

The question of the relative efficiencies of the different elements used, as regards soft X-ray excitation, was not a primary object of the present investigation, but the experimental records have been carefully examined to see if any conclusions on this point could be drawn, the ratio, at a given voltage, of the photoelectric current to the thermionic current being taken as a measure of the efficiency of soft X-ray emission. This ratio for any one target was found, however, to vary to some extent with the actual value of the thermionic current, and also to be not always constant for a given value of this current. In a few instances we have records of the examination at low voltages of several elements in rapid succession under the same conditions, and in these cases the efficiency appears to be nearly the same for all the targets.

The authors desire to acknowledge their indebtedness to the Government Grant Committee of the Royal Society for the means of purchasing some of the apparatus and materials used in this research.

The Solubility of Hydrogen in Silver.

By E. W. R. STEACIE and F. M. G. JOHNSON, Department of Chemistry, McGill University, Montreal.

(Communicated by Prof. A. S. Eve, F.R.S.—Received September 29, 1927.)

Introduction.

In a previous paper* the authors have discussed the solubility and rate of solution of oxygen in silver.

The object of the present communication is to extend these results to the system hydrogen-silver.

A number of papers of a more or less qualitative nature have been published on the solubility of hydrogen in silver. Graham† obtained an absorption of 0.2 volume of hydrogen per volume of silver wire, and 0.9 volume for silver which had been reduced from the oxide. Chabrier‡ found that hydrogen which had been activated by the silent discharge was absorbed by silver. Neumann

* 'Roy. Soc. Proc.,' A, vol. 112, p. 542 (1926).

† 'Phil. Mag.,' vol. 32, p. 503 (1866).

‡ 'C. R.,' vol. 75, p. 484 (1872).

and Streintz* obtained negative results. Baxter† found an absorption of 0·5 to 2·8 volumes for silver which had been reduced from the oxide. Richards‡ investigated the solubility of hydrogen in silver in order to determine if any error were introduced into atomic weight measurements from this source. He found no weighable amount of hydrogen. Le Chatelier§ stated that silver absorbed hydrogen at temperatures above 600° C. and that the dissolved gas lowered the melting point 30° C. Berthelot|| found that thin silver foil spattered in the presence of hydrogen at high temperatures, pointing to the formation of an unstable hydride. Heald¶ found a slight absorption of hydrogen by thin silver films deposited on glass, but Baker** found no absorption under identically the same conditions.

The first attempt at a thorough investigation of the subject was made by Sieverts,†† who obtained evidence of an absorption of 0·13 volume of hydrogen from 600° C. to 800° C. His apparatus, however, was not sensitive enough to detect as small an amount as this with any degree of certainty. There were also several serious sources of error in his determinations. He did not allow sufficient time for the establishment of equilibrium; thus in one experiment he heated the tube containing silver from 20° C. to 800° C. and cooled it again to 300° C. in 158 minutes, taking pressure readings at various temperatures en route. The amount of time taken for the whole experiment was barely sufficient for equilibrium at one temperature only, except at the highest temperatures. Most of the hydrogen which disappeared in the course of his experiments was not recovered on heating *in vacuo*. This was undoubtedly due in part to diffusion through the quartz bulb, for which no correction was made. In addition a certain amount of hydrogen may have been used up in reducing traces of oxides.

The foregoing will serve to show that there is practically nothing in the literature on the solubility of hydrogen in silver in which much confidence may be placed.

* 'Wied. Ann.,' vol. 46, p. 431 (1892); 'Monats. Chem.,' vol. 12, p. 655 (1891).

† 'J. Am. Chem. Soc.,' vol. 22, p. 362 (1899).

‡ 'Z. Anorg. Chem.,' vol. 47, p. 70 (1905).

§ 'Z. Phys. Chem.,' vol. 8, p. 186 (1891).

|| 'Ann. Chim. Phys.,' 7th series, vol. 22, p. 305 (1901).

¶ 'Phys. Rev.,' vol. 24, p. 269 (1907).

** 'Phys. Rev.,' vol. 25, p. 422 (1908).

†† 'Z. Phys. Chem.,' vol. 60, p. 129 (1907); *ibid.*, vol. 68, p. 115 (1910).

Description of Apparatus.

The apparatus employed was essentially the same as that previously used with oxygen and silver. It consisted of a manometer connected to a bulb of known volume which contained silver foil. A definite volume of gas was admitted to the bulb and the pressure was read. The temperature was measured by means of a constant volume nitrogen thermometer. Knowing the temperature and the volume of the tube containing the silver, together with the volume of the dead space above the manometer, which was at room temperature, the pressure of the gas could be calculated. If the observed pressure were lower than that calculated, then the drop in pressure was a measure of the absorption.

