APPARATUS FOR DETERMINING THERMAL-DIFFUSION COEFFICIENTS IN GAS MIXTURES

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Inzhenerno-Fizicheskii Zhurnal, Vol. 9, No. 5, pp. 616–621, 1965

UDC 533.15

A description is given of the construction of, and the technique of measuring separation effects in a single-stage thermal-diffusion apparatus. For the separation analysis, use is made of the dependence of the viscosity of gas mixtures on composition. Results are presented of a determination of the coefficient of thermal diffusion of a He/N_2 mixture in the pressure range 0.0005–0.01 MN/m^2.

In investigating the composition of a gas mixture in a thermal-diffusion separation apparatus, use has hitherto been made of thermally conducting sensors of various types [1], or of the analysis of refractive index change [2], or of mass spectrometer analysis [3], or the composition has been determined from the change of viscosity [4], etc. All these methods require special instruments, which involve difficulties due to their complexity or high cost.

We have determined the composition from the viscosity change, but in contrast to the authors of [5, 6], who used instruments with oscillating disks, we drew the gas-mixture specimens out through a capillary. This method is based on the dependence of the flow rate of a gas mixture through a capillary on its viscosity. Since the viscosity depends on the composition of the mixture, we can thus determine the composition.

It is known, for example, from [7] that for the same capillary with identical pressures at its ends, but gases with various viscosities, we have the relation

$$Q_1/Q_2 = \eta_2/\eta_1 \tag{1}$$

for the case $L_{av} < a$,

$$Q_1/Q_2 = \sqrt{\rho_2}/\sqrt{\rho_1} \tag{2}$$

for the case $L_{av} \geq 10a$.

In the region $10a > L > a$, we have

$$Q = \frac{\pi}{8\eta}\,\frac{a^4}{l}\,p_{av}(p_2 - p_1)\left[1 + \frac{L_{av}\xi}{a}\right],$$

or

$$Q = \left[\frac{\pi}{8\eta}\,\frac{a^4}{l}\,p_{av} + \frac{\pi\beta}{\rho v_{av}}\,\frac{a^3}{l}\right](p_2 - p_1).$$

In this region, (1) will have the form

$$\frac{Q_1}{Q_2} = \frac{\eta_2}{\eta_1}\,\frac{(1 + L_{av1}\xi_1/a)}{(1 + L_{av2}\xi_2/a)}.$$

Since this relation is more complex in form, it would be more convenient to choose the capillary section in such a way that either (1) or (2) would be valid. This will remain the valid also for gas mixtures of different composition. For these we may write:

$$Q_{1m}/Q_{2m} = \eta_{2m}/\eta_{1m} \quad \text{or} \quad Q_{1m}/Q_{2m} = \sqrt{\rho_{2m}}/\sqrt{\rho_{1m}}.$$

If the tests are carried out in such a way that the mixtures are drawn from different volumes at equal original pressures in the same time, then, after the withdrawal, a pressure difference will exist between the volumes.

Having determined for the reference mixtures the relation

$$\Delta p = f(x_1, x_2),$$

we may find the difference in composition of the mixtures under examination. The quantity α_T was determined from

$$\alpha_T = \frac{\Delta x}{x_1 x_2}\,\frac{\bar{T}}{\Delta T}, \tag{3}$$

which is applicable for small separations.

In our case (3) had the form

$$\alpha_T = \frac{\Delta l_t\,\Delta x_r\,\bar{T}}{\Delta l_r\,x_1 x_2\,\Delta T}.$$

In order to investigate the dependence of the thermal diffusion coefficient $\alpha_T = \alpha_T(p)$, where p is the pressure of a gas mixture in the moderately low-pressure region from 0.01 to 0.0005 MN/m^2, we constructed and set up the apparatus whose principal details are shwon in Fig. 1.

DESCRIPTION OF APPARATUS

The apparatus consists of two parts—the separating and the experimental. The former includes the thermal-diffusion separation apparatus I and II, the movable vessel for supplying it G, the manometer M for determining the pressure in the separation apparatus, and a portable furnace. Vessels I and II of the thermal-diffusion apparatus are connected through a vacuum valve before the start of separation, and disconnected after its completion.

Volume I was heated to an assigned temperature by means of a portable electric furnace supplied with stabilized current through an autotransformer. The second vessel was kept at a constant temperature of 293.1° K.

The temperature of the mixture in the vessels was followed from readings of Chromel/Alumel thermocouples and a potentiometric bridge, which allowed temperature measurement to be made with an accuracy ±0.1° K.

The silicone oil manometer M allowed the pressure in the separation apparatus to be determined to an accuracy of 266.644×10^{-3} N/m^2, since it was equipped with a cathetometer.

