[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF McGILL UNIVERSITY]

THE DIFFUSION OF OXYGEN THROUGH SILVER

BY F. M. G. JOHNSON AND P. LAROSE

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Though the diffusion of gases through metals has been studied by many, only two investigators have extended their work to the diffusion of oxygen through silver. Troost[1] studied the rate of diffusion of oxygen through silver at one temperature only, and his results will be discussed later in this paper. Sieverts[2] made some qualitative tests on a piece of silver, the thickness of which he did not mention, at 520° and 620° and found that no appreciable diffusion took place at those temperatures.

The method developed and described in this paper has for its object, the determination of the rate of diffusion of oxygen through silver under varying conditions of pressure of the gas, temperature, and thickness of silver. Results have been obtained for the rate of diffusion under such conditions.

Apparatus

The necessary apparatus required that the gas, of which the diffusion was to be measured, should diffuse through a known area of the metal under a known pressure and at a known temperature. How the apparatus used met these requirements will be discussed as the results are analyzed.

The metal was in the form of a flat disk A, Fig. 1, fixed to a circular block of silver B by means of silver sulfate C. This was done by placing a little powdered silver sulfate in the cavity formed by bending the plate around the block B and heating the latter until the silver sulfate melted. On solidifying, the sulfate forms a hard mass which gives a gas-tight joint. The block B was 0.5 cm. thick and 2.2 cm. in diameter. It

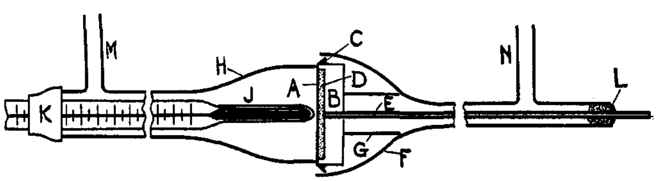

Fig. 1.

had a depression of 1.85 cm. in diameter and 1 mm. in depth, filled by a porous porcelain plate D. The area of the silver plate exposed to diffusion was taken as that of this depression, for it was found that the silver sulfate flowed between the plate and the block up to the edge of the depression, due to capillarity. In the center of the block was inserted a silver capillary tube E fixed to it by means of hard solder. The bore of this tube was about 0.4 mm. in diameter and the thickness of the wall 0.8 mm. The tubes F, G and H were of Pyrex glass and shaped as shown. These tubes were held in clamps and pressed firmly against the block B. A gas-filled quartz-glass mercury thermometer J, fitting loosely through the rubber joint K, served to indicate the temperature of the

[1] Troost, *Compt. rend.*, **98**, 1427 (1884).

[2] Sieverts, *Z. physik. Chem.*, **60**, 129 (1907).

silver plate. This thermometer. which had a scale reading from 230° to 750°, was calibrated at the boiling point of sulfur, 444.6°, and found to be correct within half a degree at this temperature, which was as close as the thermometer could be read. The end of the capillary tube E was inserted in a glass tube leading to a Toepler pump to which a McLeod gage was attached, the joint at the glass tube being made with sealing wax. The end of the tube F was closed by a plug of asbestos L and the portion of the capillary tube between L and the wax joint was cooled by a cotton wick dipping into cold water. Oxygen entered the tube H at M and nitrogen the tube F at N. The apparatus between M and N was placed in an electric furnace so that the silver plate was approximately in the middle. The nitrogen served the purpose of protecting the silver tube E and the block B from the action of oxygen, nitrogen having been found not to diffuse through silver. Due to irregularities of tubes G and F, the nitrogen had free passage out of F. The oxygen passing into the tube H escaped through the joint K as well as through the space left between the glass tube and the silver plate, due to a slight unevenness of these, so that by passing the gas slowly into H, the pressure there never appreciably exceeded atmospheric pressure.

After using this apparatus in a few tests it was found that the tube H was liable to be displaced during an experiment and consequently reduce the area of the silver plate exposed to the oxygen. In order to eliminate this trouble, a slight modification of this apparatus was used in later tests. The block B, Fig. 2, in this case had two depressions. One, D, as before, contained a porous porcelain plate and was 2.3 cm. in diameter. Into the other the silver plate was bent at right angles and the cavity filled with silver sulfate as before. This allowed the tube H to be held in position by means of a piece of silver foil P wrapped around the block, over which it was kept tight by a wire twisted around it. The combination of tubes F and G, Fig. 1, was also found to be troublesome. The tube G was therefore eliminated and the open end of F made of a diameter slightly less than that of the silver block against which it was pressed.

