which is connected to the amplifier in accordance with [3], arrives via commutator 7 at digital voltmeter 8, where it is measured and converted into code. The latter enters block 9, where it is compared with the code of the prescribed temperature, and the result of the comparison arrives, via distributor 11, at load switch 12 for switching on (off) the corresponding heater.



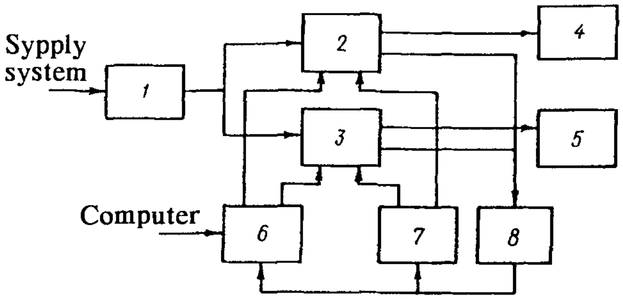


Fig. 4. Block diagram of the measuring system of the setup: 1 and 2) thermal resistors, 3) bridge, 4) current stabilizer, 5) amplifier, 6) digital voltmeter, 7) module for connection to the computer, 8) computer.

Fig. 5. Block diagram of the commutation block.

Measuring System. This is intended for measuring and recording changes in the voltage U on the sensitive element caused by changes in the composition of the gas mixture in the measuring cell. A block diagram of the measuring system is given in Fig. 4. The difference in the voltages of two sensitive elements included in a bridge circuit arrives via an F8024-S4 amplifier at an F30 digital voltmeter and is recorded by the computer.

To carry out automatic control of the operation of the valves the setup uses a control module that is connected to the computer and, via the commutation block, ensures the opening of the valves. The commutation block (Fig. 5) contains: power-supply block 1, controlled gates 2 and 3, electromagnets 4 and 5 of the valves of the upper and lower cylinders (vessels), blocks 6 and 7 for programmed and manual operation of the gates, block 8 to indicate the state of the gates. The electric circuit for controlling gates 2 and 3 is made so that, when power-supply block 1 is switched on, the gates remain closed until arrival of a control signal from block 6 or 7. This a signal can appear when there is a signal from block 8 about the state of the gates and their readiness for operation. When a signal arrives at gates 2 and 3 (from block 6 or 7), they are opened and the supply voltage from block 1 arrives at electromagnets 4 and 5, which open the valves of the upper and lower cylinders. An operator can control the gates manually using block 7 or automatically by the arrival of a signal from the computer via block 6. Moreover, separate and simultaneous opening of gates 2 and 3 is also possible; this can be needed in preparatory operations or to trigger the process of thermal diffusion.

Gas mixtures were prepared in standard cylinders by the method of partial pressure with subsequent analysis on an MX1321A-type mass spectrometer.

Analysis of the change in the composition of the mixture was done in the course of the experiment by the katharometer method. As sensitive elements we used two platinum wire-wound resistors made of PlZT-0.02 material (State Standard 21007-75) with a diameter of the spiral of 0.3 ± 0.1 mm; at 20°C they had the following resistances: 20.446 Ω and 20.452 Ω.

Procedure for Determining α_{th} and D_{12}. Before the start of the experiment we calibrated the sensitive element for the mixture investigated, i.e., we determined the dependence of U on the concentration of the heavy component x_1 of the mixture. In the majority of cases the curve of U vs. x_1 was approximated in the form of the polynomial $U = a + bx_1 + cx_1^2$.

The experiment was begun with thermostatic regulation of the cylinders of the thermal-diffusion apparatus, evacuation to a pressure of the order of $2 \cdot 10^{-2}$ mm Hg, and admission of the test mixture into the apparatus up to the pressure needed; thereafter valves 4 and 5 (see Fig. 2) closed the ends of connecting tube 3 and then the lower cylinder was evacuated again to be subsequently filled with the test mixture at the same pressure. After a certain time sufficient to heat the test mixture, both valves that closed the connecting tubes were opened simultaneously, and the change in U in time t was recorded. The maximum time t of recording $U(t)$ was prescribed equal to approximately five times the value of τ calculated for this mixture.