Owing to the fact that hydrogen is absorbed by some glasses, and also diffuses through them at an appreciable rate, preliminary trials were made with various types of glass. Soft glass obviously could not be used over a sufficiently wide range of temperature. Pyrex glass was found to absorb hydrogen at a slow but appreciable rate. Jena combustion tubing showed a similar but somewhat smaller absorption. Experiments with quartz showed that while the diffusion of hydrogen through quartz was considerable, devitrification of the tube had very little effect on the rate of diffusion. It was finally decided to use a quartz tube and to correct for the gas lost by diffusion by means of a blank experiment with an empty tube, made from the same piece of quartz, and having as nearly as possible the same wall thickness and area of surface. Incidentally this enabled us to make a series of determinations on the rate of diffusion of hydrogen through quartz at various temperatures and pressures.

The apparatus, except for the addition of the blank, was the same as that described in a previous paper (*loc. cit.*). The blank consisted of a complete duplicate of the absorption apparatus, except, of course, that the bulb was empty instead of being filled with silver.

Two samples of silver foil were used, which were 0.40 mm. and 0.12 mm. thick respectively. The silver was prepared by reducing purified silver chloride with sugar and sodium hydroxide, as previously described.

Hydrogen was prepared by the electrolysis of dilute sulphuric acid. The gas was passed through a tower containing sticks of potassium hydroxide to free it from sulphur trioxide, and then over red-hot platinised asbestos to remove traces of oxygen. It was dried by bubbling through concentrated sulphuric acid, and stored in a reservoir over phosphorus pentoxide.

Experimental Procedure.

Before commencing an experiment, the furnace was heated to about 750°C. , and both the absorption apparatus and the blank were evacuated continuously for from 6 to 10 hours. Two Langmuir condensation pumps were used in series, and the pressure maintained during the evacuation was about 10^{-5} mm. Measured amounts of hydrogen were then admitted to both the absorption apparatus and the blank at the same time. The amount of gas let in to the blank was adjusted so as to produce the same pressure as that which existed in the absorption apparatus. Readings of pressure and temperature were taken from time to time for a number of hours. Owing to the absorption, the pressure fell more rapidly in the absorption apparatus than in the blank. The pressures were kept the same, however, except at the moment when a reading was being taken, by lowering the level of the mercury in the manometer of the blank apparatus.

At the conclusion of the experiment the gas in the two tubes was pumped out, collected, and measured.

Sample Calculation.

The complete data for one experiment are given in Table I.

Absorption Apparatus.—Part of the volume, V_1 , is in the furnace at a temperature T_1 , the remainder, V_2 , is at room temperature, T_2 . Hence

$$P (V_1/T_1 + V_2/T_2) = K.$$

In this case $V_1 = 8.680$ c.c., $V_2 = 3.671$ c.c. The constant, K , can be calculated from the volume of gas admitted, 0.780 c.c., and is 0.2168 . Hence P can be calculated for any values of T_1 and T_2 . In the third column of Table I is given the observed pressure, and in the fourth column that calculated in this way. In column five is given the difference between the observed and calculated pressures (for example, 0.28 cm. at 20 minutes). This difference is due partly to the disappearance of gas by diffusion through the quartz, and partly to absorption by the silver. The amount of gas which has disappeared, expressed in cubic centimetres at N.T.P., is equal to

$$0.28 \times 273/76 (V_1/T_1 + V_2/T_2) = 0.022 \text{ c.c.}$$

Blank Apparatus.—The amount of gas which has disappeared from the blank by diffusion can be calculated in the same way. For the blank $V_1 = 12.124$ c.c., and $V_2 = 2.776$ c.c. At 20 minutes the observed pressure is lower than that calculated by 0.05 cm., which is equivalent to a loss of 0.004 c.c. of gas.

Table I.

Absorption Apparatus.

Blank.

Volume of gas (N.T.P.)
Kc.c.
0.780
0.2168c.c.
0.800
0.2225

Room temperature.	Temperature.	Absorption apparatus.				Blank.				Time.	Ab-sorption, corrected.	Ab-sorption, volumes.
		Observed pressure.	Calculated pressure.	Pressure difference.	Cubic centimetres absorbed.	Observed pressure.	Calculated pressure.	Pressure difference.	Cubic centimetres diffused.			
° C.	° K.	cms.	cms.	cms.		cms.	cms.	cms.		mins.	c.c.	
27.8	976	10.10	10.28	0.18	0.014	10.25	10.25	0.00	0.000	0.5	0.014	0.004
27.7	976	10.07	10.28	0.21	0.016	10.24	10.25	0.01	0.001	5	0.015	0.005
27.6	975	10.02	10.27	0.25	0.019	10.21	10.24	0.03	0.002	10	0.017	0.005
27.3	972	9.98	10.26	0.28	0.022	10.18	10.23	0.05	0.004	20	0.018	0.006
27.2	974	9.96	10.27	0.31	0.024	10.16	10.24	0.08	0.006	40	0.018	0.006
27.3	973	9.90	10.26	0.36	0.028	10.12	10.23	0.11	0.009	60	0.019	0.006
27.0	975	9.83	10.27	0.44	0.034	10.08	10.24	0.16	0.013	100	0.021	0.006
26.3	973	9.76	10.26	0.50	0.039	10.01	10.23	0.22	0.017	145	0.022	0.007
25.1	973	9.62	10.26	0.64	0.047	9.93	10.23	0.30	0.023	220	0.024	0.007
26.0	973	9.57	10.26	0.69	0.053	9.88	10.23	0.35	0.028	295	0.025	0.008
26.0	973	9.49	10.26	0.77	0.057	9.82	10.23	0.41	0.033	350	0.024	0.007
26.1	977	9.33	10.29	0.96	0.071	9.68	10.26	0.58	0.046	530	0.025	0.008

Absorption constant for next 12 hours.