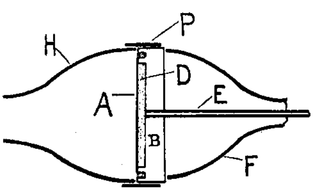

Fig. 2.

Manipulation

The oxygen and nitrogen were obtained from the ordinary commercial cylinders and underwent no other purification than that of passing through sulfuric acid before entering the apparatus. In beginning an experiment the apparatus was heated to the required temperature, and then oxygen and nitrogen were passed through for about 15 minutes at a brisk rate in order to replace the air in the tubes. During the experiment the rate was reduced to about 80 bubbles per minute. The pressure in the pump was then read on the McLeod gage at 15-minute intervals. An experiment usually lasted between one and two hours. The readings taken every 15 minutes indicated whether the diffusion was proceeding uniformly. The temperature of the furnace was regulated by means of a rheostat and could be kept constant within 5°. It was also read at 15-minute intervals and the temperature of the experiment taken as the mean of these readings. For temperatures above 530° part of the mercury thread was exposed outside the furnace but no attempt was made to correct for this as it was thought to be too indefinite. The atmospheric pressure was also noted during an experiment in order to apply a correction to the rate of diffusion for varying pressure. The temperature of the room was read, from which the volume of the gas in the pump was reduced to that at 0°. Knowing the volume of the pump which had been previously calibrated, the amount of gas passing through the silver plate could easily be calculated.

To obtain different effective pressures of oxygen on the silver plate, different mixtures of oxygen and nitrogen were prepared in a gasometer, and passed through the apparatus instead of oxygen. The mixtures were analyzed for oxygen before use and the pressure of the oxygen was thus calculated.

No correction was necessary for back pressure on the low-pressure side of the plate as this never exceeded 1 mm.

Experimental Results

The silver foil was of four different thicknesses, namely 0.0787, 0.135, 0.205, 0.248 mm. The thickness was determined from the weight of a piece of known area. The silver contained by analysis 0.02% of copper, 0.001% of iron and 0.005% of lead. The presence of tin, bismuth and antimony could not be detected in a 5g. sample. Except, possibly, for a change in crystal size, the silver did not appear to be affected in any way during the diffusion experiments.

In the tables that follow, where the area of the silver plate is taken as 2.68 sq. cm., the first apparatus described and shown in Fig. 1 was used; where the area taken is 4.16 sq cm., the modification shown in Fig. 2 was used.

Table I gives actual figures for two experiments taken from the authors' observations and illustrates the quantities involved in the calculation of the rate of diffusion.

TABLE I

DATA OF TWO EXPERIMENTS

Expt. 1. Volume of apparatus into which the gas diffused, 313 cc.; thickness of silver plate = 0.205 mm.; area of plate, 4.16 sq. cm.; room temperature, 19.0°; atmospheric pressure, 756 mm.

Time Min.	Cape feeding Cm.	Pressure Cm. of Hg	Press. diff. Cm. of Hg	Temp. °C.	Mean temp. during interval °C.
0	3.72	0.00106		493	
			0.00102		495
15	5.21	.00208		497	
			.00106		496
30	6.40	.00314		495	
			.00106		495
45	7.40	.00420		495	
			.00100		496
60	8.24	.00520		497	
			.00414		Mean 496

Reducing gas volume to 0° and correcting for a pressure of oxygen of 760 mm., the rate of diffusion = 38.4 cc. per sq. meter per hour.

Table I (*Concluded*)

Expt. 2. Volume of apparatus, 268 cc.; thickness of silver plate, 0.135 mm.; area of plate, 2.68 sq. cm.; room temperature, 23.0°; atmospheric pressure, 753 mm.

