226. *The Diffusion Coefficient of Methane and Air.*

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As no measurement of the coefficient of inter-diffusion between methane and air appears to have been recorded, and as it is not possible to deduce a reliable figure from other data, the results of some experiments on this subject are now presented.

The method used was essentially that of Loschmidt (*Sitzungsber. Akad. Wiss.*, 1870, **61**, 367). A vertical tube, closed at the ends, was divided horizontally into two halves which could be put into communication or separated as desired. Two gases were allowed to diffuse for a definite period, and the contents of the two halves of the tube were then separated and analysed. On the assumption of Fick's (second) law of diffusion, $\partial c_1/\partial t = D\partial^2 c_1/\partial x^2$, the diffusion coefficient D was calculated from the equation

$$\frac{u - o}{u + o} = \frac{8}{\pi^2}\left(e^{-\pi^2 Dt/L^2} + \frac{1}{9}e^{-9\pi^2 Dt/L^2} + \frac{1}{25}e^{-25\pi^2 Dt/L^2} + \ldots\right) \quad . \quad . \quad (1)$$

in which u and o are the percentages of the heavier gas in the contents of the lower and the upper half of the tube, respectively, L is the length of the tube, and t the time of diffusion. McKay (*Proc. Physical Soc.*, 1930, **42**, 552) gives a table which facilitates the calculation of D.

EXPERIMENTAL.

Apparatus.—The diffusion tube was made, like that of Schmidt (*Ann. Physik*, 1904, **14**, 801), from two smoothly polished rifle-barrel tubes (D, K, Fig. 1). One end of each was threaded eccentrically into a wide circular flange, the other was closed by a flat cap. The flange of the lower tube was supported by the ring of a tripod that was fastened to the floor of the laboratory. The flange of the upper tube rested on that of the lower and could be rotated, by the aid of a handle H, in an orbit accurately defined by a guard ring, J. This sliding joint is simpler than the wide-bore stop-cock used by Schmidt as an improvement on Loschmidt's sliding shutter. Moreover, it avoids the use of conical surfaces which, if they become worn, may either allow the plug of the tap to enter too far and thus destroy the symmetry of the diffusion space, or, if this be prevented, offer the possibility of leakage. A tapered pin, G, drops through the upper flange and engages the lower when the tubes are accurately in line.

The sliding joint was lightly smeared with a rubber lubricant. We were unable to prevent the intrusion of a small amount of lubricant from the joint into the diffusion space. It was distributed as a thin film when the tube was filled by mercury, and when the tube was opened a few globules of mercury were found clinging to its wall. The maximum amount of mercury thus found was 0·06 c.c. and the amount of grease was very small. It seems improbable that an appreciable error could be introduced by these.

The cap L was drilled and fitted, flush with its inner surface, with one limb of a fine capillary glass tap, N, which led to a reservoir of mercury, M. The cap, C, was fitted in the same way with a 3-way fine capillary tap, B, leading to a supply of methane, to a manometer and "Hyvac" pump, to the atmosphere, and to a gas sampler, A (Fig. 2). A two-way capillary tap, F, was fitted through the flange of the upper tube and could be brought in connexion with the lower tube by suitable rotation of the sliding joint. One of its branches led to a gas sampler, *E*, the other to a U-tube containing soda-lime and calcium chloride through which air could be drawn. The thick rubber tube connexions of the taps *B* and *F* allowed the tube *D* to be rotated.

The relevant dimensions of the apparatus were : Lengths of the lower and the upper tube, 529·4 and 528·5 mm. respectively. Volumes, 38·37 and 38·10 c.c. Mean internal diameters, 9·60 and 9·58 mm. Thickness of wall, 8·2 mm. The volume of the capillary glass tubing between steel tube and glass tap, 0·008 c.c. in both instances, was negligible.

The temperature of the diffusing gases was controlled by surrounding the diffusion tubes with Bell's asbestos "Viceroy" sectional pipe covering and by packing the ends and the middle flanges of the tubes with cotton-wool. The temperature recorded by thermometers embedded in the asbestos was found to remain constant within 0·3° during each experiment.

FIG. 1.

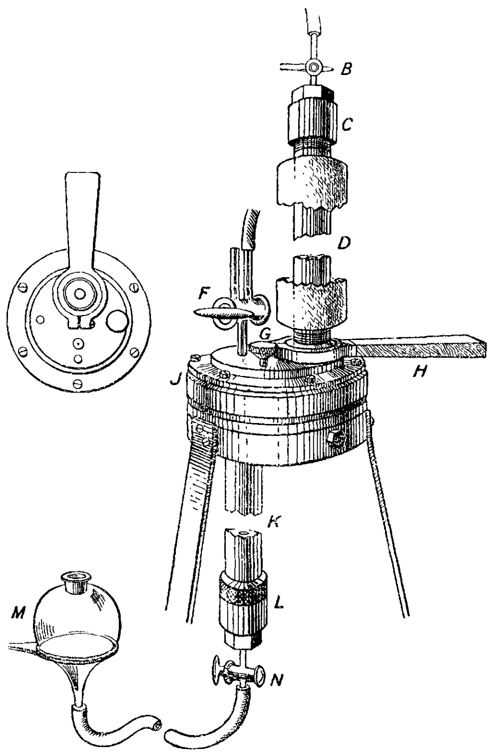
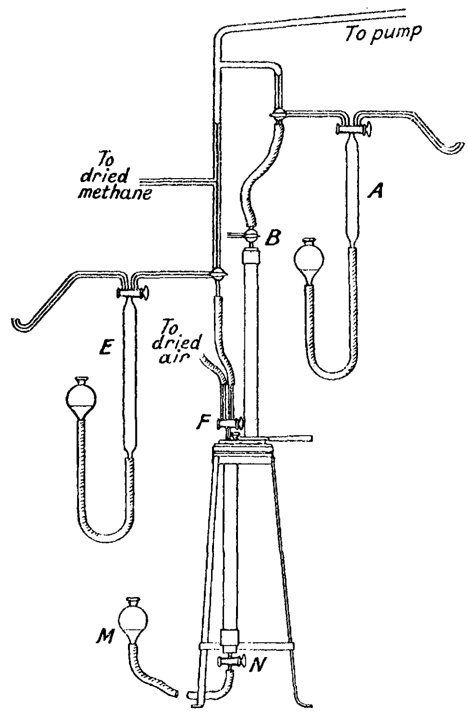


FIG. 2.