In the absorption apparatus 0·022 c.c. of gas has disappeared by absorption and diffusion, 0·004 c.c. of this is due to diffusion, hence the amount absorbed is 0·018 c.c. The silver weighed 34·08 grs.; assuming the density to be 10·5, this is equivalent to 3·25 c.c. Hence the absorption expressed in volumes of hydrogen per volume of silver is $0·018/3·25 = 0·006$.

As may be seen from Table I, about 300 minutes were required to establish equilibrium.

At the conclusion of the experiment the absorption apparatus was evacuated and the gas was collected and measured.

Volume of gas at start (cubic centimetres) at N.T.P.	= 0·780
Volume pumped out at end	= 0·701
<hr/>	
Gas not recovered	= 0·079
Gas lost by diffusion (calculated from blank)	= 0·083
<hr/>	
Difference	= 0·004

Hence all the gas absorbed by the silver was recovered, within the limits of experimental error.

Experimental Results.

Solubility of Hydrogen in Silver.—No apparent change in the silver took place, except for the development of a somewhat crystalline appearance on the surface, as previously noticed with oxygen.

The solubility of hydrogen in silver at various temperatures and pressures is given in Table II.

Table II.—Solubility of Hydrogen in Silver.

Press.	Temperature.							
	200° C.		300° C.		400° C.		500° C.	
	Absorption volumes.	\sqrt{P}/Q .	Absorption volumes.	\sqrt{P}/Q .	Absorption volumes.	\sqrt{P}/Q .	Absorption volumes.	\sqrt{P}/Q .
cms.								
5	0	—	trace	—	trace	—	0·003	748
10	0	—	trace	—	0·002	—	0·004	790
20	0	—	trace	—	0·003	1490	0·006	745
40	0	—	trace	—	0·004	1585	0·008	792
80	0	—	trace	—	0·006	1492	0·012	746

Table II—(continued).

Press.	Temperature.							
	600° C.		700° C.		800° C.		900° C.	
	Absorption volumes.	$\sqrt{P/Q}$.	Absorption volumes.	$\sqrt{P/Q}$.	Absorption volumes.	$\sqrt{P/Q}$.	Absorption volumes.	$\sqrt{P/Q}$.
cms.								
5	0.005	450	0.006	371	0.009	249	0.012	187
10	0.007	453	0.009	352	0.013	244	0.016	198
20	0.010	450	0.013	345	0.018	249	0.023	194
40	0.014	453	0.018	352	0.025	253	0.033	191
80	0.019	472	0.025	358	0.036	249	0.046	195

Diffusion of Hydrogen through Quartz.—The pressure in the blank apparatus fell rapidly at first, presumably due to the solution of hydrogen in quartz; after this the rate at which the gas disappeared was constant and was apparently due simply to diffusion. The results for the rate of diffusion are given in Table III.

Table III.—Rate of Diffusion of Hydrogen through Quartz.

Average wall thickness = 0.95 mm.

Surface area = 47.5 sq. cms.

D = rate of diffusion in cubic centimetres (at N.T.P.) per 1000 minutes.

Press.	Temperature.							
	200° C.		300° C.		400° C.		500° C.	
	D.	P/D.	D.	P/D.	D.	P/D.	D.	P/D.
cms.								
5	trace	—	0.003	1665	0.006	834	0.009	557
10	0.003	3340	0.006	1665	0.010	1000	0.017	588
20	0.006	3340	0.011	1820	0.021	955	0.033	607
40	0.013	3080	0.023	1740	0.041	975	0.066	607
80	0.023	3480	0.049	1640	0.079	1012	0.134	596
Mean		3310		1706		985		599

Table III—(continued).

	Temperature.							
	600° C.		700° C.		800° C.		900° C.	
	D.	P/D.	D.	P/D.	D.	P/D.	D.	P/D.
cms.								
5	0·014	357	0·037	135	0·071	70·5	0·137	36·5
10	0·029	345	0·071	141	0·145	69·0	0·270	37·0
20	0·058	345	0·160	125	0·294	68·1	0·550	36·4
40	0·114	351	0·325	123	0·581	68·8	1·095	36·5
80	0·230	348	0·615	130	1·160	69·0	2·226	35·9
Mean		349		131		69·1		36·5

The limit of accuracy of a single observation is about 0·002 c.c. Allowing an equal error for the corresponding blank experiment, the maximum possible error would be about 0·004 c.c., or slightly more than 0·001 volume. The values given in Table II are therefore good to about 5 per cent. at the higher temperatures and pressures. The absorptions at temperatures below 500° C. are of the same order of magnitude as the experimental error, and are therefore to be taken as merely qualitative indications of a very small absorption at low temperatures.

