LEAKAGE OF GASES THROUGH QUARTZ TUBES.

By E. C. Mayer.

Historical.

Besides the work which has been undertaken on the investigation of the flow of gases through quartz and glass, a considerable amount of attention has been given to the determination of the absorption and diffusion of gases through metals, principally iron, palladium and platinum. Among the most important work on metals may be mentioned that of Lockyer,[1] Travers,[2] Ramsay and Travers,[3] Winkelmann,[4] Graham,[5] Beetz,[6] Hoitsema,[7] Schmidt,[8] Richardson, Nicol, and Parnell,[9] Richardson,[10] and Dorn.[11] The gases investigated included hydrogen, helium, and argon.

That quartz is permeable to gases has been found by Villard,[12] Jaquerod and Perrot,[13] and Richardson and Ditto.[14]

Object.

The purpose of the present investigation was to determine the leakage of hydrogen, nitrogen and oxygen through a quartz tube, and to see whether there existed any relation between the amount of leakage and the pressure and temperature of the gas.

Apparatus.

The apparatus employed is shown in Fig. 1. The manometer consists of the long glass tube *ABCDE* joined to the cylindrical reservoir *GH* by

[1] J. N. Lockyer, Proc. Roy. Soc., 1895, vol. 58, p. 193.

[2] M. W. Travers, Proc. Roy. Soc., 1896, vol. 60, p. 449.

[3] Ramsay and Travers, Proc. Roy. Soc., 1897, vol. 61, p. 267.

[4] A. Winkelmann, Ann. d. Physik, 1901, vol. 311, p. 104; 1902, vol. 313, p. 388; 1905, vol. 321, p. 773; 1906, vol. 324, p. 1045.

[5] T. Graham, Pogg. Ann., 1869, vol. 136, p. 317; 1866, vol. 129, p. 580; 1866, vol. 129, p. 602.

[6] W. Beetz, Sitzungsber. der Bayer. Akad., 1878, p. 157.

[7] C. Hoitsema, Zeitschr. f. physik. Chem., 1895, vol. 17, p. 40.

[8] G. N. St. Schmidt, Ann. d. Physik, 1904, vol. 318, p. 747.

[9] Richardson, Nicol, and Parnell, Phil. Mag., 1904, vol. 8, pp. 1–29.

[10] O. W. Richardson, Cambridge Phil. Soc. Proc., 1905, vol. 13, p. 27.

[11] E. Dorn, Phys. Zeitschr., 1906, vol. 7, p. 312.

[12] P. Villard, Comptes Rendus, 1900, vol. 130, p. 1752.

[13] Jaquerod and Perrot, Archives des Sciences, 1904, vol. 18, p. 613; 1905, vol. 20, p. 454.

[14] Richardson and Ditto, Phil. Mag., 1911, vol. 22, p. 704.

means of black pressure tubing *FG*. *F* is a one-way stopcock. *DE* is inclined to the horizontal in the manner shown so that small differences of pressure are easily detected. A difference of pressure of 1 cm. of the gas under consideration is accompanied by a movement of the mercury in *DE* of 2.99 cm.

The eudiometer consists of a glass tube *JK* calibrated in grams of water correct at 15° C. This is joined to a tube *LM* at *L*. *R* and *N* are one-way stopcocks. *Q* is a mercury reservoir, joined to the eudiometer by means of the black pressure tubing *NP*.

Heating was obtained by means of an electric furnace. Temperature

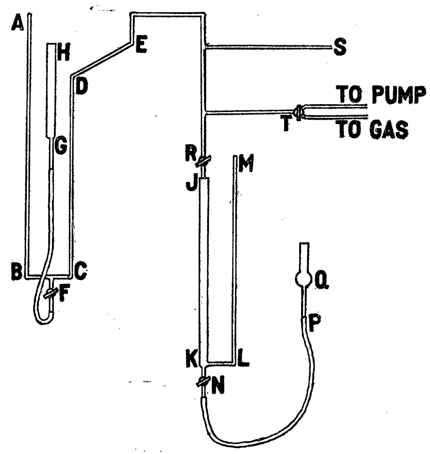

Fig. 1.

was measured by a Paul unipivot pyrometer. Specimens of Jena glass and quartz were joined to the main apparatus at *S*. The specimen of transparent quartz was 16.5 cm. long, 1.9 cm. internal diameter, 0.05 cm. wall thickness. The Jena glass specimens were of approximately the same dimensions except that they had a wall thickness of 0.18 cm.