Time Min.	Gage reading Cm.	Pressure Cm. of Hg	Press. diff. Cm. of Hg	Temp. °C.	Mean temp. during interval °C.
0	4.2	0.0011		597	
			0.0064		600.5
15	10.85	.0075		604	
			.0066		600
30	14.85	.0141		596	
			.0059		597
45	17.7	.0200		598	
			.0068		601
60	20.5	.0268		604	
			.0069		602
75	23.0	.0337		600	
			.0067		600.5
90	25.2	.0404		601	
			.0070		601
105	27.3	.0474		601	
			.0463		Mean 600

Correcting for pressure and temperature as before, rate of diffusion = 324 cc. per sq. meter per hour.

Table II

Rate of Diffusion for Various Pressures under Varying Temperature

A. Thickness of silver plate No. 1, 0.135 mm.; area exposed to diffusion, 2.68 sq. cm.; effective pressure of oxygen, 760 mm.

Temp., °C.	402	499	551	600	576	551	527	413	602	563
Rate[a]	8.7	57.8	163	390	289	175	122	11.0	407	232
Temp., °C.	437	476	513	537	580	547	592	610	565	...
Rate[a]	19.4	43.0	92.2	140	326	154	328	435	216	...

B. Thickness of silver plate No. 2, 0.135 mm.; area exposed to diffusion, 2.68 sq. cm.; effective pressure of oxygen, 760 mm.

Temp., °C.	494	555	547	601	613	620	...	...	...	...
Rate[a]	50.6	149	133	278	350	393	...	...	...	...
Temp., °C.	427	460	486	514	619	532	...	...	...	...
Rate[a]	11.8	24.4	42.2	73.2	393	96.5	...	...	...	...

C. Thickness of silver plate No. 2, 0.135 mm.; area of plate exposed to diffusion, 2.68 sq. cm.; pressure of oxygen, 392 mm.

Temp., °C.	490	542	541	583	614	430	486	...	...	...
Rate[a]	28.4	79.5	80.0	167	267	8.9	28.6	...	...	...

D. Thickness of silver plate No. 2, 0.135 mm., area exposed to diffusion, 2.68 sq. cm.; pressure of oxygen, 159 mm.

Temp., °C.	619	620	564	543	413	465	512	596	496	...
Rate[a]	209	206	89.7	62.6	4.7	13.6	35.2	148	27.7	...

[a] Rate of diffusion: cc. per sq. meter per hour.

The results of Table II are plotted in Fig. 3. It is seen that the rate of diffusion increases rapidly with temperature and the curves resemble those obtained in other investigations on the rate of diffusion of gases through metals.

The results of Table 2A and 2B are seen to differ markedly as indicated by Curves 1 and 2. Though the plates were supposed to be of the same thickness, having assumed the foil to be of uniform thickness, on measur-

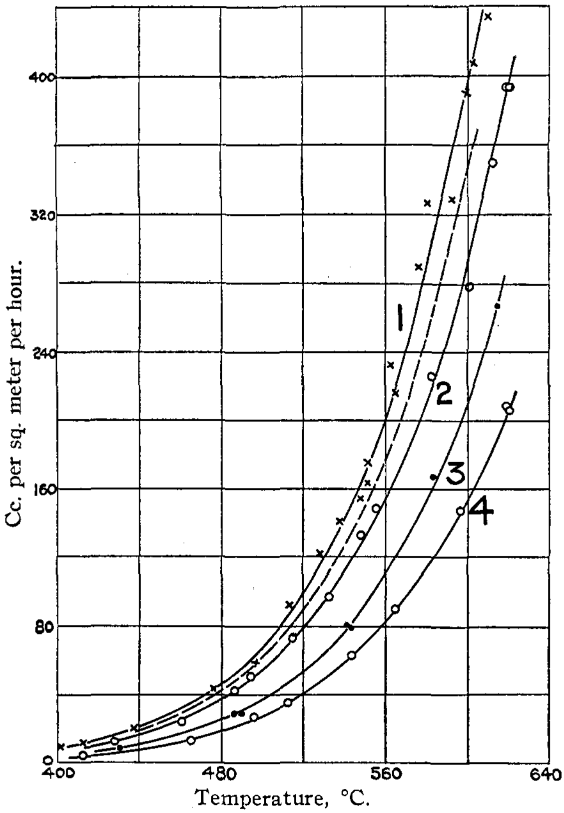

Fig. 3.—The variation of the rate of diffusion with temperature; silver, 0.135 mm. in thickness. Curves 1 and 2 at 760mm. pressure; Curve 3 at 392mm. pressure; Curve 4 at 159mm. pressure.