The rates of diffusion at higher temperatures are probably accurate to within 1 per cent. as far as the effect of temperature and pressure on the rate is concerned. The accuracy of the absolute values depends on the accuracy with which the thickness of the tube was measured. This was somewhat uncertain in the region where the capillary was fused to the wide tube. The thickness was measured at a number of places, and the average is given in Table III. This is probably uncertain to about 10 per cent.

Discussion of Results.

(I) *The Diffusion of Hydrogen through Quartz.*—From Table III it is evident that the ratio P/D (where P is the pressure and D the rate of diffusion) is constant at constant temperature, *i.e.*, the rate of diffusion is directly proportional to the pressure. This is in agreement with the results of Bodenstein and Kranendieck,* Wüstner,† and Williams and Ferguson.‡ Accordingly, the gas must diffuse through quartz as molecular hydrogen.

* 'Nernst Festschrift,' p. 100 (1912).

† 'Ann. Physik,' vol. 46, p. 1095 (1915).

‡ 'J. Am. Chem. Soc.,' vol. 46, p. 2160 (1922).

In fig. 1 the logarithms of the rates of diffusion are plotted against temperature. The points all fall on straight lines within the limits of experimental

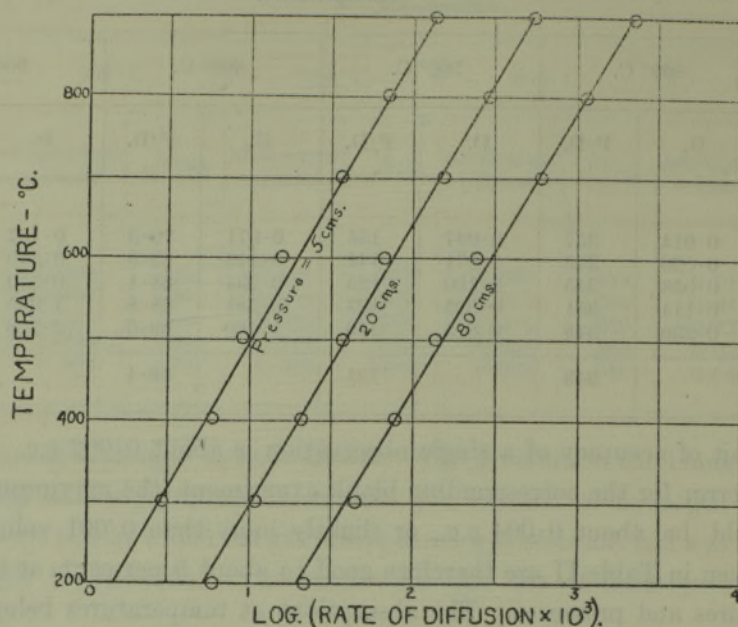


FIG. 1.—Rate of Diffusion of Hydrogen through Quartz.

error. The same relationship has been found to hold by Wüstner, and Williams and Ferguson.

The actual values obtained are similar to those of Williams and Ferguson, but the temperature coefficient is somewhat greater, and hence our results are higher than theirs at high temperatures. For the sake of comparison, the values are given in Table IV, in cubic centimetres of gas at 0° C. and 76 cms. pressure diffusing through 1 sq. cm. per hour, for a wall thickness of 1 mm.

Table IV.—Rate of Diffusion of Hydrogen through Quartz.

Temperature.	Steacie and Johnson.	Williams and Ferguson.
° C.		
440	1.2	1.6, 1.5, 1.9
610	3.5	5.1, 4.6, 6.2
727	8.1	12.0, 9.5, 8.0
881	25.0	17.7, 15.0

It is possible that the discrepancy is due to differences in the samples of quartz, although the samples used in both investigations were from the same source, the Thermal Syndicate, Ltd. The values, however, are of the same

order of magnitude, and the general effect of temperature and pressure is the same.

The fact that the rate of diffusion is proportional to the pressure, and that consequently the diffusing gas is in the molecular state, leads naturally to the conclusion that the process of diffusion is of a more or less mechanical nature, and is probably due merely to the passage of the gas through interstices in the quartz. This view receives support from the fact that the only gases which are known to diffuse through quartz are hydrogen and helium, the two lightest gases.

If the diffusion occurs in this way, however, it would naturally be expected that hydrogen, being the lighter of the two, would have the higher rate of diffusion. Actually, however, helium diffuses about 22 times as fast as hydrogen.* A possible explanation of this lies in the fact that the helium atom is symmetrical in form, while the hydrogen molecule is presumably unsymmetrical, and, taking an extreme case, a spherical atom would be expected to diffuse much more rapidly than an elongated molecule having about the same total volume. It is noteworthy that the temperature coefficients of the rates of diffusion of hydrogen and helium are almost identical, as would be the case if the process were one of capillary effusion. The temperature coefficient for helium becomes slightly greater than that for hydrogen at high temperatures, but this is to be expected, as the increased rotational energy of the hydrogen molecule would decrease the rate of diffusion to a certain extent.