Procedure.

The following procedure was adopted when it was desired to take a determination with the gas under atmospheric pressure. Connecting to the pump by means of stopcock *T*, the entire apparatus was exhausted; then turning *T* to the next position, gas was introduced. This was repeated twice so that the apparatus should be well washed with the gas. *R* was then closed and the gas trapped in the eudiometer could be placed under any pressure desirable by raising or lowering *Q*. This entire procedure was done only after the furnace had been maintained steadily at the desired temperature for at least one hour. The gas passed through a calcium chloride drier before entering the apparatus. Cock *T* was now closed. *GH* was raised so that the mercury stood somewhere in the upper part of *AB* and in the lower part of *DE* (at somewhat lower level than mercury in *AB*). *F* was then closed. By referring to a calibration curve, an amount that *GH* should be raised was noted, so that after having raised *GH* this amount, and then opened *F*, mercury in *DE* would rise to same level as mercury in *AB*. If mercury would not rise all the way to this level, *R* was opened until sufficient gas had passed from main apparatus into eudiometer, and mercury in *DE* did come to this level. *R* was then closed. Mercury in *AB*, *GH* and *DE* would then be at the same level, and gas in apparatus would be under atmospheric pressure. Cock *F* was now closed, to remain closed throughout the determination.

The procedure was entirely analogous if the gas was to be under an initial pressure greater or less than one atmosphere.

If gas escaped by absorption or diffusion through the specimen, mercury in *DE* rose. Such movements were read to an accuracy of 0.1 cm. and estimated to 0.01 cm. Readings were reduced to 76 cm. pressure and 15° C.

Theory.

Before discussing the data, it seems desirable to determine what results one may be led to expect from a theoretical consideration of the flow of gas in one direction, assuming an infinite solid (see Fig. 2) with two parallel plane faces whose distance apart is c. It may be shown that a small increment of gas dm flowing through a slab of thickness dx in a time dt is given by

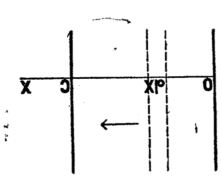

Fig. 2.

$$dm = -a^2 q \frac{\partial u}{\partial x} dt, \qquad (1)$$

where q is the cross-section of the slab, $\partial u/\partial x$ the pressure gradient, a^2 the constant of flow. a^2 is the quantity of gas traversing unit area of the slab in unit time when the pressure gradient is unity.

Let the origin be in one face and the axis of X perpendicular thereto. Consider the initial pressure in the solid any function of x and suppose the pressure of the left-hand face of the solid is a constant β, and the right-hand face at zero pressure; we must solve the equation

$$\frac{\partial u}{\partial t} = a^2 \frac{\partial^2 u}{\partial x^2}. \qquad (2)$$

We find[1]

$$\mu = \frac{2}{c}\sum_{m=1}^{m=\infty}\left[\epsilon^{-\frac{a^2m^2\pi^2}{c^2}t}\sin\frac{m\pi}{c}x\int_0^c f(x)\sin\frac{m\pi}{c}x\,dx\right] + \beta\left[\frac{c-x}{c} - \frac{2}{\pi}\sum_{m=1}^{m=\infty}\frac{1}{m}\epsilon^{-\frac{a^2m^2\pi^2}{c^2}t}\sin\frac{m\pi x}{c}\right] \tag{3}$$

as our required solution.

Since $u = f(x)$ when $t = 0$, if $u = 0$ when $t = 0$, $f(x) = 0$ when $t = 0$.

Differentiating[2] u with respect to x and integrating[3] with respect to t between the limits $t = 0$ and $t = T$, we obtain

$$M = a^2q\frac{\beta}{c}T - \frac{2\beta qc}{\pi^2}\left[\left(\sum_{m=1}^{m=\infty}\frac{1}{m^2}\epsilon^{-\frac{a^2m^2\pi^2}{c^2}T}\right) - \frac{\pi^2}{6}\right], \tag{4}$$

where M is the total mass of gas which has passed in a time T through the left-hand face of the solid.