The experimental part of the equipment consisted of two symmetrical halves, designed for samples from vessels I and II, respectively. Their volumes were made equal to a high degree of accuracy (difference < 0.1 cm^3), the main part of the volumes being vessels A and B, which were located in a water thermostat Q, whose temperature was kept constant to an accuracy of ±0.1° K. The vessels comprised about 96% of the total volume, the remainder being that of the connecting tubes, which were thin-walled capillaries of internal diameter 2.5 mm, and well insulated thermally.

The samples flowed out from vessels A and B through the measuring capillary MC, of internal diameter 10μ and length 100 mm.

The most complex item from the constructional point of view was the drop micromanometer DM which was used to determine differences in the mixture composition between the hot and cold ends of the thermal-diffusion apparatus. The accuracy of determination of the composition difference was $\Delta x = 0.017\%$ for 1 mm of the micromanometer scale. The construction difficulties consisted of:

1. Choosing a tube of constant section along its length, in order to minimize the error associated with nonuniformities in diameter; this being the major part of the instrument error.
2. Locating the manometer measuring tube to be accurately horizontal, in order to reduce the part of the experimental error arising from movement of the drop due to gravity.

If these requirements are fulfilled and there is no heating of one half of the experimental part relative to the other, nor leakage of the mixture through the drop, then the manometer will operate reliably and accurately.

The drop micromanometer required a long time—20–30 min—to settle down. To decrease the measurement time, it seemed expedient to use a drop micromanometer similar to that described in [8], or a capacitance-type sensor as in [9], or any accurate pressure-measuring device with a small response time. For rough measurement of the pressure in vessels A and B, as well as for setting them equal, manometer M1 was used. The accuracy of measurement was $266.644 \cdot 10^{-3}$ N/m^2.

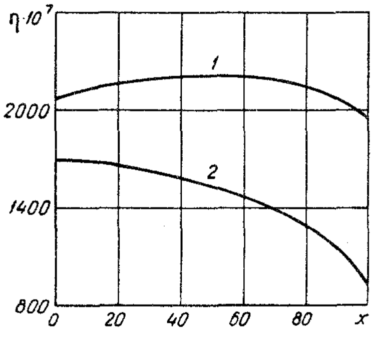

Fig. 2. Dependence of viscosity on mixture composition (t = 273.16° K); 1)He—Ar [14]; 2)H_2—N_2 [15].

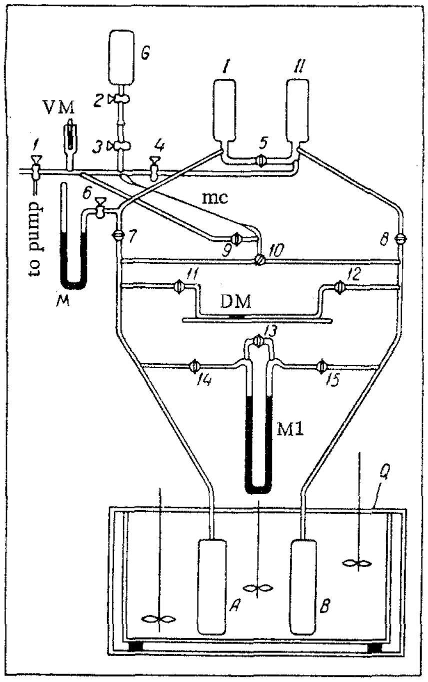

Fig. 1. Equipment for investigation of coefficients of thermal diffusion in gas mixtures. 1–15) Vacuum and chemical valves; M) absolute oil manometer; VM) vacuum manometer.

MEASUREMENT TECHNIQUE

We shall now examine the sequence of operations in the apparatus. After separation is finished, valve 5 is closed and the furnace removed. When vessel I is cooled to the temperature of vessel II and of vessels A and B, the samples are transferred to the experimental part through valves 7 and 8. Vessels A and B are filled so that their pressures are equal (in our case the pressure was always constant and equal to 490.33 N/m^2). The equality of the pressures could be judged roughly from the readings of manometer M1, and then, to make the pressures accurately equal, A and B were connected to the differential drop manometer DM, and with the aid of the subsidiary volume (0.1 cm^3), between valves 14 and 15, the pressures were made equal. When the pressures in the two halves of the apparatus were sufficiently equal so that on joining them to DM the drop remained motionless in the central part of the tube, we proceeded with the outflow. This passed through the capillary from vessels A and B for identical times, during which manometer DM was disconnected from A and B. After the outflow the drop micromanometer was connected and the displacement of the drop determined, from which the difference in composition of the samples from the upper and lower ends of the thermal-diffusion apparatus was evaluated. The zero was checked prior to the start and at the end of each series of measurements.

