

electrodes. However, the mercury, mercuric oxide, calcium hydroxide electrodes compared very favorably in speed of reaching equilibrium and in constancy with those containing barium hydroxide. It may be seen from the table that the maximum deviations between the electrodes read at the various temperatures is considerably greater than with the barium hydroxide half-cells, reaching a maximum of about two millivolts. This was the usual situation with these half-cells. A number of electrodes were made up using ordinary materials, "technical" calcium oxide, ordinary c. p. red and yellow mercuric oxide, etc., and these were found to give potentials usually well within ± 0.002 volt of the above value.

Summary

1. The electrode $\text{Hg}/\text{HgO}(\text{s}), \text{Ba}(\text{OH})_2(\text{s})$ has been studied from the standpoints of ease of prepa-

ration, constancy, reproducibility and effect of temperature change.

2. The potential of the electrode including a liquid junction, compared to the hydrogen electrode at zero is $+0.1462 - 0.00060(t - 25^\circ) \pm 0.0002$ volt.

3. Likewise the potential of the electrode using ordinary materials is $\pm 0.1462 - 0.00060(t - 25^\circ) \pm 0.001$ volt.

4. The electrode using ordinary materials is very satisfactory for ordinary work.

5. The electrode $\text{Hg}/\text{HgO}(\text{s}), \text{Ca}(\text{OH})_2(\text{s})$ has been studied from the standpoint of ease of preparation, constancy, reproducibility and temperature coefficient.

6. The potential of the electrode against the normal hydrogen electrode is $+0.1923 + 0.00010(t - 25^\circ) \pm 0.0010$ volt.

LINCOLN, NEBRASKA

RECEIVED JULY 29, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, UNIVERSITY OF TORONTO]

The Diffusion of Helium through Fused Silica

BY E. O. BRAATEN AND G. F. CLARK

Introduction

It has been established by many observers¹ that the lighter gases can diffuse readily through fused silica. Over a wide range of temperatures and pressures it has been found that the rate of diffusion is proportional to the pressure, and that the diffusion process has a temperature coefficient expressed by an exponential relation (equation 1). Most of the results have been obtained at high temperatures where rates of diffusion are larger and experimental procedure less tedious. Sufficient data are not yet available at the lower temperatures to permit of construction of a theory valid over the whole temperature range where diffusion occurs.

Theory

It has been shown that when the Lennard-Jones² theory for diffusion is applied to systems of inert

(1) P. Villard, *Compt. rend.*, **130**, 1752 (1900); A. Jacquero and F. L. Perrot, *ibid.*, **139**, 789 (1905); E. C. Mayer, *Phys. Rev.*, **6**, 283 (1915); G. A. Williams and J. B. Ferguson, *THIS JOURNAL*, **44**, 2160 (1922); Johnson and Burt, *J. Opt. Soc. Am.*, **6**, 734 (1922); Steacie and Johnson, *Proc. Roy. Soc. (London)*, **117A**, 662 (1927); J. W. McBain, "The Sorption of Gases by Solids," Geo. Routledge & Sons, Ltd., London, 1932, where a complete bibliography is given up to the date of publication; *Trans. Faraday Soc.*, "A General Discussion on the Adsorption of Gases by Solids," 1932.

(2) J. E. Lennard-Jones, *Trans. Faraday Soc.*, **28**, 333 (1928).

gases in silica the resulting equations do not fit experimental results. It appears, therefore, that the diffusion of monatomic gases through silica does not involve the mechanism of surface adsorption followed by subsequent diffusion. An extension of the theory was made by Alty,³ who postulated that the gas enters the solid directly from the gas phase after which it penetrates the solid in the manner described by Lennard-Jones. Before the gas can enter the cracks in the solid it must have an energy, W_0 , sufficient to overcome a potential barrier composed of two overlapping fields at the entrance to each pore, a comparatively small energy E_0 being also required for the atom to diffuse along the cracks.