Since approach to a steady state follows an exponential law so that $U(t) = U_t = U_\infty[1 - \exp(-t/\tau)]$ [4], on the basis of the measured values of U_∞ we can determine the relaxation time from the relation

TABLE 1. Comparison between Experimental Values of U and Ones Calculated from the Polynomial for an He–Ar Mixture

x_1	$U_{\text{exp}} \cdot 10^3$	$U_{\text{cal}} \cdot 10^3$	δ, %
0.2	0.968	0.965	0.31
0.25	11.810	11.76	0.42
0.4	17.438	17.390	0.27
0.5	20.551	20.550	0.0
0.75	28.280	28.370	0.34

TABLE 2. Experimental Results on the Temperature Dependence of α_{th} and D_{12} for He–Ar and Ar–CO Mixtures

T_1	T_2	T_{m}	S, %	α_{th}	τ	D_{12}
He–Ar ($x_1 = 0.5$; $P = 0.1$ MPa)						
291.4	325	307	1.006	0.369	583	0.759
	354	321	1.815	0.373	570	0.809
	394	337	2.895	0.384	556	0.869
291.8	404	342	3.183	0.389	553	0.887
Ar–CO ($x_1 = 0.4996$; $P = 0.5$ MPa)						
294.6	340.7	316.5	0.23	0.063	930	0.419
295.3	347	319	0.26	0.064	900	0.427
294.9	370	329.6	0.36	0.065	860	0.480
	424	352	0.62	0.068	843	0.528

$$\frac{1}{\tau} = \frac{\ln U_\infty - \ln (U_\infty - U_t)}{t}. \tag{1}$$

Using the value of τ found, we calculated the coefficient of mutual diffusion for binary gas mixtures from the relation [5]

$$\tau = K \frac{L}{A} \left[\frac{T_1}{V_1} + \frac{T_2}{V_2} \right]^{-1} \left(\frac{T}{D} \right)_{\text{m}}, \tag{2}$$

where $(T/D)_{\text{m}}$ is the mean value of T/D along the connecting tube; K is a correction for deviation from a quasistationary state; in a first approximation this correction was calculated as follows [6]:

$$K = 1 + \frac{AL}{2V_1} \frac{T_1}{\overline{T}_D} \left[1 + \frac{1}{2} |\ln q| \right]. \tag{3}$$

The value of $(T/D)_{\text{m}}$ is equal to the actual value of T/D at a ceratin mean temperature $\overline{T}_D$ (between T_1 and T_2). As $\overline{T}_D$ for D_{12} we used the logarithmic mean temperature determined from Braun's formula [1]:

$$T_{\text{m}} = \frac{T_1 T_2}{T_2 - T_1} \ln \frac{T_2}{T_1}, \tag{4}$$

experimental results on thermodiffusion were referred to this temperature.

The magnitude of thermodiffusion separation was determined from the formula

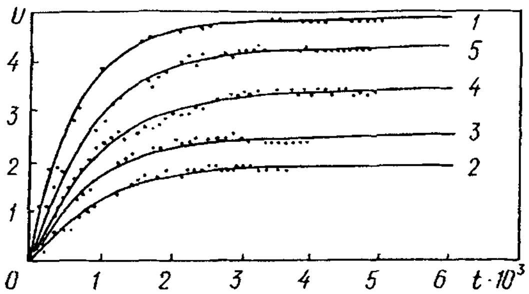


Fig. 6. Dependence of U of the bridge on the time t of thermodiffusion separation of mixtures: 1) He–Ar $(U \cdot 10^{-3})$ for $x_1 = 0.5$ at $T = 321$ K; 2, 3, 4, 5) Ar–CO $(U \cdot 10^{-5})$ for $x_1 = 0.4996$ at $T = 316.5$, 319, 329.6, 352 K, respectively. U, V; t, sec.

$$S = \Delta x \left(1 + \frac{V_1 T_2}{V_2 T_1} + \Delta\right), \tag{5}$$

where

$$\Delta x = \frac{U_\infty}{(\partial U/\partial x)} = \frac{U_\infty}{b + 2cx}; \tag{6}$$

Δ is a small correction for the gas volume contained in the connecting tube; calculations made by the relation suggested in [7] showed that at a temperature drop of 80–100°C this correction does not exceed 0.5% of the magnitude of separation S.

