PHYSICOCHEMICAL MEASUREMENTS

MEASURING GAS DIFFUSION COEFFICIENTS BY MEANS OF A CAPILLARY OPEN AT ONE END

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An apparatus and improved diffusion cell are described along with the method of use; the results are compared with published ones.

Gas mutual diffusion coefficients can be determined by many methods (Loschmidt's, the two-bulb one, Frank-Kamenetskii's, by the use of a capillary open at one end, and so on), in which one employs a volume-mean frame of reference. In the method based on a capillary open at one end, one measures the amount of material diffusing from a large volume into a capillary closed at one end in a set time interval, where the diffusion coefficient is measured by means of a device [1] constituting a diffusion tube sealed at one end, while the other end communicates with a large-volume chamber. The volume of the chamber is much greater than that of the capillary, so the concentration change in the volume can be neglected. The diffusion tube is filled with one gas and the chamber with another. After a set time τ, the open end is closed and the gas mixture is sampled. One uses the length L of the diffusion tube, the initial concentration c_c^0, the final concentration of the material c_c^τ diffusing into the tube, and the concentration in the chamber c_0 to derive the diffusion coefficient D from [1]

$$\frac{c_0 - c_c^\tau}{c_0 - c_c^0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left\{ - \left[\frac{\pi(2n+1)}{2} \right]^2 \frac{D\tau}{L^2} \right\} . \tag{1}$$

One employs a gas analyzer that can determine concentrations in small volumes. For example, in [2], the capillary volume was $V = 1.72 \cdot 10^{-8}$ m^3 (L = 22 mm, d = 1 mm) and a mass spectrometer was used for the analysis.

A special device is used to sample the gas mixture from the capillary, which complicates the equipment.

We have improved this method [3] by combining the diffusion cell with the measurement one, which also enables one to examine the diffusion dynamics.

The diffusion cell (Fig. 1) is located in the body of the interferometer 12 (e.g., an ITR-1). It consists of the diffusion capillary 17 and slot channel 19 having connecting tubes 9 and 18. The comparison tube 11 with connecting tube 13 is in parallel with the diffusion capillary.

The diffusion capillary and the comparison tube are closed at one end by the optical plates 15 and 16. The other end of the capillary communicates with the slot channel, while the tube is closed by the optical plate 10. The slot channel has the optical window 8, which is above the ends of the tube and capillary. A constant boundary condition is attained by flushing the open end of the capillary with a gas mixture having a constant composition or with a pure gas.

Before the experiment starts, one needs to set the volume flow rate for the gas flowing above the diffusion capillary and fill the capillary and comparison tube with the gas mixture or pure gas, and also to set the zero reading on the scale.

The pressure cylinder 1 contains one of the gas and operates with the reduction valves 2, ministate 3, buffer vessel 4, rheometer 5, and capillary system 6 to pass a non-pulsating gas flow initially through the stopcock 7 to the atmosphere. The reduction valves and the monostate produce a set flow rate, which is recorded by the rheometer. At the same time, the diffusion capillary and reference tube are evacuated through the stopcock 14 and 20 by a forevacuum pump. As the pumping is continued to a pressure of about 1 mm Hg (133 Pa), the operation should be repeated by filling the diffusion cell and comparison tube

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TABLE 1

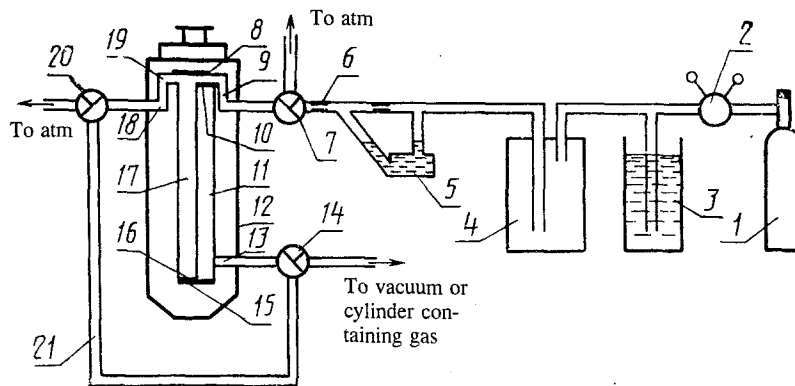| Gas system	Flushing rate, $cm^3 \cdot sec^{-1}$	Regular mode rate, $10^4 \cdot sec^{-1}$	Standard deviation in determining regular mode rate, %	Diffusion coefficient, $cm^2 \cdot sec^{-1}$
He — Ar	2,0	1,992	0,1	0,733
	5,0	1,983	0,4	0,745
	5,0	1,962	0,3	0,738
	10,0	1,982	0,2	0,753
Mean value				0,742 ± 0,007
Published value [7]				0,74
Calculated value				0,72
He — N_2	5,0	1,970	0,3	0,683
	5,0	1,900	0,3	0,678
	10,0	1,923	0,3	0,675
	10,0	1,927	0,3	0,677
	10,0	1,946	0,3	0,681
Mean value				0,679 ± 0,003
Published value [7]				0,695
Calculated value				0,70

Fig. 1. Apparatus containing improved diffusion cell.

with the test gas through stopcock 14 after pumping. This eliminates a correction for the residual part of the gas when one measures the concentration during diffusion. Then one refills the diffusion cell and comparison tube with the test gas to a pressure somewhat above atmospheric to avoid any flow of the other test gas into the diffusion capillary at the start of the diffusion. The stopcock 20 equalizes the pressure in the diffusion capillary and comparison tube to atmospheric. Then stopcock 14 is used to cut off the comparison tube from the diffusion capillary, and one takes the reading from the interferometer compensator scale. This is the initial reading. The test gas passes through stopcock 7 into the slot channel 19 as a non-pulsating flow with a given volume flow rate. When the gas attains the open end of the capillary, the interference pattern begins to shift. That instant is recorded as the start of the diffusion.