The diffusion equation which Alty derived is

$$M = Bp e^{-(W_0 + E_0)/kT} \quad (1)$$

where $E_0 \ll kT$, p is the pressure, M is the mass flowing through the solid per unit time, k is Boltzmann's constant, B is a constant, and T the absolute temperature. Equation (1) is found to be valid for temperatures above 200° , but below this temperature the rates are higher than would be expected according to the equation. Barrer⁴

(3) T. Alty, *Phil. Mag.*, **15**, 1035 (1933).

(4) R. M. Barrer, *J. Chem. Soc.*, 376 (1934).

has shown that one may expect a decrease in energy of activation E_0 below 200° , this decrease being attributed to the formation of a new surface phase removable by treatment of the surface with hydrofluoric acid.

Experimental

Two different types of apparatus were used. The first arrangement, Fig. 1a, consisted of two tubes, the inner one of fused silica and the outer of soft glass, held together by means of a waxed ground joint. The capillary neck between the silica bulb and the ground joint prevented any appreciable error in the measurements if the top part of the system should be at a slightly lower temperature than the bulb itself. (This error would, in any case, be small between the temperatures 25 and 130° .) The second apparatus, Fig. 1b, was designed to work over all ranges of temperature. It consisted of a silica bulb attached to a Pyrex bulb by means of a graded seal which permitted the complete submersion of the bulb in the heating bath.

In the first apparatus bulbs of thicknesses 1.8, 1.0 and 0.5 mm. were used. They were made from the same sample of clear fused silica of good quality.⁵ A further silica bulb 20 cm. long, 2 cm. diam. and 0.19 mm. thick was used in the second apparatus. An estimate of the average thickness of a bulb was made both by averaging the measured wall thicknesses, and by calculation from the weight of the bulb. The gas used was helium (99.9% pure).

The systems were heated by an electric furnace and the temperature, measured on a mercury thermometer, was kept constant to about 1° by means of a brass-invar thermostat. The pressure measurements were made on a sensitive McLeod gage and the mass of gas diffusing through the bulbs was calculated from the volumes of the different parts of the system and the densities of the gas in those parts. A small amount of gas diffuses through the Pyrex-silica graded seal connecting the silica bulb to the McLeod gage. This has been calculated to be less than 0.1% of the mass of gas diffusing through the silica bulb. Calculations show that no corrections were necessary for thermomolecular flow. It may be noted that in Fig. 1a the gas diffuses from the inside out while in Fig. 1b the diffusion is from outside the fused silica to the inside.

Results

Tables I to V show the values obtained for the mass of helium in grams diffusing through 1 sq. cm. of silica surface per hour for different pressures, sets of values being given for several temperatures and thicknesses of silica.

These values have been plotted in Fig. 2 and show that the rate of diffusion varies linearly with pressure, in agreement with earlier work. Fig. 3 shows that the rate of diffusion is inversely proportional to the thickness, the graph being linear within the limits of experimental error.

(5) Made by the Thermal Syndicate, England.

Table VI shows the values for the mass diffusing through 1 sq. cm. at a fixed pressure of 76 cm. for different temperatures. A set of values has been

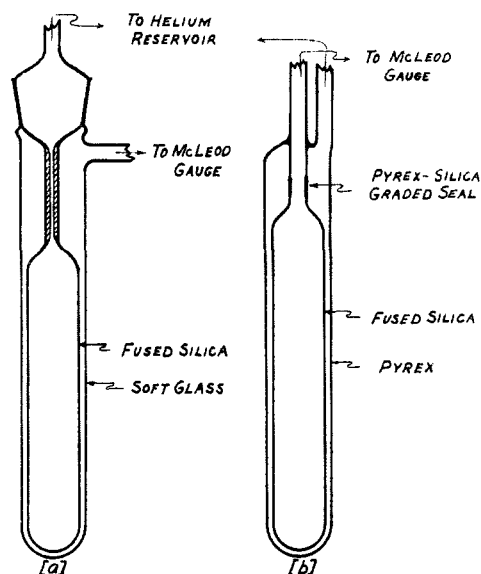


Fig. 1.

obtained for each thickness of silica. In Fig. 4 it will be observed that when the logarithm of the mass of gas diffusing is plotted against $1/T$ a