If $f(x)$ is not zero when $t = 0$, but if $f(x) = b$, constant, then it may be shown that M becomes

$$M = a^2q\frac{\beta}{c}T - \frac{2\beta qc}{\pi^2}\left[\left(\sum_{m=1}^{m=\infty}\frac{1}{m^2}\epsilon^{-a^2\frac{m^2\pi^2}{c^2}T}\right) - \frac{\pi^2}{6}\right] + \frac{4bqc}{\pi^2}\left[\left(\sum_{m=1}^{m=1,3,5\ldots}\frac{1}{m^2}\epsilon^{-a^2\frac{m^2\pi^2}{c^2}T}\right) - \frac{\pi^2}{8}\right]. \tag{5}$$

If $u = \beta$ when $x = 0$, $u = \gamma$ when $x = c$, and if $u = f(x) = b$, constant, when $t = 0$, M becomes

$$M = a^2q\frac{(\beta-\gamma)}{c}T - \frac{2(\beta-\gamma)}{\pi^2}qc\sum_{m=1}^{m=\infty}\left[\frac{(-1)^m}{m^2}\epsilon^{-a^2\frac{m^2\pi^2}{c^2}T} + \frac{\pi^2}{12}\right] - \frac{4(\beta-b)}{\pi^2}qc\sum_{m=1}^{m=1,3,5\ldots}\left[\frac{1}{m^2}\epsilon^{-a^2\frac{m^2\pi^2}{c^2}T} - \frac{\pi^2}{8}\right]. \tag{6}$$

RESULTS.

In the experiments with Jena glass, there were no indications of leakage. It was impossible to use higher temperatures than 800° C. as the Jena glass became too soft. Also at the higher temperatures it was not feasible to use pressures much lower or higher than one atmosphere because of the softness of the glass. From the results it seems probable that Jena glass is not permeable to the common gases at moderately high temperatures.

[1] W. E. Byerly, Fourier's Series and Spherical Harmonics, 1893, pp. 38, 105.

[2] Byerly, p. 68. E. Goursat and E. R. Hedrick, Mathematical Analysis, 1904, vol. 1, p. 365. H. S. Carslaw, Fourier's Series and Integrals, 1906, pp. 55, 62.

[3] Goursat and Hedrick, p. 364.

A series of determinations at atmospheric pressure and room temperature were taken to see whether hydrogen or oxygen leak through quartz with the result that no leakage was found.

The results for hydrogen at temperatures 330°, 430°, 550°, and 710° C. are shown by the curves, Figs. 3 to 6. Time in minutes is plotted as

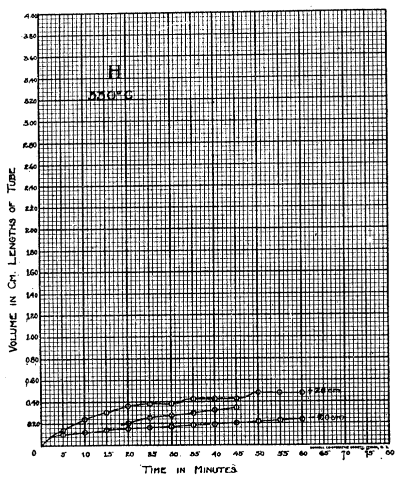

Fig. 3.

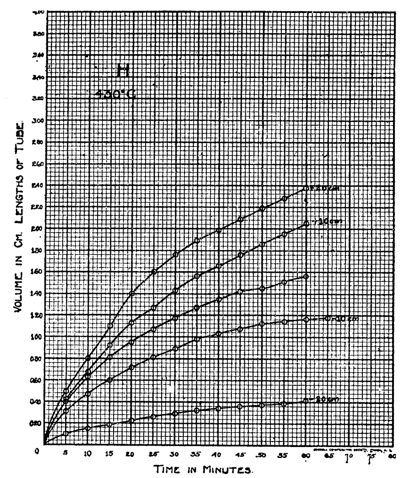

Fig. 4.