ing with a micrometer after the experiments, they were found to vary. By taking the mean of numerous readings, one gave 0.114 mm., the other 0.129 mm. for the thickness. A new piece of silver was measured over a large area in the same way and gave 0.123 mm., while by weighing, the thickness obtained was 0.135 mm. Since the latter is considered the more accurate and the corresponding micrometer measurement, 0.123 mm., happens to be nearly equal to the mean of 0.114 and 0.129 mm., the diffusion for a plate of 0.135mm. thickness is fairly well represented by the mean of the results obtained and indicated by the dotted curve, Fig. 3. If we assume that the diffusion is inversely proportional to the thickness, the difference between Curves 1 and 2 is largely accounted for but there still remains an error of about 7%. This may be due either to temperature or to area of the silver plate. In Fig. 4, are plotted the logarithms of absolute temperature against the logarithms of diffusion velocity.

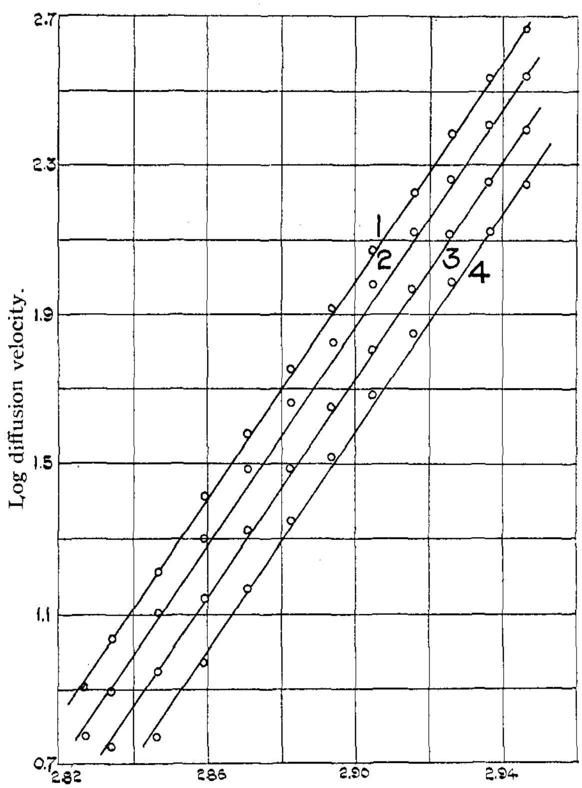

Fig. 4.—Curves plotted from data of curves of Fig. 3 showing the relation between the log of the absolute temperature and the log of the rate of diffusion. Slope, 14.62.

It will be noted that the straight lines thus obtained all have the same slope, 14.62. This shows that the temperature effect is independent of the pressure of the gas and at the same time that the temperature is not the main cause of the discrepancy between the two curves noted above. The area of the silver plate exposed to diffusion was taken as that of the depression in the silver block. An error of 3.5% in the diameter of the latter will account for the difference in the results. It is quite possible that the silver sulfate had crept beyond the edge of the depression or not quite to it and thus introduced an error in the area, although on removing the plates from the block this did not appear to be so. By plotting results in the manner followed in Fig. 4, straight lines were also obtained by Ryder,[3] for the diffusion of hydrogen, nitrogen and carbon monoxide through steel. Plotting in the same way the results given by Richardson, Nicol and Parnell[4] for the diffusion of hydrogen through platinum a straight line is again obtained. Deming and Hendricks[5] have recently measured the diffusion of hydrogen through nickel. They did not plot the logarithms of the temperature against the logarithms of the rate of diffusion in their paper but this has been done in Fig. 5 and here again a straight line is obtained. It seems very probable, therefore, that this relation is a general one in the diffusion of gases through metals. It must be noted, however, that any change in the state of the metal would probably alter the slope of the curve as Ryder found[3] at the critical point of the steel.