Jacquerot and Perrot† have obtained a ratio for hydrogen and helium with porcelain which agrees with that calculated for a simple case of capillary diffusion. It would appear probable that the capillary spaces through which the gas diffuses are considerably larger in the case of porcelain than with quartz. Consequently, the effect of the shape of the molecules would be outweighed by their relative masses. It is only when the size of the pores is just slightly larger than the size of the gas molecule that the shape would become the predominating factor in the process of diffusion.

If the diffusion of hydrogen through quartz is a simple case of effusion, the temperature coefficient can be calculated from the kinetic theory. The chance of a molecule hitting an opening is proportional to its velocity and hence to \sqrt{T} . The rate of diffusion depends on both the chance of collision with an opening and on the number of molecules present. At constant pressure the number of molecules will be proportional to $1/T$. Hence the rate of diffusion will be

* Williams and Ferguson, *loc. cit.*

† 'Arch. Sci. Phys. Nat. Genève,' vol. 20, p. 128 (1905).

proportional to $1/\sqrt{T}$. The actual increase in the rate of diffusion with increasing temperature is far greater than this. There is, however, another factor which might account for this, and that is the increase in the size of the pores due to the thermal expansion of the quartz.

(II) *The Solubility of Hydrogen in Silver*.—As previously mentioned, the results in the literature are very conflicting. The values obtained in this investigation are given in Table II, and are plotted in fig. 2. They are much smaller than any of those obtained in previous investigations, with the exception of that of Neumann and Streintz, who obtained negative results. The explanation of this lies in the fact that most of the previous workers did not exhaust their apparatus for a sufficiently long time before making observations. As we have mentioned in the previous paper, the last traces of dissolved gases are only very slowly removed from metals. The same point has recently been emphasised by Bircumshaw* in connection with the solubility of hydrogen in aluminium and tin. Consequently most of the excess absorption reported has been due to loss of hydrogen by combination with residual oxygen. In the case of the investigation of Sieverts, this conclusion receives support from the fact that he was unable to recover the majority of the hydrogen which had disappeared. Silver which has been fused in air and rapidly cooled will contain practically the entire amount of oxygen which it dissolved at the melting point, say, from 0.3 to 0.4 volume of gas per volume of silver. Hence, if it is not thoroughly pumped out, as much as 0.6 to 0.8 volume of hydrogen may be used up in the formation of water. It is not surprising, therefore, that in the earlier investigations absorptions of about 0.6 to 0.8 volume of hydrogen were obtained, and that the gas was not recovered on heating *in vacuo*.

An outstanding example of this kind is the investigation of Bone and Wheeler.† In connection with their work on the catalysis of the hydrogen-oxygen reaction by hot surfaces, they measured the absorption of hydrogen by silver, and obtained the very high value of 11.4 volumes at a dull red heat. Of this only about 1.3 volumes were given off on heating *in vacuo*. The excess hydrogen was undoubtedly used up in combining with dissolved and adsorbed oxygen, the majority of which had not been removed by exhaustion as they merely used a "moist vacuum." There still remains, however, the comparatively large absorption of 1.3 volumes to be accounted for. The silver gauze had been repeatedly used as a catalyst and had developed a more or less spongy surface, as evidenced by photomicrographs given in their paper. Owing to the large

* 'Phil. Mag.,' 7th series, vol. 1, p. 510 (1926).

† 'Phil. Trans.,' A, vol. 206, p. 1 (1906).

surface, therefore, adsorption would come into play as well as absorption, and their results are not comparable with those obtained with silver in massive form.

The conclusion of Richards that, for atomic weight purposes, silver melted in hydrogen is as good as that melted in a vacuum is verified by our determinations. The maximum absorption found was 0.046 volume of hydrogen per volume of silver, or about 4.1×10^{-7} grams of hydrogen per gram of silver.

The observation of Le Chatelier, that the melting point of silver is lowered 30° by the presence of dissolved hydrogen, has not been confirmed. We were unable to detect any difference in the melting point of silver in hydrogen and in a vacuum. This is to be expected, as the amount of gas absorbed is so small that it could not have any appreciable effect on the melting point.

Effect of Temperature.—In fig. 2 the absorption is plotted against temperature at various pressures. Below 400°C. the absorption is extremely small; above

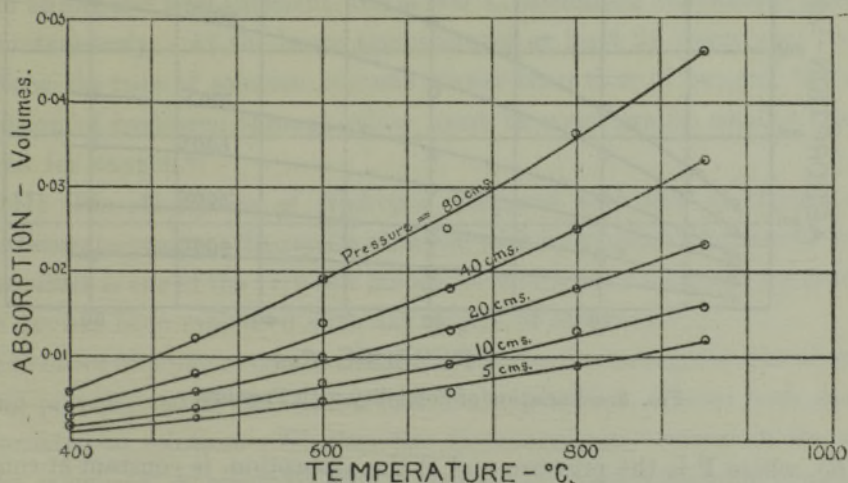


FIG. 2.—Variation of Solubility with Temperature.