The thermodiffusion factor α_{th} was determined from the relation

$$\alpha_{\text{th}} = \frac{S}{x_1 x_2 \ln (T_2/T_1)}. \tag{7}$$

Discussion of Experimental Results. To calibrate the thermodiffusion setup we used an He–Ar mixture of equimolecular concentration as the most thoroughly investigated mixture according to the literature data. The sensitive element of the katharometer was calibrated for pure gases and five He–Ar mixtures of different concentrations at a temperature of the lower cylinder $T_1 = 291.4$ K and pressure $P = 0.1$ MPa. As a result of using the least-squares method to process the dependence of U of the sensitive element on the concentration we obtained the following coefficients for the polynomial $U = bx_1 + cx_1^2$: $b = 0.05298$ and $c = -0.02376$. As is seen from Table 1, the deviation of the experimental points from the averaged curve approximated by the given polynomial does not exceed 0.4%.

Figure 6 presents, as an example, experimental dependences of U of the bridge on the time t of thermodiffusion separation for an He–Ar mixture of equimolar concentration at $P = 0.1$ MPa, as well as for Ar–CO mixtures with a concentration close to equimolar at $P = 0.05$ MPa and different temperatures. Values of α_{th} and D_{12} calculated from these dependences are presented in Table 2.

For the composition of the mixtures we used gases of the following purity: high-purity helium (99.993% He), pure argon of grade A (99.96% Ar), and carbon monoxide (98% CO).

We estimated the error of determination of α_{th} for the mixtures: for He–Ar of the order of 2% and for Ar–CO 5–7%. For D_{12} the error is equal to no more than 5–6% for He–Ar and 6–8% for Ar–CO. In calculations of errors we adopted a level of confidence equal to 0.95.

Figure 7 compares experimental results on the thermodiffusion factor and the coefficient of mutual diffusion obtained for He–Ar on our setup and taken from the literature. As is seen from the graphs, there is an agreement between them within the limits of the estimated errors.

Averaged values of α_{th} and D_{12} for an Ar–CO mixture obtained from results of 3-5 measurements are listed in Table 3. The temperature dependences of α_{th} and D_{12} were approximated by the polynomials

TABLE 3. Experimental Results on the Temperature Dependence of the Thermodiffusion Factor and the Coefficient of Mutual Diffusion for Ar–CO Mixtures of Different Concentrations

x_{Ar}	T_1	T_2	T_m	α_{th}	D_{12}
0.2655	294.6	340.7	316.5	0.066	0.419
	295.3	347	319	0.067	0.428
	294.8	370	329.6	0.068	0.455
	294.6	390	338	0.067	0.480
	294.5	424	352	0.071	0.518
0.4996	294.6	340.7	316.5	0.063	0.419
	295.3	347	319	0.064	0.431
	294.9	370	329.6	0.065	0.459
	294.9	390	338	0.066	0.485
	294.9	424	352	0.068	0.525
0.7633	294.6	340.7	316.5	0.065	0.424
	295.3	347	319	0.066	0.437
	294.7	370	329.6	0.066	0.465
	294.6	390	338	0.065	0.505
	294.9	424	352	0.066	0.528

TABLE 4. Coefficients of Eqs. (8) and (9)

x_{Ar}	b_1/d_1	$b_2\cdot 10^3/d_2\cdot 10^2$	$b_3\cdot 10^6/d_3\cdot 10^5$	δ, %
0.2655	0.4090/–0.8547	–2.1606/0.5162	3.4078/–0.3587	±1.5/±0.2
0.4996	0.0355/–0.8246	0.0490/0.4821	0.1231/–0.2804	±0.1/±0.2
0.7633	0.1050/–2.1501	–0.2454/1.2850	0.3809/–1.4887	±1.5/±0.5

$$\alpha_{\mathrm{th}} = b_1 + b_2 T + b_3 T^2 , \tag{8}$$

$$D_{12} = d_1 + d_2 T + d_3 T^2 . \tag{9}$$

The coefficients of Eqs. (8) and (9) as well as deviations of experimental values of α_{th} and D_{12} from those calculated from polynomials (8) and (9) are presented in Table 4.

