

The ice used for these tests was crushed, averaging 1 or 2 centimeters in dimensions. When a single large piece of ice was used the temperature dropped very slowly, reaching  $-14^{\circ}$  in one and one-half hours. A lower temperature would probably be reached if sufficient time were given. If snow or shaved ice were used the cooling would probably be rather slow also, since the packing of the snow would hinder convection.

The inside cylinder of the basket is made to take a 500-cc. flask or an 800-cc. beaker. As a test, using the vacuum jar, 500 cc. of ethyl alcohol was put in a flask at room temperature, and the flask placed in the already cold brine. At the end of half an hour the alcohol was lightly stirred for a moment and its temperature was read as  $-17^{\circ}$ . At the end of the first hour the temperature was down to  $-20.5^{\circ}$ . During the observations the temperature dropped as low as  $-20.8^{\circ}$  and it might have approached the eutectic temperature of  $-21.1^{\circ}$  even more closely.

Obviously this device may also be used with other salts and mixtures of salts. However, temperatures below  $-30^{\circ}$  are difficult to obtain with calcium chloride (either alone or with the aid of sodium chloride) because of the unfavorable heat relations and because of the decreased convection due to the greatly increased viscosity.

This device is a double application of the "dissolving cone" principle.<sup>2</sup> A further modification has been successfully used for many years by Professor W. C. Bray of the Chemistry Department for maintaining unstirred water-baths close to  $0^{\circ}$ . Since water has a maximum density at about  $4^{\circ}$ , Professor Bray uses a screen or cage to hold the crushed ice near the bottom of the  $0^{\circ}$  bath.

<sup>2</sup> "The Laboratory," Fisher Scientific Co., Pittsburgh, Pa., Vol. V, No. 1, p. 10, 1932.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF JOHNS HOPKINS UNIVERSITY]

## FURTHER STUDIES IN THE RARE GASES. I. THE PERMEABILITY OF VARIOUS GLASSES TO HELIUM<sup>1</sup>

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During the course of a research<sup>3</sup> on the computation of the age of iron meteorites by the "Helium method"—the ratio of helium to uranium and thorium—it was necessary to determine the loss of helium on heating for

<sup>1</sup> The following paper presents the results of experiments on the diffusion of helium and hydrogen through Pyrex glass, Jena 16''' glass, soda glass and lead glass. The results are discussed from a theoretical standpoint in formulating a theory of the mechanism of the diffusion process.

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<sup>3</sup> Paneth and Urry, *Z. physik. Chem.*, A152, 127 (1931).

several hours in a vacuum at 1000°. This loss was surprisingly low, being in no case greater than 6.0% of the total helium content. It therefore became of interest to ascertain if possible how the radioactively produced helium is so tightly bound in the iron-nickel structure and eventually to apply the principle to the minerals, basalts, etc., which have recently been microanalyzed for helium, radium and thorium. Before attempting to make measurements on such factors as adsorption, solubility and diffusion of helium through crystalline substances, these factors have been determined for supercooled liquids.

The diffusion of helium through many types of glass is now a well-established fact. Paneth and Peters,<sup>4</sup> who have showed an extremely sharp differentiation between the diffusion of helium and neon through hot glass, have ably summarized the literature on the diffusion effects. Apart from the work of Williams and Ferguson,<sup>5</sup> who have made a few measurements at comparatively high temperatures through silica glass, no attempt has been made to determine accurately the effect of the variables, pressure, temperature and constitution of the glass.

### Experimental

The apparatus shown in Fig. 1 is sealed at A to the "Analysis apparatus" for the study of minute quantities of the rare gases, developed in the laboratory of Professor Paneth and used by the author in several series of researches. In its present form it is best described in a lecture publication to the Bunsen Gesellschaft, 1928, forming "Heliumuntersuchungen."<sup>3,6</sup> The apparatus is also connected to the pumping system through stopcock 1. C represents the diffusion apparatus, immersed in water, of exactly similar construction to the palladium oven described in the above publication. D is a heating coil wound on a separate tube. B is a tube of the glass whose permeability to gases is to be measured and is fitted to the vacuum mantle through a glass

<sup>4</sup> Paneth and Peters, *Z. physik. Chem.*, **B1**, 253 (1928). About 1% of neon is the maximum present after diffusion through glass contrasted with the ratio of neon to helium in the atmosphere of 3 to 1.

<sup>5</sup> Williams and Ferguson, *THIS JOURNAL*, **44**, 2160 (1922). Richardson and Ditto, *Phil. Mag.*, **22**, 704 (1911), observed a diffusion of helium and neon from the atmosphere through quartz at 1000°. The statement of Williams and Ferguson that this is improbable and that the helium may come from the quartz itself should, however, be corrected. A quartz tube is surrounded by a vacuum mantle and heated for several hours until helium is no longer spectroscopically visible. Air is then let into the jacket and within thirty minutes or less the helium spectrum appears. That this is not due to leakage can be shown by the absence of neon as described in the publications in the following footnote. Moreover, Paneth and Peters have observed a continuous diffusion of helium from the atmosphere through soda glass.