this it increases rapidly with increasing temperature. The temperature coefficient is, however, much smaller than that observed with oxygen and silver. That the absorption is an exponential function of the temperature is shown by Table V. The values of $\log. \text{Absorption}/\text{Temperature}$ are practically constant, except for the one value at 400°C. , which is too low. Owing to the very small absorption at this temperature, however, the value is rather uncertain. If the absorption at 400°C. were increased by an amount equal to the probable experimental error, the value of $\log. \text{Abs.}/T$ would be brought into agreement with that at higher temperatures.

Table V.—Variation of Absorption with Temperature.

Pressure = 80 cms.						
Temperature ° K.	673	773	873	973	1073	1173
$\frac{\log_{10} \text{Abs.}}{T} \times 10^4$	1.15	1.40	1.46	1.44	1.45	1.42

Effect of Pressure.—The effect of pressure on absorption is shown in Table II, and the results are plotted in fig. 3. As may be seen from Table II, the ratio

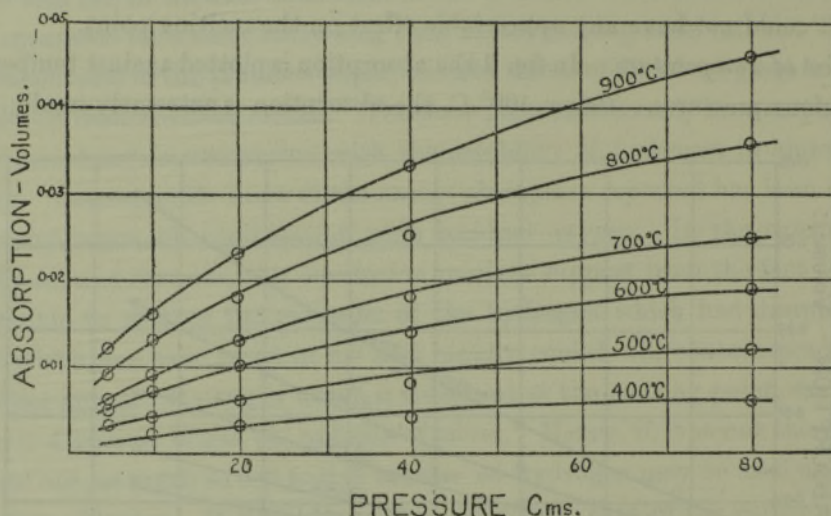


FIG. 3.—Variation of Solubility with Pressure.

$\sqrt{P/Q}$, where P is the pressure and Q the absorption, is constant at constant temperature. It accordingly follows from Henry's Law that the dissolved hydrogen must be dissociated into atoms, or else that it must exist in the form of a dissolved hydride containing one atom of hydrogen to the molecule. This seems to be a general relationship which holds for the solubility of all gases in metals, with the exception of hydrogen in palladium,* and in some of the rare earth metals.†

Effect of Surface.—Identical values for the absorption were obtained with silver foil of two different thicknesses. Hence the effect of adsorption is negligible compared with that of solution. The high values obtained by Bone

* Hoitsema, 'Z. Phys. Chem.,' vol. 17, p. 1 (1885); Holt, Edgar, and Firth, *ibid.*, vol. 82, p. 513 (1913); Sieverts, *ibid.*, vol. 88, p. 105 (1914).

† Sieverts, Müller-Goldegg, and Roell, 'Z. Anorg. Chem.,' vol. 131, p. 65 (1923); vol. 146, p. 149 (1925); vol. 150, p. 261 (1926); and vol. 153, p. 289 (1926).

and Wheeler make it possible that even at a red heat adsorption will predominate if the surface is sufficiently large. On the other hand, Benton and Elgin* obtained no evidence of adsorption at 110° C. with silver sponge. As adsorption usually decreases with increasing temperature, it seems likely that Bone and Wheeler are in error, especially in view of the inaccuracies in their experiments which we have pointed out above.

The Rate of Solution.—Owing to the small amount of hydrogen absorbed at the lower temperatures, and to the speed with which equilibrium was established at the higher temperatures, the measurement of the rate of solution was not practicable, as comparatively small errors in the amount of gas absorbed would have a very large effect on the rate of solution. The rate of solution is, however, rather slow compared to that of oxygen. At 700° C. from 50 to 100 minutes were required for equilibrium, depending on the pressure. At 800° C., 10 or 15 minutes were sufficient, and at 900° C. saturation was reached practically instantaneously. At the lower temperatures at least 24 hours were required.