The concentration averaged along the diffusion cell was measured with an ITR-1 interferometer as follows. A set value of the optical path length is set on the compensator scale for the rays passing through the diffusion cells, comparison tube, and compensator. When the optical paths are equal for the rays passing through the test gas and the compensation system, the moving interference pattern coincides with the fixed one. This instant is recorded by a timer. Then another value for the optical path difference is set, and the time is recorded when the interference patterns coincide again. One can make from 10 to 50 readings in a single experiment. The mean concentration $\bar{c}$ is plotted against τ in semilogarithmic coordinates. Figure 2 shows a form of this dependence. In the initial stage, $\bar{c}$ varies rapidly (part 1 in Fig. 2), which is followed by slower change (part 2). Subsequently, i.e., at longer times (part 3), the logarithm of the concentration varies linearly:
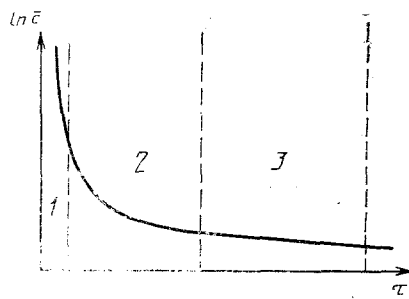
$$\ln \bar{c} = f(\tau). \tag{2}$$

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Fig. 2. The τ dependence of the mean
concentration.

The (1) series converges rapidly, and if the Fourier diffusion coefficient $F_{oD} < 0.25$, one can neglect all the terms in the series apart from the first. The regular diffusion state sets in form that instant [4], in which the mutual-diffusion coefficient is proportional to the regular-mode rate m, which is equal to the slope of the rectilinear part of the relationship [2]:

$$D = Km. \tag{3}$$

The coefficient K in (3) is dependent on the geometrical parameters and the diffusion-cell shape. For a one-dimensional cells, $K = 4L^2/\pi^2$.

The improved diffusion cell was tested with the above equipment in an ITR-1 interferometer. The measurement tube in the interferometer was replaced by the diffusion cell, with one of the interfering rays passing along it. This was made as a brass tube 100.0 cm long with interval diameter 8.0 mm. The open end of the tube was located in the slot channel, while the other end was closed by an optical plate cemented to the tube. The slot channel was of rectangular cross section, h = 3.0 mm and b = 10.0 mm, and was made of dural. The sealing of the diffusion cell was checked from the pressure change in it over several days after evacuation by the forevacuum pump. The air leak was not more than 10 mm Hg (1.3 kPa) per day, which could be neglected. The diffusion cell with slot channel and comparison tube was placed in the interferometer body, in which the necessary holes had been made for the gas pipes. The interferometer was used in the vertical position, which is not always convenient. It can be placed in an inclined position, but the inclination should not be such that ordinary gas displacement occurs. Then the capillary was filled with the heavier gas, the open end was flished with the light gas and was at the top. When the capillary contained a light gas, the open end was at the bottom. The diffusion capillary and comparison tube were placed in a cylindrical water jacket, which received water from a U-1 thermostat.

We used flow rates in the range 2.0-10.0 $cm^3 \cdot sec^{-1}$ to examine the effects of the flushing rate at the open end of the capillary on the result for the diffusion coefficient, and it was found that the flushing rate did not affect the latter.

To calculate the diffusion coefficients from the formulas for methods in which the gas is diffused through the capillary (tube), a correction was applied for the finite gas propagation rate in the volume whence it was diffusing. The effective length exceeds the geometrical length by about 0.8 of the diameter [5]. When the open end is flushed to produce a set boundary condition, there is entrainment of the material in the capillary, which reduces the diffusion path below the geometrical one. Cinematographic study has shown [6] that the entrainment is dependent in a complicated way on the Reynolds number. These corrections are opposite in sign, but it was not always possible to cause them to balance under certain conditions. In our case, the first correction was 0.67% and the mean value of the second was 0.32%. These corrections are of the same order but different signs, so they were neglected and the geometrical length of the diffusion tube was used in (3).

We used this apparatus to measure mutual diffusion coefficients for helium—argon and helium—nitrogen mixtures, for which there are non-conflicting data in the reference literature [7]. Table 1 gives the measurements. The diffusion coefficients have been referred to normal pressure. The regular-mode rate was calculated from the points on the (2) rectilinear relationship derived by least-square fitting. Table 1 also gives the values calculated for the Lennard—Jones potential from the Chapman—Enskog formula. The necessary quantities were taken from [8].

The error in the result was examined in the usual way [8], which showed that it did not exceed 1.2% for 0.95 fiducial probability. It follows from (3) that the error in the diffusion coefficient is dependent on the error in determining the regular-mode rate since the error in the form coefficient can be neglected ($\delta K \approx 10^{-2}\%$). The standard deviation in determining the regular-mode rate was about $10^{-1}\%$. The error in the position of the experimental point was governed by the errors in measuring the concentration and time. Error in determining the instant when diffusion starts does not influence the slope, since

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time shift produces a parallel displacement of part 2 of the curve (Fig. 2), so that error can be neglected. The error in measuring the concentration with the interferometer is usually small and is depended on the concentration itself. The concentration range for the rectilinear part is about 30% (from 40 to 10%), and the relative error in that case varied from 0.7 to 1.3%. This error explains the discrepancies of over 1.2% between the diffusion coefficients in the different measurements.

It is quite possible to reduce the error in measuring the concentration by using another type of interferometer or a laser source, which enables one to obtain an error in measuring the diffusion coefficient of less than a percent.
of less than a percent.

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