<sup>6</sup> Paneth and Peters, *Z. physik. Chem.*, **134**, 353 (1928); Paneth and Peters, *ibid.*, **B1**, 170 (1928); Paneth and Peters, *ibid.*, **B1**, 253 (1928); Paneth, Gehlen and Peters, *Z. anorg. allgem. Chem.*, **4**, 175 (1928); Paneth, *Z. Elektrochem.*, **9**, 83 (1928); Paneth, Petersen and Chloupek, *Ber.*, **62**, 4, 801 (1929). Paneth and Urry, *Mikrochemie*, 233, "Emich-Festschrift" (1930); Paneth and Urry, *Z. physik. Chem.*, **A152**, 110 (1931).

joint E. By the use of a standard interchangeable ground-glass joint at E, various tubes B of different glasses may be inserted. These tubes are connected to the helium supply through the ground-glass joint F. In order that C may be easily removable, a ground-glass joint connects C with stopcock 2 and the analysis apparatus: A platinum-platinum-rhodium thermocouple sealed through the ground soda glass cap G passes down the center and touches the inner wall of B, giving the temperature of the tube. H is an aluminum electrode, the use of which is described later. The rest of the apparatus constitutes the helium supply to the inside of B which supply may be shut off at stopcock 3. I is the manometer for pressure readings from 5 mm. upward. K is a McLeod gage for pressure readings from  $10^{-3}$  to 5 mm. L is a charcoal tube shut off by stopcock 4 from the main lead and from the helium store M by stopcock 5. Manometer N checks the pressure in the store. Stopcock 6 shuts off the calcium oven used in the purification of the helium.

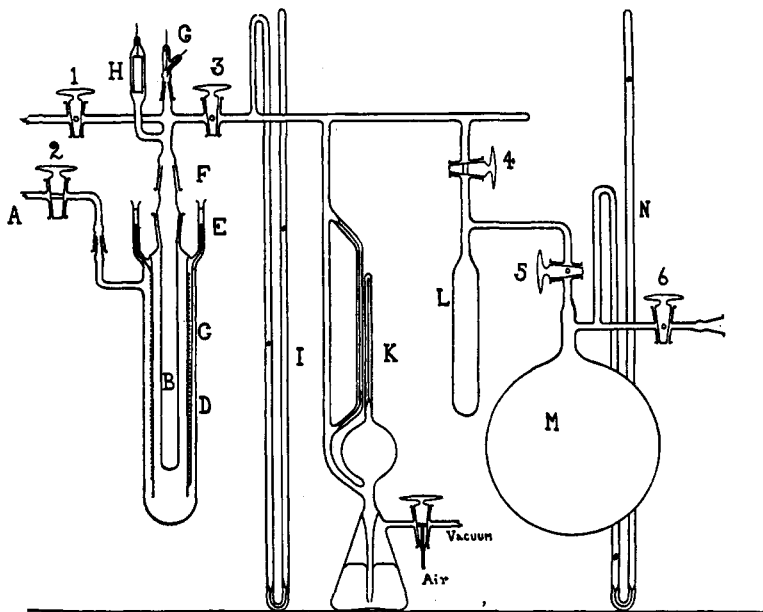


Fig. 1.

### Procedure

**The Purification of the Helium.**—The apparatus on the "Helium side" including the calcium oven and the leads to the helium bomb are completely evacuated through stopcock 1 and the charcoal activated. The apparatus is then flushed out with electrolytic oxygen,<sup>6</sup> stopcock 4 shut off and helium streamed over the calcium at  $350^{\circ}$ , previously heated in a vacuum, until about 760 mm. is indicated by N. The supply tube is then shut off and by alternately immersing the charcoal tube L and another charcoal tube at the incoming end of the calcium oven in liquid air, a circulation of the gases over the calcium is brought about. After three to four hours stopcock 6 is shut off and the charcoal tube L immersed in liquid air for four hours. Stopcock 5 is then shut and the charcoal evacuated and activated once more through 4. To obtain a given pressure in B, L is once again immersed in liquid air and stopcock 5 carefully turned to admit a small quantity of helium into L. With stopcock 1 shut

and 3 and 4 open, B fills with helium to a pressure given by I or K. After adsorbing for two hours 4 is shut and the liquid air removed. The experimental order is so arranged as to start with a pressure of about 200 mm. and to pump off through 1 small quantities of helium as the next lower pressure is required. By drawing small amounts of this helium through a separate lead into the "Analysis apparatus" it was found that the spectrum of this gas gave no neon and no hydrogen lines, only the helium lines being visible—0.001% of neon in helium is visible under the conditions of the spectroscopic analysis described previously.<sup>6</sup> It is also arranged that the apparatus from 1 to 5 can be filled with electrolytic air-free hydrogen purified by adsorption of any oxygen in L.

**Control Experiments.**—To test for possible leakage in tube B or in C, tube B is filled with air at atmospheric pressure. The "Analysis apparatus" and C, stopcock 2 being open, are flushed out with oxygen, evacuated and shut off from the pumping system. Maintaining 2 open, the tube B is heated for ten to twelve hours at 290°. It is then cooled off, stopcock 2 shut, and the residual gases examined spectroscopically in a 0.1-mm. capillary on the McLeod gage, after purification as previously described.<sup>6</sup> If any leakage occurs, the residual rare gases must be in the same proportion as found in the atmosphere. In such control experiments, however, only pure helium was observed due to a diffusion of the helium through the glass from the atmosphere varying from  $10^{-7}$  to  $10^{-9}$  cc., depending upon the glass of which B is constructed and the duration of the heating.<sup>7</sup> To demonstrate that there is no accumulation of helium from any extraneous source during the progress of an experiment, tube B is connected to the pump through 1 as is C through the "Analysis apparatus" and heated for ten hours to drive out any helium in the glass. The "Analysis apparatus" is then shut off from the pump, stopcock 2 left open, and the evacuated tube heated for a further period of four hours, whereupon less than  $10^{-10}$  cc. of helium or neon is present.<sup>8</sup>