Since the rate of solution is much slower than that of oxygen, the rate of diffusion of hydrogen through silver must be considerably smaller than that found for oxygen.†

(III) *The Absorption of Hydrogen compared with that of Oxygen.*—It is interesting to compare the results obtained with hydrogen with those for oxygen, since silver is one of the very few metals for which the absorption for more than one gas has been measured with any degree of accuracy.

The effect of pressure on absorption is the same for both gases, the absorption being proportional to the square root of the pressure. Hence both gases are dissociated in solution. Whether the dissociated gas remains in the atomic state, is ionised, or reacts to form a hydride or oxide containing one atom of hydrogen or oxygen to the molecule, cannot be decided by pressure measurements alone. The state of the dissolved gas will be discussed further later.

The amount of hydrogen absorbed by silver is much less than that of oxygen. This is not surprising, since silver has a much greater affinity for oxygen than for hydrogen, as shown by the fact that it forms one definite stable oxide Ag_2O , and perhaps others, such as Ag_2O_3 , and Ag_2O_2 , while there is no reliable evidence that a hydride of silver has ever been prepared.

The effect of temperature on the absorption of hydrogen by silver is entirely different from that with oxygen. With oxygen there is a clearly defined

* 'J. Am. Chem. Soc.,' vol. 48, p. 3027 (1926).

† Johnson and Larose, 'J. Am. Chem. Soc.,' vol. 46, p. 1377 (1924), and vol. 49, p. 312 (1927).

minimum at about 400°C. , after which the absorption increases rapidly with increasing temperature. With hydrogen there is no such minimum. In a previous paper it was concluded from a consideration of the effect of temperature on the solubility and rate of solution of oxygen in silver, that the minimum in the solubility at 400°C. must be due either to a change in the manner of combination of the oxygen, or to a change in the silver from one allotropic modification to another. The fact that there is no similar behaviour with hydrogen seems to render unlikely the possibility of another form of silver existing above 400°C. , and the cause of the peculiar behaviour of oxygen and silver must be the state in which the oxygen exists in solution. It is noteworthy that the minimum in the solubility of oxygen in silver at 400°C. corresponds exactly with the minimum in the heat of formation of silver oxide, calculated by Keyes and Hara* from their measurements of the dissociation pressure of oxygen in equilibrium with silver oxide.

General Discussion.

The Diffusion of Gases through Metals.—The absorption of gases by metals and the diffusion of gases through metals are phenomena which are dependent upon each other. Since a gas molecule or atom must diffuse into the metal before it can be absorbed, it is of interest to discuss the mechanism of diffusion before considering absorption. The system oxygen-silver has been fairly thoroughly investigated, and it will be used as a typical system for purposes of discussion.

The fact that the rate of diffusion is proportional to the square root of the pressure points to diffusion taking place by means of atoms and not molecules. As indicated above, the absorbed gas is also in the dissociated condition. Since the diffusion of oxygen through silver is due to atomic and not to molecular oxygen, it is natural to suppose that the rate of diffusion will depend on the concentration of atomic oxygen outside the metal.

If we accept Langmuir's theory of the mechanism of adsorption,† and assume that every oxygen molecule which strikes a silver surface condenses, while the rate at which oxygen atoms evaporate from the surface depends on the temperature, then adsorption will be a time lag between the rate of condensation and the rate of evaporation. The amount of gas adsorbed will decrease as the temperature is raised because the rate of evaporation increases, while the rate of condensation remains almost constant.

* 'J. Am. Chem. Soc.,' vol. 44, p. 479 (1922).

† 'J. Am. Chem. Soc.,' vol. 38, p. 2221 (1916).

Atomic oxygen will be in existence only at the moment when an adsorbed atom evaporates from the surface. At low temperatures the life of an adsorbed atom is comparatively long, and consequently there will be very few leaving the surface, and hence very little free (*i.e.*, unadsorbed) atomic oxygen in contact with the surface. At high temperatures, the life of an adsorbed atom on the surface will be extremely short. The surface will thus have very little adsorbed gas. Every molecule which strikes the surface will still be condensed, but will almost immediately leave again in the form of atoms. Hence as the temperature rises, although the actual amount of adsorption decreases, the concentration of atomic oxygen in the neighbourhood of the surface will increase rapidly. Those atoms which leave the surface in an outward direction will recombine at once to form molecular oxygen. Some, however, will leave it in an *inward* direction and will diffuse into the metal. The number entering the metal, *i.e.*, the rate of diffusion, will depend on the concentration of free atoms at the surface, and will consequently increase very rapidly with rising temperature. The rate of diffusion will thus depend simply on the rate of formation of atomic oxygen at the surface, that is, on the rate of evaporation of adsorbed atoms from the surface. The effect of temperature on the rate of evaporation from the surface is given by

$$M = A\sqrt{T} \exp.(-\lambda/RT),^*$$

where A is a constant and λ is the internal latent heat of evaporation. It has been shown by Johnson and Larose (*loc. cit.*) that the rate of diffusion of oxygen through silver is expressed by Richardson's equation

$$Q = K\sqrt{T} \exp.(-q/RT),$$

where Q is the rate of diffusion and q and K are constants. Richardson's equation also holds for the diffusion of hydrogen through platinum,[†] nickel,[‡] and steel.[§] The above two equations are identical in form, and hence it seems fairly well established that the rate of diffusion depends on the rate of evaporation of adsorbed atoms from the surface.