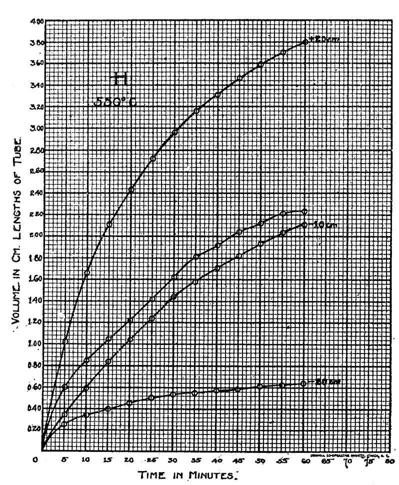

Fig. 5.

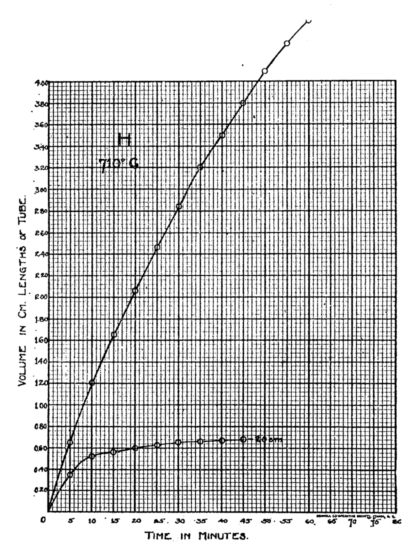

Fig. 6.

abscissas and volume of leakage reduced to 15° C. and 76 cm., in centimeter lengths of the tube *DE* as ordinates. The pressures used were

20 cm. above atmospheric pressure, 10 cm. above, atmospheric pressure, 10 cm. below, and 20 cm. below. Curves are designated to show under what pressure they were obtained. Determinations were taken for one hour.

One centimeter length of the tube *DE* corresponds to a volume of 0.217 cu. cm.

From an inspection of the curves, it is seen that temperature remaining constant, leakage increases with an increase in pressure. Furthermore it appears that the gas leaks more rapidly at the beginning of a determination than later. With the apparatus in the present work it is impossible to distinguish between the loss of gas by diffusion and by absorption by the walls of the specimen. However it is believed that the loss by absorption had been reduced to a minimum as the specimen was always maintained at the desired temperature for at least one hour before readings were taken, and furthermore the apparatus was washed with the gas twice immediately before the final gas was introduced for experimentation.

If curves are plotted to show the leakage of hydrogen under like conditions of pressure, it will be noted that the leakage increases with temperature, the increase being considerably more marked at the higher pressure.

The results for oxygen at temperatures 280°, 420°, 550° and 690° C. are shown by curves, Figs. 7 to 10.

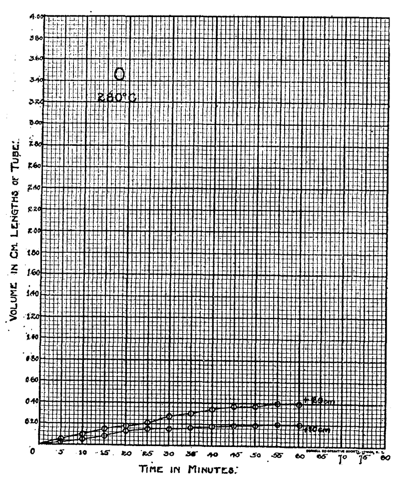

Fig. 7.

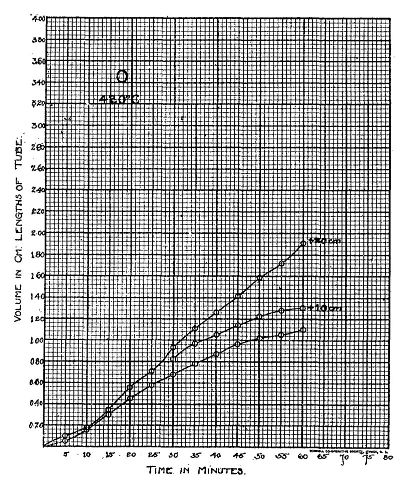

Fig. 8.