Press., cm.	Mass $\times 10^{10}$
42.8°	
75.5	107.0
57.0	83.0
33.0	48.1
19.4	27.5
7.4	10.4

102.7°	
75.7	371.0
47.1	231.3
29.6	140.5
10.7	50.6

Press., cm.	Mass $\times 10^{10}$
42.8°	
75.5	47.4
57.0	36.5
33.0	22.9
19.4	13.9
7.4	5.3

102.7°	
75.7	166.5
47.1	105.9
29.6	63.8
10.7	22.9

Press., cm.	Mass $\times 10^{10}$
134.5°	
75.8	157.2
34.1	68.7
9.2	16.4

Press., cm.	Mass $\times 10^{10}$
134.5°	
75.8	274.6
34.1	118.5
9.2	36.0

Press., cm.	Mass $\times 10^{10}$
42.8°	
75.3	293.2
60.6	236.4
39.0	154.2
20.7	81.4
8.1	31.5

TABLE VI
PRESSURE CONSTANT AT 76.0 CM.

Thickness, mm.	T, °C.	Mass (grams) × 10 ¹⁰
0.5	0.0	32.9
	25.4	68.0
	60.5	155.2
	79.5	234.4
1.0	131.0	574.0
	0.0	13.6
	25.4	31.2
	60.5	71.1
1.0 (ground)	79.5	106.0
	131.0	255.3
	42.9	51.4
	80.0	110.0
1.8	134.5	274.6
	42.9	27.4
	80.0	62.4
	134.5	157.2

straight line is obtained in every case over the whole temperature range, namely, from 0 to 135°. Curves A, B, C and D are all parallel which suggests that the energies of activation are the same for samples of fused silica with the same silicate content. The energy of activation determined from the graph is 4800 cal./gram atom. The data for curve E obtained previously⁵ lead to an activation energy of 4120 cal. E was not from the same melt as the other samples; Barrer⁴ has already reported that the activation energy depends on the sample.

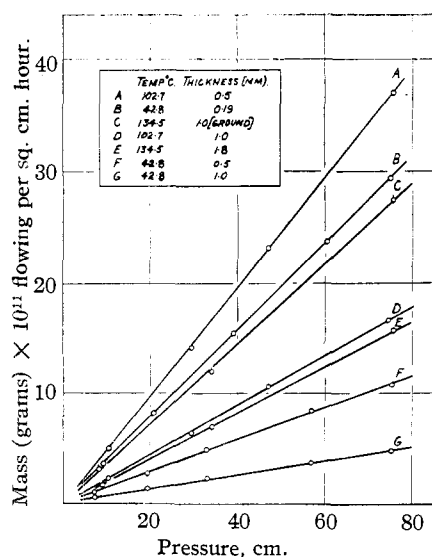


Fig. 2.

After measurements had been completed on the tube of thickness 1.0 mm., its outer surface was ground with fine carborundum and the measurements repeated. The rates were very slightly

higher but the same value of $W_0 + E_0$ was obtained. (These results are not in the graph.)

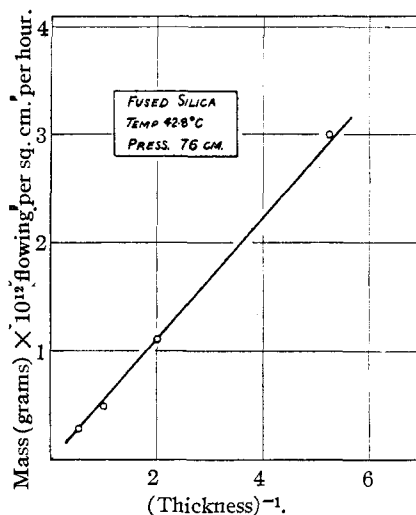


Fig. 3.

Table VII shows the values obtained for the 0.19-mm. bulb at a constant pressure and a wide range of temperatures.