The Absorption of Gases by Metals.—In the absorption of oxygen by silver, the higher the temperature the farther is the system removed from the dissociation temperature of Ag_2O . It might, therefore, be expected that the

* Langmuir, 'J. Am. Chem. Soc.', vol. 35, p. 122 (1913).

† Richardson, 'Phil. Mag.', 6th series, vol. 7, p. 266 (1904); Richardson, Nicol and Parnell, *ibid.*, vol. 8, p. 1 (1904).

‡ Deming and Hendricks, 'J. Am. Chem. Soc.', vol. 45, p. 2857 (1923).

§ Ryder, 'Elect. J.', vol. 17, p. 161 (1920).

absorption would decrease with increasing temperature. Actually, the reverse occurs once the minimum at 400°C . is passed, and in general with almost all gases and metals the absorption increases with increasing temperature. It is possible to account for this on much the same basis as Langmuir has used for adsorption.

As we have shown above, oxygen atoms diffuse through silver at a rate which is proportional to the concentration of atomic oxygen outside the metal. If we assume that every oxygen atom which hits a silver atom in the *interior* of the silver reacts to form a compound, and that the oxide thus formed dissociates at a rate which depends on the temperature, the absorption will be a time lag between the rate of combination and the rate of dissociation. With adsorption the rate of condensation increases only slowly with rising temperature, while the rate of evaporation increases rapidly; hence adsorption decreases with increasing temperature. With absorption, however, while the rate of dissociation increases rapidly with rise in temperature, the rate of combination depends on the number of atoms diffusing through the metal and this increases very rapidly with increasing temperature. Hence in general absorption will increase as the temperature increases.

From this point of view, absorption and adsorption are fundamentally similar. Adsorption takes place on the surface and depends on the number of hits registered by gas molecules. Absorption takes place inside the metal and depends on the number of hits by diffusing atoms.

The amount of gas absorbed is thus a balance between two opposing factors. In the case of silver and oxygen, the rate of diffusion is extremely small at low temperatures. It is therefore possible that the minimum in the solubility at 400°C . is due to the fact that the rise in temperature above the dissociation temperature causes a greatly increased rate of dissociation of silver oxide which is not outweighed by the increased rate of diffusion until 400°C . is reached. It is noteworthy that the rate of diffusion only becomes appreciable in the neighbourhood of 400°C . It is probable that minima would be discovered with other gases and metals if sufficiently accurate measurements were made at low temperatures.

There are very few cases in which the absorption does not increase with increasing temperature. Decreases are shown with rising temperature in the absorption of hydrogen by palladium, and by some of the rare earth metals. For these, as mentioned above, the absorption is not proportional to the square root of the pressure, and hence is not due to atomic hydrogen, but either to molecular hydrogen or to compound formation. The only other cases of this

sort are the absorption of hydrogen by vanadium and titanium,* and the absorption of nitrogen by iron,† where there seems to be little doubt that definite compounds are formed.

It appears probable that the absorption of gases by metals is only a particular case of a much more general phenomenon. If a gas and a solid possess a mutual attraction for one another, as manifested by the formation of a definite chemical compound at low temperatures, it is very unlikely that this affinity will cease altogether at some sharply defined dissociation temperature. Thus with oxygen and silver, although much above the dissociation temperature of Ag_2O , the gas still possesses sufficient affinity for the silver to dissolve in it at high temperatures. It seems probable that if any gas and solid unite to form a definite compound at low temperatures, then the gas will dissolve in the solid to some extent at temperatures above the dissociation temperature of the compound. Thus, for example, we would expect oxygen to dissolve in the lower oxide of a metal at temperatures above that at which the higher oxide dissociates. Similarly, water would be expected to dissolve to some extent in solid salts above the dissociation temperature of hydrates. A certain amount of evidence exists for the solubility of oxygen in lower oxides. Thus Leblanc and Sachse‡ have obtained evidence of the absorption of oxygen by NiO at 350°C ., and Leblanc§ detected the absorption of oxygen by litharge.

Summary.

The solubility of hydrogen in silver has been investigated from 200° to 900°C . at pressures from 5 to 80 cms. The solubility first becomes appreciable at 400°C . The solubility increases exponentially with increasing temperature. It is proportional to the square root of the pressure.

A mechanism has been suggested for the absorption of gases by metals, and the connection between absorption, adsorption, and diffusion has been discussed.

The diffusion of hydrogen through quartz has also been measured from 200° to 900°C . It has been shown that the assumption that the diffusion of hydrogen through quartz is of a mechanical nature is in accord with the observed facts.

* Sieverts, Huber and Kirschfeld, 'Ber. d. Chem. Ges.,' vol. 59, p. 2891 (1926).

† Neumann, 'Stahl und Eisen,' vol. 34, p. 252.

‡ 'Z. Elektrochem.,' vol. 32, p. 204 (1926).

§ 'Ann. Chim. Phys.,' vol. 6, p. 480 (1846).