Figure 8 compares our experimental data on the temperature dependence of α_{th} for an Ar–CO mixture with literature data for the concentration Ar ~0.5, as well as with results of calculations by the Chapman–Enskog theory [13] and semiempirical relation (3) of [14]:

$$\alpha_{\mathrm{th}} = \alpha_{\mathrm{th.sol.sph}} / \exp \left[\sum_{i=1}^{n} c_i (\ln T^*)^{i-1} \right] , \tag{10}$$

derived by correlating experimental data. The coefficients of the polynomial are: $C_1 = 2.38257$; $C_2 = -1.52495$; $C_3 = 0.330919$. The values of $\alpha_{\mathrm{th.sol.sph.}}$ were determined from the relation [15]

$$\alpha_{\mathrm{th.sol.sph}} = (\sqrt{m_1} - \sqrt{m_2})/(x_1 \sqrt{m_1} + x_2 \sqrt{m_2}) . \tag{11}$$

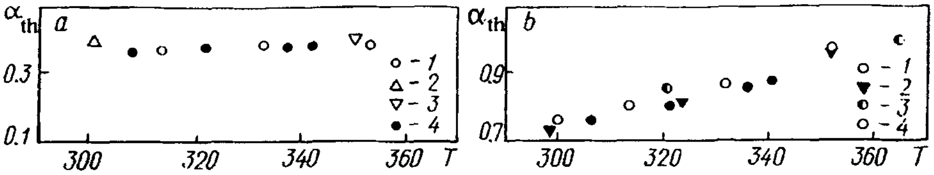


Fig. 7. Temperature dependence of α_{th} (a) and D_{12} (b) for an He–Ar mixture ($x_1 = 0.5$); a: 1) [9]; 2) [9]; 3) [10]; 4) present data; b: 1) [8]; 2) [11]; 3) [12]; 4) present data. T, K.

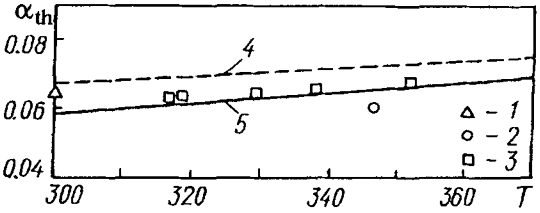


Fig. 8. Temperature dependence of the thermodiffusion factor for an Ar–CO mixture ($x_1 \sim 0.5$). Experimental data: 1) [15], 2) [16], 3) present data. Calculation: 4) by the Chapman–Enskog theory for the Lennard-Jones (12-6) potential, 5) by formula (3) [14].

Agreement between the experimental data and those predicted by formula (10) is within 3–7%, which does not exceed the experimental error in determining α_{th}.

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NOTATION

α_{th}, thermodiffusion factor; D_{12}, coefficient of mutual diffusion, cm^2/sec; x_1, x_2, molar concentrations of the heavy and light components of the initial (unseparated) mixture; U, $U(t)$, sensitive-element voltage, V; U_∞, value of U in the stationary state, i.e., when $t \gg \tau$, V; t, τ, time, relaxation time, sec; T_1, T_2, temperatures of the cold and hot vessels of the apparatus, K; V_1, V_2, volumes of the cold and hot vessels, cm^3; A, L, cross-sectional area, cm^2, and length of the tube, cm; $\ln q = \alpha_{th} \ln (T_2/T_1)$, separation factor; S, mixture separability, %; δ, ratio of the difference of the experimental and predicted values of the quantity considered to the experimental value. Subscripts: exp, experiment; cal, calculation; load, loading; sol. sph., solid sphere; m, mean.

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