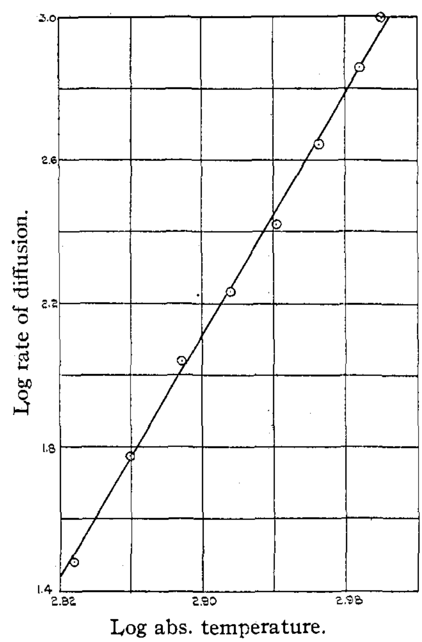

Fig. 5.—The relation between the log of the absolute temperature and the log of the rate of diffusion for hydrogen through nickel. (Ref. 5.)

The rate of diffusion is plotted against the square root of the pressure for these results in Fig. 6. Curve 2 is thus obtained for 505° and Curve 4 for 581°. Curves 1 and 3 represent results obtained from Curves 1, 2 and 3 (Fig. 3) for 450° and 600° and are plotted in the same manner. In each case the points lie sensibly on a straight line, the deviations being well within the experimental error. It appears from these results that the rate of diffusion varies as the square root of the pressure. Richardson, Nicol and Parnell,[4] in their

Table III

Rate of Diffusion for Various Pressures at Two Temperatures

Thickness of silver plate No. 3, 0.135; area exposed to diffusion, 2.68 sq. cm.

Temp., °C.	581	505	581	505	581	505
Rate of diff.	252	67.9	116	34.1	175	49.5
Press. of O_2, mm. of Hg	760	760	159	159	392	392

[3] Ryder, *Elect. J.*, **17**, 161 (1920).

[4] Richardson, Nicol and Parnell, *Phil. Mag.*, [6] **8**, 1 (1904).

[5] Deming and Hendricks, This Journal, **45**, 2857 (1923).

experiments on the rate of diffusion of hydrogen through platinum found the same relation. Winkelmann[6] in his investigation of the diffusion of hydrogen through palladium found also that the rate of diffusion varied as a power of the pressure. From his results which, however, are not very reliable, he found this power to be about 0.7. Troost[1] found that the diffusion of oxygen through silver of 1mm. thickness was 1.70 liters per sq. meter per hour when using oxygen and 0.89 liter when air was used, both at atmospheric pressure. With silver of 0.5mm. thickness, the figures obtained were 3.33 liters for oxygen and 1.64 liters for air. The ratio of the square roots of the

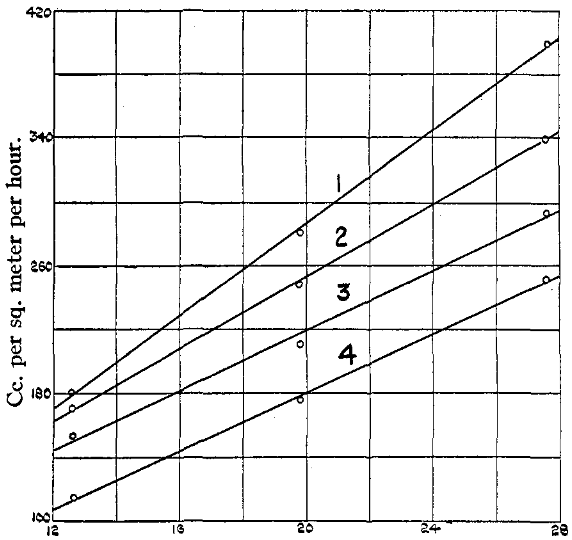

Fig. 6.—The relation between the square root of the pressure and the rate of diffusion. Curves 1 and 3 with silver 0.135mm. thick at 450° and 600°, respectively; Curves 2 and 4 with another plate of the same thickness at 505° and 581°, respectively. For Curve 1 the rate of diffusion has been multiplied by 20, and for Curve 2 by 5.

pressures is 2.08 while the ratio of the rates of diffusion is 1.91 in the first case and 2.03 in the second case. Troost's figures then show also that the rate of diffusion varies as the square root of the pressure. It will be noted that the diffusion obtained by Troost for silver of 0.5mm. thickness is just about twice that obtained when the silver was 1.0mm. thick. That the rate of diffusion is inversely proportional to the thickness is also shown by the following results.