**A Diffusion Experiment.**—Tube B is filled to a given pressure of helium and heated to the temperature at which the experiment is to be conducted for about six hours, after which time equilibrium conditions are reached. During this period C is left open to the "Analysis apparatus," which in turn is continuously on the pumping system. The tube B is again cooled to room temperature, the "Analysis apparatus" and C are flushed out with oxygen and evacuated and the pumping system shut off but stopcock 2 left open. One of the "Analysis apparatus" charcoal tubes is immersed in liquid air to produce a standard vacuum as the zero point of the diffusion. In about five minutes the tube attains the working temperature, which can be maintained within 3–4° between 150 and 300° and somewhat closer below 150°. Exactly at the end of 120 minutes the heater D is switched off and the liquid air removed. After fifteen minutes more the entire apparatus is once again at room temperature. Stopcock 2 is shut off and the gases are treated as previously described. The McLeod gage is run up and the helium spectroscopically viewed. If neon free and spectroscopically pure, the helium is measured as described in previous publications.<sup>9</sup> The tube B is again heated

<sup>7</sup> The gases from the heating coil D then also contained  $< 10^{-10}$  cc. of neon and therefore  $< 4.10^{-8}$  cc. of air, after the preliminary heating before the first control experiment.

<sup>8</sup> The heating coil D therefore contained no helium.

<sup>9</sup> See the previously mentioned publications of Paneth and co-workers, especially "Heliumuntersuchungen VIII," for an accurate method of measurement. In order to determine the total helium by diffusion, the ratio of the McLeod volume to the total volume of the "Analysis apparatus" including C must be determined as outlined in the above publication. According to the amount of helium expected, a McLeod capillary can be chosen of the correct diameter to give a suitable length of gas column. They are easily interchangeable in one glass-blowing operation.

at the same temperature for six hours with C open to the pump and the experiment repeated. This usually gave the same result, showing that after heating for six hours with a vacuum on the one side equilibrium had been established. The factors recorded in each experiment are the total helium diffusing, the temperature, the time of diffusion (120 minutes) and the pressure in B when at the working temperature and at the room temperature. The factors recorded for each series are the length and the internal and external diameters of the tube B and hence the wall thickness = 1.0 mm. average thickness for all specimens. An allowance is made in calculating the surface for the closed hemispherical end of B. The results have been checked at decreasing pressures from 200 to 0 mm. and at increasing pressures up to 200 mm.

Theoretical

Consider the diffusion process, representing the apparatus diagrammatically in Fig. 2. A represents the "Analysis apparatus" initially at a high vacuum. B represents the glass wall through which the diffusion occurs and C the helium reservoir. Suppose  $c_1$  is the saturation concentration at the wall in contact with the helium and  $c_2$  the concentration on the wall in contact with the evacuated apparatus. The rate of accumulation of helium in A will be dependent primarily on two factors—the rate of evaporation from the  $c_2$  surface =  $k_1c_2$  and the rate of condensation on the same surface =  $-k_2p$ , if the concentration of the helium on the surface is sufficiently low. When these two factors are equal and opposite, the pressure in A is fixed and the diffusion of helium

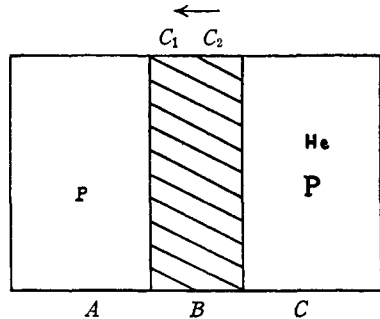


Fig. 2.

no longer occurs. The pressure in A is then the "vapor pressure" of helium in glass but as long as  $c_2$  is less than  $c_1$  these two factors cannot be equal, owing to an increase in  $c_2$  by diffusion in the glass phase which we shall assume obeys Fick's law. Equilibrium is then reached when the glass wall is saturated throughout its thickness,  $c_2 = c_1$  and the rate of evaporation = the rate of condensation. The pressure of helium in A may then be termed the "vapor pressure" of helium in glass at the concentration  $c_2 = c_1$ , and the volume  $Q$  of helium in A at N. T. P. is now independent of time. It will at once be seen that the time required to reach this state will depend on the size of A,  $pV = Q \times 760$ , where  $V$  is the volume of A. Therefore  $p = k_3Q$ , where  $k_3 = 760/V$ . Figure 3 diagrammatically represents the increase of  $Q$  with time (1) and on the same diagram is shown the change in concentration  $c_2$  with time (2). Curve 3 shows the increase with time of  $c_2$  if no evaporation occurred, that is, if the diffusion process finished at the glass surface in contact with A and is the curve given by Fick's law. Thus at first, owing to evaporation,  $c_2$  tends greatly to decrease but at the same time tends greatly to increase by the oncoming helium in the glass phase and will

take a course roughly shown by the lower portion of Curve 2. As  $Q$  increases, however, the rate of condensation greatly increases and the net evaporation is smaller.  $c_2$  starts increasing again and  $dQ/dt$  falls off.

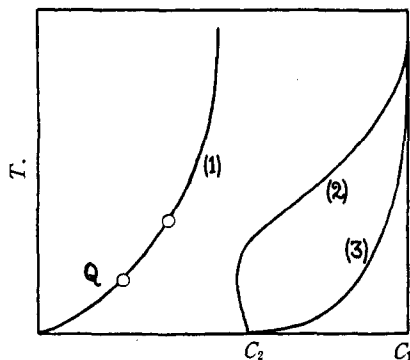


Fig. 3.