Among the curves no data are given corresponding to pressures smaller than one atmosphere. Under these conditions not a single trace of leakage of oxygen was detected.

The data for oxygen, like that for hydrogen, show an increase in leakage with increase in pressure at constant temperature, and a greater leakage with increase in temperature, pressure remaining constant.

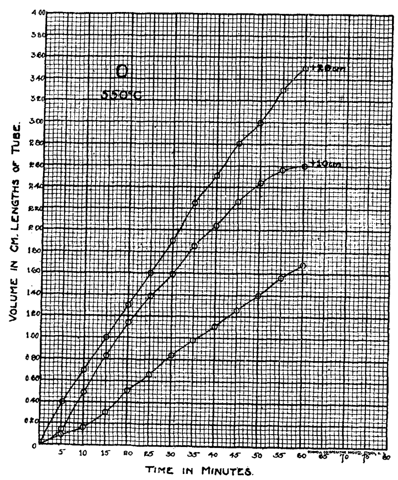

Fig. 9.

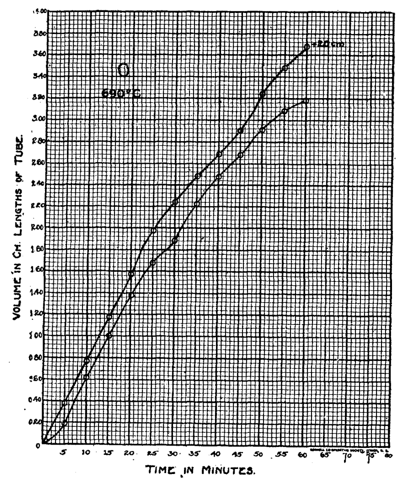

Fig. 10.

The data for nitrogen for temperature 430°, 550° and 700° C. are plotted in Figs. 11 to 13. No leakage of the gas was detected at the lowest temperature of about 300° C. as in the case of hydrogen and oxygen, nor was there any indication of leakage corresponding to a pressure lower than one atmosphere. Here again, at constant tempera-

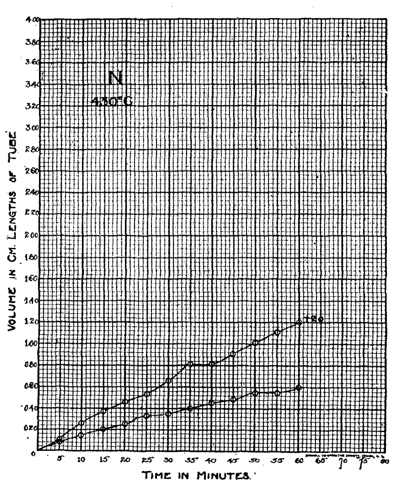

Fig. 11.

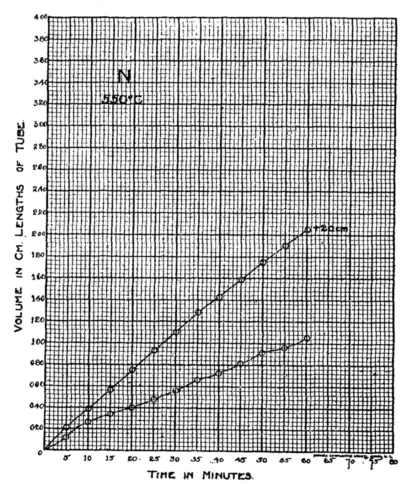

Fig. 12.

ture, leakage increase with an increase of pressure, and at constant pressure, leakage increases with an increase in temperature.

Curves, of which Fig. 14 is an example, are interesting, as they show the relative leakage of hydrogen, oxygen and nitrogen under like conditions of pressure and approximately like conditions of temperature. In every instance, it is seen that hydrogen leaks most rapidly, and nitrogen least rapidly.

The theoretical treatment outlined above furnishes equations (4),

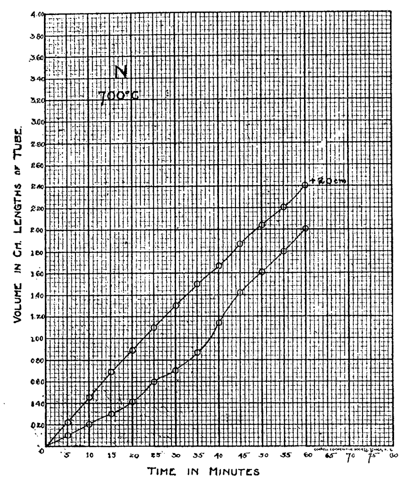

Fig. 13.