TABLE VII

T, °C.	Mass in g. × 10 ¹⁰	T, °C.	Mass in g. × 10 ¹⁰
-78.0	2.47	121.6	1362
-58.4	8.24	164	2478
-42.9	17.2	231	5520
-21.0	43.5	314	11720
0.0	90.4	412	23000
42.8	296	497	36050
80.4	660	562	46720

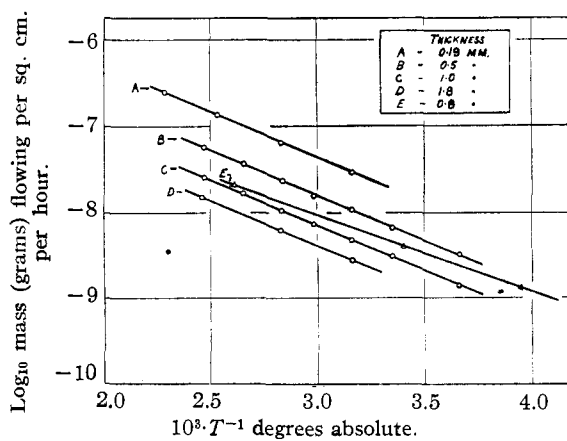


Fig. 4.

Theory³ predicts that, at least at higher temperatures, the graph showing the relation between the logarithm of the mass and $1/T$ should be a straight line. These results have been plotted in Fig. 5 and certainly a straight line is indicated above 180°. At this temperature there seems to

be a change of slope, the points corresponding to lower temperatures apparently fitting a second straight line. The value for the activation energy as calculated for the region between 180 and 562° is 5390 cal., in fair agreement with the results of other observers who worked in this temperature range, while the magnitude of $W_0 + E_0$ for the region 180 to -78° is 4800 cal. per gram atom. It should be noted that no decrease of activation energy is found below -20°. Previous results suggesting a decrease⁶ were not corroborated, and it appears that the discrepancy is due to the use of a bulb which could not be kept at sufficiently uniform temperature.

The change in the slope for the graph in Fig. 5 has also been obtained by Van Voorhis⁷ and T'sai and Hogness⁸ for the passage of helium through fused silica, although no values were obtained by them for temperatures below 180°. It is generally agreed upon that the activation energy remains constant for temperatures from 250 to 1000°.

The heat treatment which the thin bulb received did not appear to affect its properties for diffusion.⁴ In obtaining the results for the thin-walled tube the initial temperature 42.9° was gradually increased to 562°. The rates of diffusion were measured again while changing from high to low temperature. The appearance of the tube remained unchanged during the work.

It is a pleasure to thank Professor E. F. Burton for his valuable advice and encouragement throughout this work, and Mr. Chappell for his assistance in constructing the apparatus.

(6) E. F. Burton, E. O. Braaten and J. O. Wilhelm, *Can. J. of Res.*, **8**, 463 (1933).

(7) C. C. Van Voorhis, *Phys.*, **A32**, 557 (1924).

(8) T'sai and Hogness, *J. Phys. Chem.*, **36**, 2595 (1932).

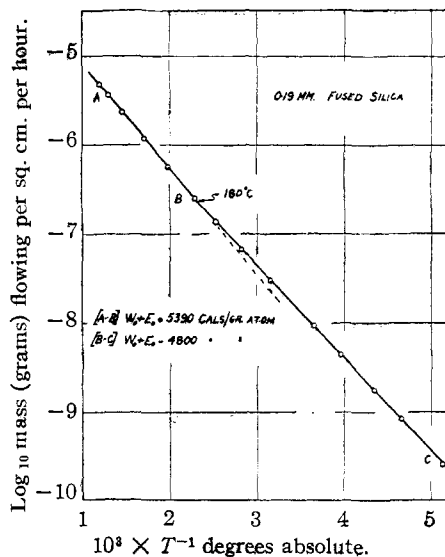


Fig. 5.

Summary

It has been found for the diffusion of helium through fused silica that (a) the gas passing through is proportional to the pressure, (b) increasing the emergent surface many times only slightly increases the rate of diffusion and (c) the rate of diffusion is inversely proportional to the thickness, which is in accord with Fick's law of diffusion.

Two values for the activation energy have been obtained depending on the temperature region for which the experiments were carried out. The magnitude for $W_0 + E_0$ was found to be independent of the thickness of the sample and to depend on the silicate content.