Hereafter  $dQ/dt$  approaches zero and  $c_2$  approaches  $c_1$  until the equilibrium state is reached. The two points on the  $Q$ - $T$  curve were experimentally realized, the diffusing times being ten and thirty hours, while the volume of A was about 700 cc.

Hence the time required to come to such a state of equilibrium is practically speaking infinite. If we observe what occurs in a period of two hours from zero time, we note that over this period  $c_2$  remains almost constant. It will be shown how this was experimentally verified. Hence a period of 120 minutes was chosen for the diffusion time.

What is actually determined is the relation of  $Q$  to the pressure  $P$  of helium in the tube B.

The concentration  $c$  at any plane  $x$  after a time  $t$  is given by

$$\frac{dc}{dt} = \frac{Dd^2c}{dx^2}$$

where  $D$  is the diffusion coefficient.<sup>10</sup> On integrating, expanding into a

<sup>10</sup> Andrews and Johnston, THIS JOURNAL, 46, 640 (1924) have dealt with the integration of the above equation for several cases, the full equation for the case under consideration being

$$\frac{c_1 - c}{c_1} = \frac{4}{\pi} \sum_{m=1}^{\infty} \frac{\cos \left[ \frac{(2m-1)\pi x}{a} \right]}{(2m-1)(-1)^{m+1}} e^{-(Dl/a^2)(2m-1)^2\pi^2}$$

and hence after a given time  $t$ ,  $c_2$  is directly proportional to  $c_1$ . On differentiating equation (1)

$$\frac{dc_2}{dt} = \frac{D\pi^2}{a^2} (c_1 - c_2)$$

giving the rate of increase of  $c_2$  with time due to diffusion in the glass phase. To determine what concentration  $c_2$  exists previous to the commencement of an experiment and after pumping for six hours on A, during this time  $p = 0$  and the condensation is zero. The increase in  $c_2$  is given by

$$\frac{dc_2}{dt} = K(c_1 - c_2), \text{ where } K = \frac{D\pi^2}{a^2} \quad (3)$$

The decrease in  $c_3$  due to evaporation is given by

$$-\frac{dc_3}{dt} = k_1 c_3 \quad (4)$$

and at equilibrium  $c_3 = \bar{c}_3$ , the initial concentration for a diffusion experiment. From equations (3) and (4) we obtain

series and neglecting the higher terms, putting  $x = a$ , the thickness of the glass wall, and therefore  $c = c_2$  and collecting the separate constants under one constant, we obtain

$$\frac{c_1 - c_2}{c_1} = A e^{-Dl\pi^2/a^2} \quad (1)$$

or, when  $l$  is constant as in these experiments

$$\frac{c_1 - c_2}{c_1} = A e^{-B} \text{ and } \log(c_1 - c_2) + B = \log A c_1$$

Putting  $\log E = B$

$$c_2 = c_1 \left[ 1 - \frac{A}{E} \right] \quad (2)$$

Thus  $Q$  is directly proportional to the saturation concentration on the reservoir wall  $c_1$ . If Henry's law were obeyed in this particular case, then  $c_1 = \bar{K}P$ , where  $P$  is the helium pressure in the tube  $B$ , and hence  $Q = \text{const.} \times P$ . Since this is not the case, the results are discussed with reference to phenomena at the  $c_1$  surface, since  $c_1 \neq \bar{K}P$ .

$$\bar{c}_2 = \frac{Kc_1}{(K - k_1)} \quad (5)$$

If the diffusion coefficient is smaller than the evaporation coefficient, then the concentration  $c_2$  is zero at the commencement of the experiment and the oncoming helium is immediately evaporated off the  $c_2$  surface. Consider the concentration  $c_{2t}$  on the  $c_2$  surface at a given time  $t$  after the experiment has been started, taking the complete surface of the tube to express the concentration terms, then

$$c_{2t} = \bar{c}_2 - Q_t + c_t \quad (6)$$

$Q_t$  being the net quantity evaporated in time  $t$  and  $c_t$  the increase in concentration due to the diffusion in the glass phase. The increase in concentration due to the diffusion in the glass phase  $= (dc/dt)_{2t} = K(c_1 - c_{2t})$ . The condensation on the  $c_2$  surface, proportional to the pressure  $= (dc/dt)_{2t} = k_2 p$ . The evaporation off the  $c_2$  surface proportional to the concentration  $= (dc/dt)_{2t} = -k_1 c_{2t}$ . Then

$$\frac{3dc_{2t}}{dt} = K(c_1 - c_{2t}) + k_2 k_3 Q_t - k_1 c_{2t} \quad (7)$$

remembering that  $p = k_3 Q_t$ . By putting  $c_{2t} = f(t^n)$ , equation (7) can be brought into an integrable form and the desired relation between  $Q_t$  and  $c_t$  obtained.