The results in Tables IV, V and VI are plotted in Fig. 7 and the corresponding curves in Fig. 8 are obtained by plotting the logarithms of absolute

[6] Winkelmann, *Ann. Physik*, [4] **6**, 104 (1901).

temperature against the logarithms of the rate of diffusion. Straight lines are obtained having the same slope, 14.62 as those in Fig. 4. This indicates that the temperature effect on the rate of diffusion is independent of the thickness. In Fig. 4, there seems to be a tendency for the points to lie on slightly curved lines instead of the straight lines drawn through

RATES OF DIFFUSION FOR VARIOUS THICKNESSES OF SILVER

TABLE IV

Thickness of silver plate, 0.0787 mm.; area of plate exposed to diffusion, 4.16 sq. cms.; pressure of oxygen, 760 mm.

Temp., °C.	407	433	461	500
Rate of diff.	13.1	28.7	52.5.	97.0

TABLE V

Thickness of silver plate, 0.205 mm.; area of plate exposed to diffusion, 4.16 sq. cms.; pressure of oxygen, 760 mm.

Temp., °C.	479	491	535	559	584	590	627	...	...
Rate[a]	21.3	35.4	74.8	142	222	248	422	...	...
Temp., °C.	639	633	411	649	431	445	463	...	...
Rate[a]	544	495	4.6	533	9.0	13.1	21.0	...	...
Temp., °C.	518	548	574	593	610	620	413	...	...
Rate[a]	65.3	105	164	235	296	378	5.5	...	...
Temp., °C.	X552	584	603	540	618	631	625	...	...
Rate[a]	99.5	170	193	83.8	300	399	356	...	...
Temp., °C.	X478	496	406	413	421	...	...	...	...
Rate[a]	26.5	38.4	4.5	6.4	8.5	...	...	...	...
Temp., °C.	505	500	518	527	538	...	...	...	...
Rate[a]	45.2	43.8	57.3	68.3	82.5	...	...	...	...
Temp., °C.	433	443	455	469	477	485	...	...	...
Rate[a]	11.6	14.5	18.1	21.5	32.7	31.6	...	...	...
Temp., °C.	551	564	575	587	598	610	...	...	...
Rate[a]	106	136	152	190	230	284	...	...	...

[a] Rate of diffusion: cc. per sq. meter per hour.

X Denotes that the plate was changed for another of the same thickness.

TABLE VI

Thickness of silver plate, 0.248 mm.; area exposed to diffusion 4.16 sq. cm.; pressure of oxygen, 760 mm.

Temp., °C.	590	622	637	617	565	502
Rate of diff.	156	252	326	232	102	44.8
Temp., °C.	410	442	482	530	603	627
Rate of diff.	5.7	11.6	27.3	65.0	199	292

them. This is not so marked in Fig. 4 as in Fig. 8. This curve would be more accentuated if a stem correction had been made for the temperature, and the relation found is therefore probably only an approximate one. Further work, however, over wider ranges of temperature and with a more suitable means of measuring the temperature will no doubt settle this point.

The curve in Fig. 9 is obtained by plotting the rate of diffusion at 580°, obtained from the curves of Fig. 3 and Fig. 7, against the reciprocal of the thickness. Similar straight lines are obtained for any other temperature. The curve shows that the rate of diffusion is inversely proportional