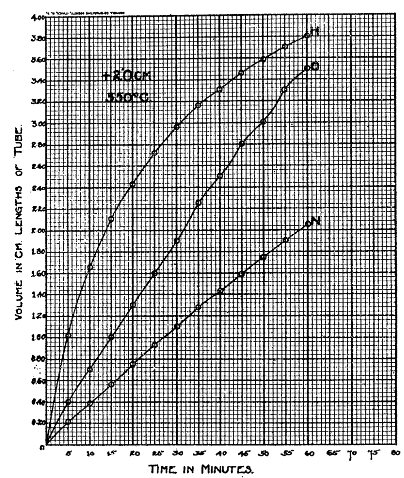

Fig. 14.

(5) and (6), by means of which it is possible to check the experimental data. In the case of hydrogen leaking into the atmosphere, if $b = 0$, equation (4) may be applied.

By equation (4) and the leakage for hydrogen at one atmosphere, 430° C., and after 60 minutes, an approximate value (0.000003474) of a^2 was computed and this used to calculate data for curves for hydrogen at 430° C. The first four terms only of the infinite series in equation (4) were taken. M was expressed in centimeter lengths of the tube DE (see Fig. 1), q in square centimeters, β in meters of mercury and T in minutes.

A comparison of the curves so determined with those obtained experimentally does not indicate a close agreement, particularly for a pressure 20 centimeters below atmospheric.

If $b = \gamma =$ constant, the curves computed on basis on equations (4) and (6) will be similar.

If b constant (to be determined from data as stated below), and $\gamma = 0$, equation (5) may be applied. Now if curves be drawn showing the relation between the quantity of hydrogen leaking at 430° C. (for example, in equal time), and the pressure, the positive X-intercept indicates that under a pressure represented by this intercept, hydrogen does not leak, irrespective of the time. If b is taken equal to 25 centimeters (the average positive X-intercept) and an approximate value (0.00000917) of a^2 is computed, and curves plotted from calculations by means of equation (5), these curves again do not check with those found experimentally, the largest deviation occurring for a pressure of 56 centimeters.

However it appears hardly probable that hydrogen exerting a definite pressure b exists in the interstices of the quartz as would be assumed by the theory summed up in equation (5). If quartz does contain occluded hydrogen, it seems reasonable to assert that this gas is in equilibrium and forms, as it were, a constituent part of the quartz itself. So that of the two ideas proposed, the one based on equation (4) appears the more likely. Inasmuch as this does not explain the results adequately, we cannot offer any positive explanation of the leakage of hydrogen through quartz. Possibly some other theory may be more applicable. The experimental results for oxygen and nitrogen seem to differ even more widely from the corresponding results obtained by theory.

Summary and Conclusion.

A quartz tube of the transparent variety was found to be pervious to hydrogen at temperatures ranging from 330° C. to 710° C., and at pressures varying from 20 cm. mercury below to 20 cm. mercury above atmospheric pressure. In the case of oxygen and nitrogen, no leakage could be detected for pressures less than one atmosphere. Nitrogen did not seem to escape until a temperature of about 430° C. was obtained. At constant temperature, the results for all gases showed considerable increase in leakage with increasing pressures. Under approximately like conditions, hydrogen leaks most rapidly and nitrogen least rapidly.

The results may possibly be explained by assuming that if the quartz contains occluded gas, that this gas is in equilibrium and forms a constituent part of the quartz itself. It is reasonable to believe that this occluded gas does not effect the process of diffusion in any other manner.

The writer wishes to acknowledge his indebtedness to Prof. J. S. Shearer, at whose suggestion the work was begun, and particularly to Prof. E. G. Merritt, who has aided and encouraged the work in every possible way. Valuable assistance has been received from Dr. R. P. Anderson, Dr. E. H. Kennard and Prof. F. R. Sharpe.