The following experiments, however, verify the fact that  $c_{2t}$  does not vary and therefore is equal to  $\bar{c}_2$  for the 120 minutes. After attaining equilibrium, a 120-minute diffusion was run giving a certain value for  $Q$ . The "Analysis apparatus" was pumped out and a second 120-minute run made immediately. This gave the same value for  $Q$ , a third run immediately after the conclusion of the second also gave the same value.  $c_{2t}$  and  $c_t$  are both functions of  $c_1$  and therefore of  $\bar{c}_2$  and hence from equation (6) if  $\bar{c}_2$  were to vary  $Q_t$  would also vary.  $Q_t$ , however, was the same in all three experiments and therefore the initial concentration on the  $c_2$  surface must have been the same. Hence the concentration during the course of the first experiment could not have changed, since the final concentration which is the initial for the following experiment must have been the same as the initial concentration of the first experiment. Then equation (7) becomes  $0 = K(c_1 - \bar{c}_2) + k_2 k_3 Q - k_1 \bar{c}_2$  and substituting for  $\bar{c}_2$  from equation (5)

$$Q = \frac{2k_1 K c_1}{(K - k_1) k_2 k_3} \quad (8)$$

TABLE I

(A) PYREX GLASS					
<i>P</i> , mm.	<i>t</i> , °C.	<i>Q</i> <sup>a</sup>	<i>P</i> , mm.	<i>t</i> , °C.	<i>Q</i> <sup>a</sup>
175.0	283	5642	55.0	125	265
175.0	220	2711	55.0	81	128
175.0	172	1452	47.0	283	1759
175.0	125	699	29.0	283	1115
175.0	81	338	20.0	283	828
175.0	20	112	20.0	220	404
153.0	283	5020	20.0	172	213
125.0	283	4150	20.0	125	109
125.0	220	2032	20.0	81	53
125.0	172	1082	10.0	283	436
125.0	125	541	10.0	220	215
125.0	81	264	9.0	283	401
100.0	283	3429	5.5	283	268
100.0	221	1695	5.5	220	133
98.0	172	803	5.5	172	64
97.0	125	401	5.5	125	26
95.0	81	223	5.5	15	6
65.0	283	2320	1.2	283	57
55.0	283	2005	0.098	283	18
55.0	220	994	0.022	283	3
55.0	172	525			

(B) LEAD GLASS					
<i>P</i> , mm.	<i>t</i> , °C.	<i>Q</i> <sup>a</sup>	<i>P</i> , mm.	<i>t</i> , °C.	<i>Q</i> <sup>a</sup>
209.0	283	200.5	45.0	283	80.9
160.0	283	173.5	20.0	283	49.7
129.0	283	143.5	9.2	283	33.0
80.0	283	113.0			

(C) SODA GLASS					
<i>P</i> , mm.	<i>t</i> , °C.	<i>Q</i> <sup>a</sup>	<i>P</i> , mm.	<i>t</i> , °C.	<i>Q</i> <sup>a</sup>
185.0	283	69.3	43.5	283	23.6
140.0	283	53.1	10.0	283	9.7
93.5	283	43.3	10.0	283	10.36
47.0	283	24.2	10.0	283	9.7

(D) JENA 16''' GLASS					
<i>P</i> , mm.	<i>t</i> , °C.	<i>Q</i> <sup>a</sup>	<i>P</i> , mm.	<i>t</i> , °C.	<i>Q</i> <sup>a</sup>
204.0	283	55.3	121.0	283	37.0
202.0	221	21.4	79.0	283	29.2
201.0	172	7.8	50.0	283	18.8
200.0	134	3.1	45.0	283	19.3
194.0	22	0.2	12.0	283	8.9
175.0	283	46.9	11.0	283	7.3

<sup>a</sup> The value of *Q* is given in units of  $10^{-12}$  cc. and is the volume of helium, reduced to N. T. P., diffusing through a unit area of wall equal to 1.0 sq. cm. of thickness 1.0 mm. per second.



Baxter, Starkweather and Ellestad<sup>11</sup> have determined the loss in weight of a Pyrex globe containing 75 cm. pressure of helium at 20° with an internal surface of 500 sq. cm. After attaining a constant daily loss, 0.0047

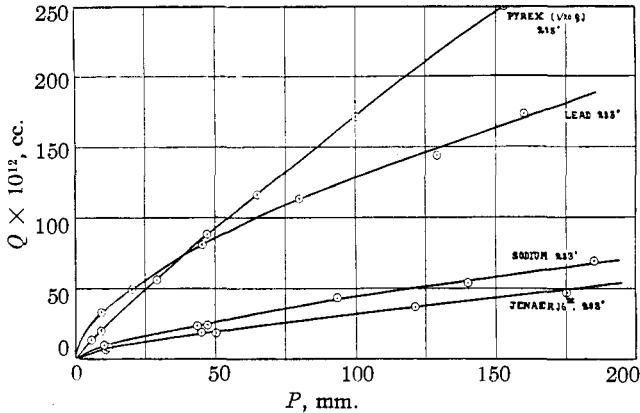


Fig. 4.—The relation between  $Q$  and  $P$  at 283°, for four types of glass (Pyrex glass;  $1/20$  diminished).

mg. of helium leaked out per twenty-hour hours, approximately equal to  $6.8 \times 10^{-10}$  cc. per second per sq. cm. per mm. wall at room temperature.

By extrapolation of the data in Table I,  $4 \times 10^{-10}$  cc. at 20° c for 750 mm. of helium through a 1-mm. Pyrex wall into a vacuum is obtained. The partial pressure of helium in the atmosphere being of the order of  $5 \times 10^{-6}$  mm., these two results are comparable and of good agreement. If the logarithm of  $Q$  is plotted against  $\log P$ , straight lines result and  $Q = \alpha P^n$ . Similarly for a given pressure  $Q = \beta T^m$ , where  $T$  is the absolute temperature.

Table II gives the values of  $\alpha$  and  $\beta$  and of  $m$  and  $n$  for the four glasses studied.