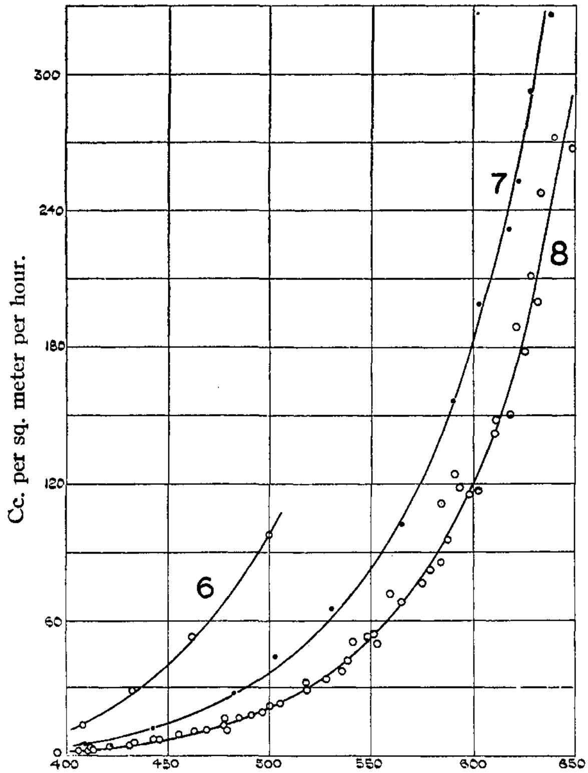

Fig. 7.—The variation of the rate of diffusion with temperature for three different thicknesses of silver; Curve 6 for a thickness of 0.0787 mm.; Curve 7 for 0.205 mm.; Curve 8 for 0.248 mm.

to the thickness. This is a relation which was often assumed by investigators studying the diffusion of gases through metals but for which there was very little experimental evidence.

Having now found how the rate of diffusion varies with temperature, pressure and thickness, we may derive a formula which will give the rate of diffusion of oxygen through silver for any condition of pressure, thickness, and temperature of silver, at least between 400° and 630°, and beyond if the relations found are assumed to be the same for other temperatures.

Since the slope of the curves in Fig. 4 and 8 is 14.62, the rate of diffusion, X, in cc. per sq. meter per hour, can be expressed as $X = aT^{14.62}$ where a is a constant depending on the thickness and pressure, and T is the absolute temperature. The rate of diffusion varies as the square root of the pressure and inversely as the thickness, so that instead of a we may put

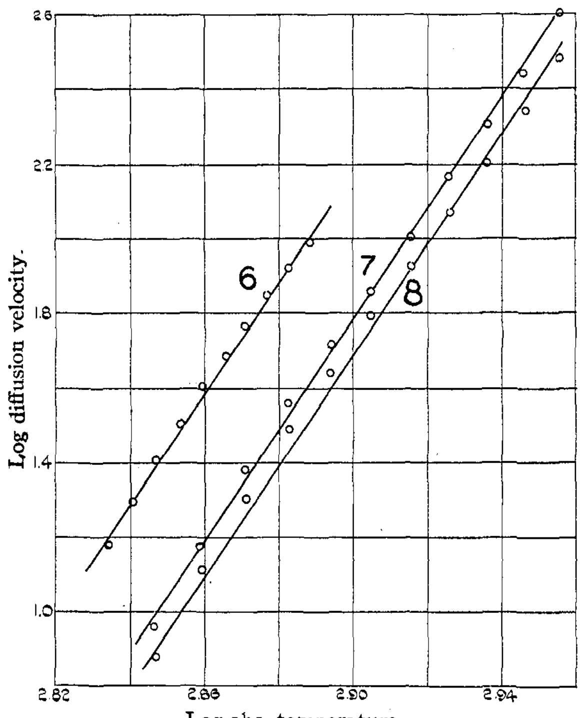

Fig. 8.—Data from curves of Fig. 7 plotted to show the straight line relationship between the log of the absolute temperature and the log of the rate of diffusion. Slope of line 14.62.

$(c/h)\sqrt{p}$, where p is the pressure of the gas in millimeters of mercury, h the thickness of the silver in millimeters and C a constant. The formula thus becomes $X = \frac{C}{h}\sqrt{p}\ T^{14.62}$. In order to evaluate C, it is necessary only to substitute values for h, p and T for any one point taken from the curves. In this way C is found to be 1.71×10^{-43}, so that the final form of the equation is $X = \frac{1.71}{10^{43}}\sqrt{\frac{p}{h}}\ T^{14.62}$.

Making use of this equation to calculate the rate of diffusion of oxygen through silver of 1mm. thickness under atmospheric pressure and at a temperature of 778°, X = 707 cc. per square meter per hour. This is less than half that obtained by Troost under these conditions.

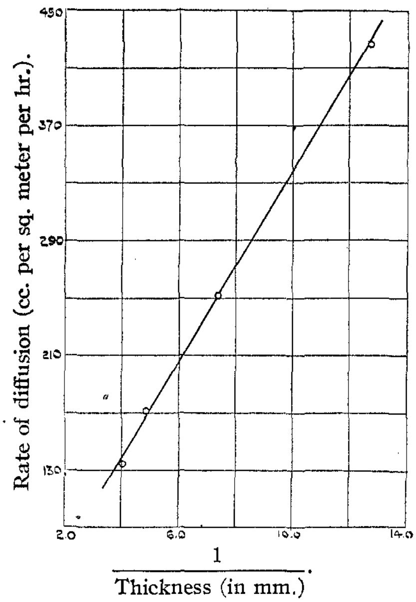

Fig. 9.—The relation between the rate of diffusion and thickness of silver at a temperature of 580°.