Gases.—The methane used was prepared from a good sample (94% pure) of fire-damp, twice liquefied and distilled, the first and last thirds of the distillate being rejected each time. The product was indistinguishable from pure methane by analysis in a Bone and Wheeler apparatus. The air used was drawn slowly over soda-lime and calcium chloride.

Method of Experiment.—At the beginning of each experiment the two halves of the diffusion tube were put in connexion and the air in them was displaced, through *B*, by mercury from *M*. Meanwhile the system between the methane holder and the diffusion tube was evacuated and then filled to the taps *B* and *F* with methane. By suitable manipulation of *M* and *B*, *D* was flushed with methane and finally filled with that gas at slightly more than atmospheric pressure. The two halves of the diffusion tube were then disconnected. The lower half was well flushed and finally filled with air, the mercury being left at a point just above the barrel of the tap *N*, which was then closed. The gases in *D* and *K* were brought to atmospheric pressure by momentarily opening the taps *B* and *F* to the air.

The interdiffusion of the gases was started by turning the upper tube until the pin *G* fell and locked the tubes in line. During each experiment the temperatures of thermometers embedded in the asbestos were read at intervals, and the barometer reading was taken. Just before the end of the diffusion period the branches of the apparatus were evacuated, tap F being turned so that the capillary space between it and the sliding joint was also evacuated. Tap F was then shut and, at a definite moment, the diffusion was stopped by turning the upper tube out of line with the lower. The apparatus was allowed to stand overnight to permit the contents of the two halves of the tube to become homogeneous. Samples were then withdrawn by means of A and E, and analysed.

According to Fick's law, which is true or nearly so for all gases with which it has been tested, the diffusion coefficient is independent of time. Hence for these experiments a period of diffusion was chosen (about one hour) in which the errors of experiment would least affect the results.

The apparatus was tested at intervals for leakage, but none was detected, either between the halves of the diffusion tube when fully turned out of line or between the tube and the atmosphere.

Results.

As a preliminary check, the diffusion coefficient of carbon dioxide and air was determined. The value found was 0·139 ± 0·003 cm.²/sec., corrected to 0° and 760 mm. pressure, in comparison with previous determinations ranging from 0·130 to 0·142 cm.²/sec.

The measurements for the diffusion of methane and air are given in the table; u and o have virtually the same significance as on p. 1085, but actually they refer to the methane found in the

Duration of expt., mins.	u.	o.	$u + o$.	Temp.	Press., mm. Hg.	D.	$D_{0°,760}$. $m = 2$.	$m = 1·75$.
60	70·6	29·8	100·4	16·8°	750	0·218	0·191	0·194
60	70·0	30·0	100·0	18·7	749	0·222	0·192	0·195
60	70·5	29·5	100·0	18·3	754	0·215	0·187	0·190
60	70·3	29·9	100·2	16·9	753	0·220	0·193	0·196
60	69·8	30·1	99·9	15·8	756	0·225	0·200	0·203
60	70·1	29·5	99·6	15·8	759	0·216	0·193	0·195
60	69·9	30·0	99·9	17·6	763	0·223	0·198	0·201
60	69·7	29·9	99·6	18·1	761	0·222	0·196	0·199
63	69·4	30·6	100·0	17·0	760	0·221	0·196	0·199
61	69·5	30·3	99·8	17·2	760	0·225	0·199	0·202
60	70·0	30·0	100·0	18·6	751	0·222	0·192	0·196
60	69·7	30·2	99·9	17·5	749	0·226	0·197	0·200
60	69·5	30·3	99·8	19·5	755	0·228	0·197	0·201
60	70·0	30·2	100·2	21·3	763	0·225	0·195	0·198
60	69·5	30·5	100·0	21·6	763	0·230	0·198	0·202
60	69·7	30·2	99·9	20·6	763	0·226	0·196	0·200
60	70·1	30·0	100·1	19·2	765	0·222	0·195	0·198

upper and in the lower half of the tube at the end of the experiment. The values of $u + o$ serve to check the tightness of the apparatus against diffusion from the outer air; they show that rarely, if ever, was error introduced by leakage to the outer air while the contents of the separated halves of the tube stood overnight before they were removed; for the analytical error in $u + o$ may approach 0·4. As the lower half of the tube was about 0·7% larger than the upper, the actual value of $u + o$ in these experiments would be $100 - 0·7 \times 0·30 = 99·8$.

The values of D may be reduced to a common temperature and pressure by means of the equation $D_{0°, 760} = D_{t,p}(p/760)(273/T)^m$. The value of m is unknown, but for other pairs of gases it lies between 2·00 and 1·75. The values of $D_{0°, 760}$ are tabulated for each of these values of m. Their means, which are 0·195 and 0·198 respectively, do not differ enough, in view of the experimental errors, to warrant a determination of m for the sake of the reduction of D to 0°. The true value of $D_{0°, 760}$ is probably close to 0·196 cm.²/sec.

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