Since the value of  $\alpha$  is the value of  $Q$  for  $P = 1$  mm., a comparison of  $\alpha$  for the various glasses gives the relative diffusion through the various types of glass at 1 mm. pressure. On account of the variation of  $n$  for the

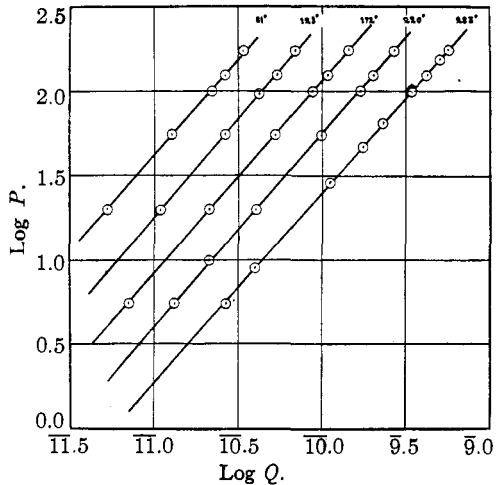


Fig. 5.—The log-log isotherms for the diffusion of helium through Pyrex glass.

<sup>11</sup> Baxter, Starkweather and Ellestad, *Science*, November 23, p. 516 (1928).

TABLE II<sup>12</sup>

$t_i$ , °C.	Pyrex glass $Q = \frac{\alpha P^{0.88}}{\alpha}$	Lead glass $Q = \frac{\alpha P^{0.86}}{\alpha}$	Soda glass $Q = \frac{\alpha P^{0.64}}{\alpha}$	Jena 16''' glass $Q = \frac{\alpha P^{0.66}}{\alpha}$
283	$58.2 \times 10^{-12}$	$8.8 \times 10^{-12}$	$2.2 \times 10^{-12}$	$1.6 \times 10^{-12}$
220	29.5	.....	.....	.....
172	15.7	.....	.....	.....
125	7.9	.....	.....	.....
81	3.7	.....	.....	.....
$P$ , mm.	$Q = \frac{\beta T^{0.88}}{\beta}$			$Q = \frac{\beta T^{0.62}}{\beta}$
202.0	.....	.....	.....	$3.24 \times 10^{-35}$
175.0	$10.00 \times 10^{-23}$	.....	.....	.....
100.0	5.96	.....	.....	.....
20.0	1.50	.....	.....	.....
5.5	0.32	.....	.....	.....

different glasses, however, the relative diffusion through the various types of glasses will vary with pressure.

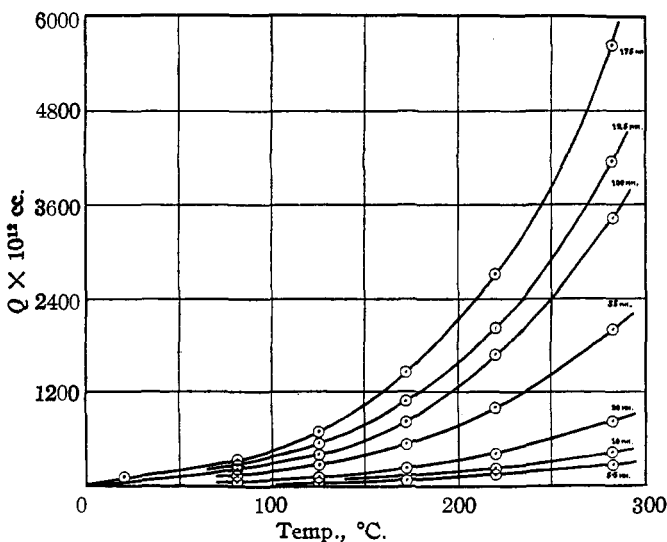


Fig. 6.—The variation of  $Q$  with temperature for various pressures.

Although glasses of as widely different composition as possible were used, no significant connection between the composition and the relative diffusion rate can be found. Table III gives the analyses of the glasses.

It will be noticed that the glasses of highest and lowest silica content have a higher permeability than those of medium content. Such physical constants as density, viscosity and dielectric constant also cannot be correlated. The values of  $n$  for the various glasses, however, are proportional, within the

<sup>12</sup> With the exception of Pyrex glass, which was selected from a new laboratory stock, the glasses were supplied by Hanff and Buest, Berlin, Germany.

TABLE III

	SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	B <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>3</sub>	PbO	ZnO	Mn <sub>2</sub> O <sub>4</sub>	Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub>
Pyrex glass	80.75	4.1	0.1	0.3	12.0	0.4	..	...	...	2.20
Lead glass	56.0	...	12.1	...	...	...	31.2	...	...	0.70
Soda glass	69.0	11.1	...	12.5	...	...	..	...	...	7.4
Jena 16'''	67.3	14.0	...	7.0	2.0	...	..	7.0	0.2	2.5

experimental limits, to the percentage of SiO<sub>2</sub> + B<sub>2</sub>O<sub>3</sub>, as may be seen from Table IV.

TABLE IV

Type	SiO <sub>2</sub> + B <sub>2</sub> O <sub>3</sub>	$\eta$ calculated	$\eta$ found
Pyrex	92.75%	0.88	0.88
Lead	56.00	.53	.56
Soda	69.00	.655	.64
Jena 16'''	69.30	.66	.66

We have seen that under the conditions of the experiments the quantity of helium measured  $Q$  must be directly proportional to the concentration on the wall in contact with the helium,  $c_1$ . If Henry's law were obeyed  $Q$  is proportional to  $c_1$ , is proportional to  $P$ . Now suppose that the helium is first adsorbed on the glass surface  $c_1$  and passes into the glass phase only through this adsorbed phase. We should then have in general  $Q \propto c \propto P^n$ .