Table VII gives values for the rate of diffusion of oxygen through silver under various conditions. In one row are the values calculated from the formula deduced and in the following the observed values. On the whole, considering the number of factors which enter into a determination of this kind, the agreement is as good as might be expected.

The authors are extending the investigation over larger ranges of temperature, pressure and thickness and further work will also include the determination of the solubilities of various gases in metals under varying conditions. The investigation of the rate of diffusion of other gases through other metals will also be undertaken.

Table VII

Comparison of the Rate of Diffusion Calculated from the Formula with That Observed

A. Thickness of silver, 0.135 mm.; pressure of oxygen, 760 mm.

Temp., °C.	420	450	480	500	550	600
Rate[a] calc.	11.9	22.0	40	59	147	347
Rate[a] obs.	11.5	22.5	42	62	150	342

B. Thickness of silver, 0.135 mm.; pressure of oxygen, 392 mm.

Temp., °C.	420	450	480	500	550	600
Rate[a] calc.	8.5	15.8	28.7	42	105	249
Rate[a] obs.	8.5	14.0	26	37	92	210

C. Thickness of silver, 0.135 mm.; pressure of oxygen, 159 mm.

Temp., °C.	420	450	480	500	550	600
Rate[a] calc.	5.4	10.1	18.3	26.8	67	159
Rate[a] obs.	4.5	9.4	18	27	70	154

D. Thickness of silver, 0.248 mm.; pressure of oxygen, 760 mm.

Temp., °C.	420	460	500	540	580	620
Rate[a] calc.	6.5	14.7	32	67	134	264
Rate[a] obs.	6.0	16.5	37	73	134	253

TABLE VIII (*Concluded*)

E. Thickness of silver, 0.205 mm.; pressure of oxygen, 760 mm.

Temp., °C	420	460	500	550	600	640
Rate[a] calc	7.8	22.9	39	97	229	442
Rate[a] obs	7.0	19.0	43	99	239	495

F. Thickness of silver, 0.0787 mm.; pressure of oxygen, 760 mm.

Temp., °C	400	425	450	475	500	...
Rate[a] calc	13.3	22.7	37.8	62	101	...
Rate[a] obs	10.5	22.5	39.5	64	98	...

[a] Rate of diffusion: cc. per sq. meter per hour.

Summary

1. An apparatus has been described for the investigation of the rate of diffusion of oxygen through silver.

2. The rate of diffusion of oxygen through silver has been measured at temperatures varying between 400° and 630°, at oxygen pressures of 159 mm. 392 mm. and 760 mm., and for thicknesses of silver of 0.0787 mm., 0.135 mm. 0.205 mm. and 0.248 mm.

3. The relation between the rate of diffusion and the gas pressure, temperature and thickness of silver has been deduced from the curves obtained, and it has been found that the rate of diffusion varies as the 14.62 power of the absolute temperature, as the square root of the pressure and inversely as the thickness of silver.

4. An equation has been derived from which the rate of diffusion of oxygen through silver can be calculated for any pressure, temperature and thickness of silver. This equation is in the form $X = \frac{1.71}{10^{43}}\sqrt{\frac{p}{h}}\,T^{14.62}$ where X is the rate of diffusion in cc. per sq. meter per hour, p the pressure of the oxygen in millimeters of mercury, h the thickness of the silver in millimeters, and T is the absolute temperature.

MONTREAL, CANADA

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

A METHOD FOR THE DETERMINATION OF CALCIUM CARBIDE[1]

BY J. Y. YEE AND H. J. KRASE

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In connection with an investigation on the thermal decomposition of calcium cyanamide and of calcium carbide, an accurate method for the determination of the latter was necessary. The commonly used methods involve the measurement of the total gas liberated when the carbide is treated with water, the gas volume being dependent on such variables as

[1] The method described in this paper has also been successfully used in this Laboratory for the analysis of sodium carbide.