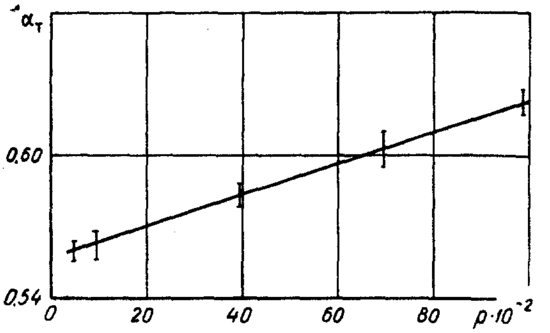

Fig. 3. Dependence of thermal-diffusion coefficient on pressure for the mixture He 68.4%, N_2 31.6%.

The measurements for one separation test were repeated 3–5 times, and the results gave good agreement within the limits of experimental error. The zero was verified by filling A and B with the same mixture, equating pressures as before, and carrying out flow through the capillary. Volumes A and B were then connected again with the micromanometer. If the zero is correct, the drop must then remain motionless, or return to its initial position after some displacement. If it fails to return, the most probable cause is inequality of volumes A and B of the experimental part. To determine the difference in mixture composition of the samples from the drop displacement in the micromanometer, calibration with mixtures of known composition was necessary.

For standardization, mixtures were chosen which were, firstly, close in composition to the original mixture in the thermal-diffusion separating apparatus (it is best to have it as one of the standards), and, secondly, did not differ in composition from one another by more than 2–4%. This was done so that in the region of small changes of concentration of the components of the mixture, the dependence of viscosity on composition could be regarded as linear. We could therefore take the dependence of drop displacement on composition to be linear for small changes of composition.

The dependence of viscosity on mixture component concentration has the form shown in Fig. 2. In very small sections of the curve we may take the dependence of viscosity on composition to be linear. In using this method of determining composition, it is important to have prior knowledge of the position of any extremum on the curves of dependence of viscosity on composition, in order to avoid operating close to it. When data on the dependence of viscosity on mixture composition are not available, the formulas of [10, 11, 12] may prove of great value. When standards have been chosen in accordance with the above considerations, calibration is performed. The standard mixtures are placed in A and B, and then all the operations are carried out in a similar way to that described above.

Before making a determination of the thermal-diffusion coefficients in the experimental apparatus, we carried out control tests to check the possibility of a mixture being separated in the connecting capillaries because of inequality of pressure in vessels I and II when filling A and B, as well as inequality of their diameters. The tests showed that there was no separation.

EXPERIMENTAL RESULTS

The mixture composition was N_2 31.6%, He 68.4%, and the pressures $0.98 \cdot 10^4$; $0.686 \cdot 10^4$; $0.392 \cdot 10^4$; $0.098 \cdot 10^4$; $0.049 \cdot 10^4$ N/m^2. At each pressure 8–12 tests were made, the results of which showed good agreement among themselves and with results obtained on another apparatus for a N_2-He mixture of the same composition. In this apparatus thermistor sensors were used for measuring the separation.

A dependence of the thermal-diffusion coefficient on both mixture composition and pressure was observed. With reduction of pressure from $0.98 \cdot 10^4$ to $0.049 \cdot 10^4$ N/m^2, the coefficient for a N_2 31.6%, He 68.4% mixture decreases from 0.62 to 0.56, i.e., by 10%. The results of the measurements are shown in Fig. 3.

The results will not be discussed in detail, since that is done elsewhere. The main purpose of the present paper was to describe the construction of, and the method of measurement in, the experimental apparatus.

NOTATION

Q) amount of gas flowing through the cross section of the capillary in unit time; l) length of capillary; ξ) slip; β) coefficient of proportionality $\simeq 1$; p_1, p_2) pressures at the ends of the capillary (when the outflow is to a vacuum, this may be taken as $p_1 \simeq 0$); v_m) arithmetic mean velocity of the molecules; Δp) pressure drop; x_1, x_2) molar fractions of components of the mixture; α_T) thermal-diffusion coefficient; Δx) difference in molar fractions of components in the standard mixtures; Δl_t) displacement of the drop in the micromanometer after outflow through the capillary of samples of mixture from the hot and cold ends of the thermal-diffusion separation apparatus; Δl_r) the same for the standard mixtures; T_1 and T_2) temperatures of the hot and cold ends, respectively, of the thermal-diffusion apparatus; η_1 and η_2) viscosity of the gases; ρ_1 and ρ_2) density of the gases; L_m) mean free path of molecules; a) capillary diameter.

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1 February 1965

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