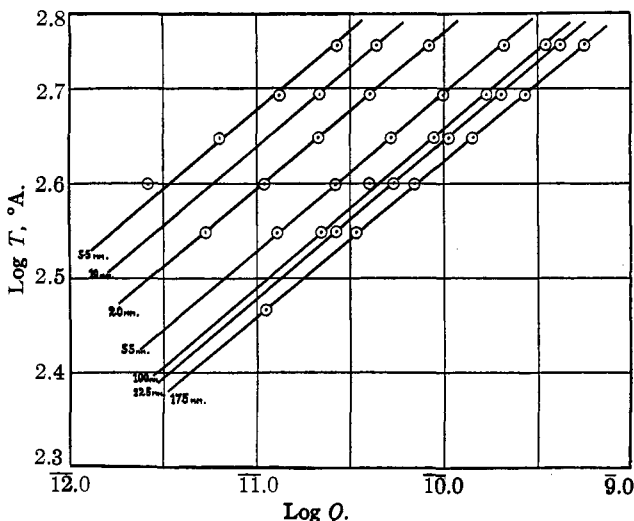


Fig. 7.—The log-log isobars for Pyrex glass.

Paneth and Peters<sup>4</sup> found that if a helium-containing glass is heated in a vacuum until  $< 10^{-10}$  cc. is given off, by the addition of 3 mm. of hydrogen and reheating for a short period a further spectroscopically detectable amount of helium is obtained. With a helium-free Pyrex glass, the diffusion rate of hydrogen was obtained in a similar manner to the helium

determinations. Table V shows the relative diffusion rates of helium and hydrogen.

TABLE V

	Pressure, mm.	Temp., °C.	$Q^a$
Hydrogen	7.0	283	$18 \times 10^{-12}$
Helium	7.0	283	$320 \times 10^{-12}$

<sup>a</sup> Denotes the volume of helium in cc. diffusing per second per sq. cm., per mm. wall.

Since the diffusion of hydrogen into the glass during a short period is negligible compared to that of helium, it seems reasonable to propose that the hydrogen replaces an adsorbed layer of helium in much the same way as replacement takes place on charcoal. Moreover, if glass, previously heated in hydrogen until no more helium is given off, is left for twenty-four hours in the air, and reheated in hydrogen for a short while, helium and a little neon are given off. On heating again a practically neon-free helium is obtained. Thus helium is preferentially adsorbed from the atmosphere and the much smaller amount of neon quickly replaced by hydrogen when heated. Glass tubes of 50 sq. cm. surface when filled for one hour with neon and helium in the air ratio (3 to 1) and then pumped out, give on heating  $10^{-5}$ – $10^{-6}$  cc. of helium and very little neon. After the third fractional heating a neon-free helium is obtained.

More significant perhaps is the fact that instead of heating, the electric discharge in hydrogen can be used to bring about the same effect. Experiments described in the following pages show that the rate of diffusion of hydrogen (and helium) is not affected by a discharge through the glass wall, whether a high frequency 800,000 volt discharge or a 60 cycle 20,000 volt discharge. This being the case and remembering that the walls are at water cooled temperatures and therefore the rate of diffusion of hydrogen about 50 times smaller than in Table V, the observed effect must be a surface phenomenon.<sup>13</sup> If hydrogen can replace the adsorbed helium layer on a glass surface, which adsorbed layer is itself very stable, not being removed at 400° in a vacuum, then by the addition of an excess of hydrogen to the helium in the reservoir the helium adsorbed layer is partially displaced and the concentration in the first layer  $c_1$  decreased,  $Q$  being correspondingly decreased. This was found to be the case, as may be seen from Table VI.

That the diffusion rate is not affected by a discharge through the glass was also shown. A Tesla coil using a 2 KV, 60 cycle, 2 kilowatt transformer for supply was connected to the electrode H. One of the heating

<sup>13</sup> A repetition of Paneth and Peters' experiment showed that  $10^{-8}$  cc. of helium can be removed from an otherwise apparently helium-free Pyrex glass surface in twenty-two minutes using 18,000 volt, 60 cycle discharge in 5 mm. of hydrogen; temperature of the walls, 10°.

coil leads was earthed.<sup>14</sup> The calculated voltage output of the Tesla coil was 800,000 volts. At low frequency the transformer was connected to H and one lead of the heating coil. Table VI gives the results obtained, the experiments being conducted as previously over two hours.

TABLE VI

Expt.	Composition and pressure of gas in tube B, mm.	Temp., °C.	Q <sup>a</sup>	Remarks
3A	5.5 He	283	275 × 10 <sup>-12</sup>	
12A	5.5 He	283	275	
13A	5.5 He	283	277	
14A	5.5 He			
	+ 5.5 H <sub>2</sub>	283	275	
15A	5.5 He			
	+27.5 H <sub>2</sub>	283	268	
7A	12.0 He	283	522	
8A	12.0 He	283	522	H. F. discharge
9A	12.0 He	283	522	L. F. discharge
21A	7.0 H <sub>2</sub>	283	18	
22A	7.0 H <sub>2</sub>	283	20	H. F. discharge
23A	7.0 H <sub>2</sub>	283	17	L. F. discharge; atomic hydrogen visible

<sup>a</sup> Q being in the same units as in the foregoing tables.

In the case of hydrogen the total diffusion rate is so small that accurate measurements could not be made but the mean value shows that any effect is very small. The "clean-up effect" of hydrogen in helium is another example where a layer of hydrogen is adsorbed entirely on the glass surface since the discharge does not affect the very low rate of diffusion of hydrogen into the glass and the hydrogen is sometimes removed in a matter of seconds in a thoroughly outgassed 0.2-mm. capillary. With helium, neon and the rare gases, however, no "clean-up effect" occurs.

Williams and Ferguson,<sup>5</sup> in attempting to find the solution to the problem that helium diffuses 22 times faster than hydrogen at 760 mm. pressure and 500° through silica glass,<sup>15</sup> measured the relative solubility of these two gases in glass and found them not to differ appreciably. Supposing, however, that hydrogen is very strongly bound in the surface as we have seen is likely to be the case,<sup>16</sup> then, on outgassing the glass to determine the amount "dissolved," the main body of hydrogen would be that adsorbed or absorbed in the surface. With helium, however, where the time allowed

<sup>14</sup> The discharge did not affect the heating but had to be shut off when making temperature readings with the thermocouple.

<sup>15</sup> See also Table V through Pyrex glass.

<sup>16</sup> The same authors could detect no diffusion of hydrogen through Pyrex or Jena glass at 760 mm. and 640°, probably owing to a limited sensitivity, but the glass blackened. This latter fact appears to point to the presence of at least physico-chemical forces between the hydrogen and the glass.

for saturation was sufficient for quite a large diffusion into the glass, the "solubility" would be the chief factor. This result, then, instead of increasing the difficulties of the solution of the problem, may itself be a solution. The hydrogen being bound very strongly in the surface layer cannot to any great extent diffuse into the glass; the helium, being less strongly bound, diffuses.

The value of  $n$  in the equation  $Q = \alpha P^n$  indicates the relative strength of the forces holding the adsorbed gas in the surface. On turning to Table IV, we see that the value of  $n$  decreases proportionately to the decrease in the silica + boric oxide content.<sup>17</sup> As the percentage of the metals and therefore of the metallic atoms in the surface increases, so the relative strength of the forces holding the gas in the surface increases. The other constant,  $\alpha$ , which cannot be correlated in any way with the composition or physical properties of the glass, varies enormously for the four types of glass. Two factors obviously play an important part in fixing  $\alpha$ , (1) the true surface of a given measured surface of the glass, (2) the true solubility in the bulk of the glass. Thus upon the extent of the true surface depends the concentration of the adsorbed layer and hence  $c_1$ . Nothing can be said at present, however, of the relative effect of these two factors on the constant  $\alpha$ . An attempt will be made to determine the extent of the true surface by the radioactive indicator method of Paneth and Vorwerk.<sup>18</sup> That the solubility may substantially vary is to be expected from analogous experiments on the solubility in mixed liquid solvents of varying composition. That the true surface will vary is equally apparent from the very different composition, melting point, annealing and drawing temperature of each glass tube studied.<sup>19</sup>

The change of permeability with temperature agrees very closely with the equation  $Q = \beta T^m$ . In order to determine the chief factor affecting the increase of permeability with increasing temperature, the following series of experiments were conducted. The rate of diffusion was determined for six temperatures at one pressure, running the experiments consecutively and only evacuating a few minutes before each determination, working from 283° down to room temperature and back again to 283°. A second series was then made but after each determination the tube B was held for six hours at the next temperature, C being on the pump. The two series of results were identical within the experimental limits. If considerable changes in the concentration conditions at the different temperatures occur, these two series cannot give the same results since in the first set of determinations no time is allowed for a readjustment of such changes on going

<sup>17</sup> It may be of interest to note that these two elements are the only ones present in glass forming volatile hydrides.

<sup>18</sup> Paneth and Vorwerk, *Z. physik Chem.*, **101**, 445, 480 (1922).

<sup>19</sup> See "International Critical Tables," Vol. II, pp. 92-101.

to the next lower or next higher temperature, whereas in the second series a period of six hours is allowed for the attaining of any new equilibrium conditions. Thus the chief factor involved in the change of permeability with temperature must be the rate of change of the diffusion coefficient  $D$  with temperature in the glass phase, this being independent of concentration and adsorption changes. In this respect the relative diffusion may be related to the viscosity of the medium since Cohen and Brun<sup>20</sup> found the Stokes-Einstein equation to hold approximately for the diffusion of one organic liquid into another

$$D = \frac{RT}{N} \frac{1}{6\pi\eta r}$$

where  $\eta$  is the viscosity of the medium and  $r$  the radius of the diffusing atom or molecule.

Assuming  $r$  to be independent of temperature  $D\eta = KT$ , or for helium through various glasses at one temperature,  $D\eta = K'$ , where  $\eta$  and  $D$  are the viscosity and diffusion coefficient for each particular glass. Owing to a lack of viscosity data for glass below 500°, this question must be dealt with after a study of the viscosity of glasses at comparatively low temperatures.

Further work is in progress dealing with the diffusion and adsorption of the rare gases through and on crystalline bodies.

### Summary

1. A method of determining accurately the rate of diffusion of helium, neon and hydrogen through glass at comparatively low temperatures and pressures is outlined and the results are given for Pyrex glass, lead glass, soda glass and Jena 16''' glass.

2. The results are discussed in the light of previous experiments on the helium content of glasses, outgassing effects and the "clean-up effect."

3. It is concluded that in the process of diffusion through glass, helium and hydrogen are first adsorbed on the glass surface and solubility and diffusion proceeds from this adsorbed or absorbed (in the case of hydrogen) layer. This theory may be extended to other gases equally well.

4. In the above conclusion lies an explanation of the hitherto inexplicable contrast between the rates of diffusion of hydrogen and helium through glass.

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<sup>20</sup> Cohen and Brun, *Z. physik. Chem.*, **103**, 404 (1923).