

follows from equilibrium considerations. The extrapolation in Fig. 7 shows that there is no bonding whatsoever for the ethoxyethanol at infinite dilution. This means that any bonding which the molecule undergoes in actual solutions must be of the intermolecular type. On the other hand, the substituted propanol and butanol show considerable bonding even at infinite dilution. This is to be attributed to ring formation. Moreover, ethoxypentanol shows only small hydrogen bonding at zero concentration. This can be associated with the fact that the pentanol would form a ring too long for stability.

It appears from these results that the most stable rings involving hydrogen bonds contain 6 or 7 atoms, including the hydrogen. These numbers are greater by one than those usually given for rings involving only the ordinary electron pair type of bond. No explanation seems immediately forthcoming as to why a five-membered hydrogen bond ring should be unstable, yet there seems to be no doubt as to the absence of ring formation in 2-ethoxyethanol-1.

Conclusion

The infrared absorption spectra of carbon tetrachloride solutions of various glycols and ethoxyalcohols have been studied in the neighborhood of

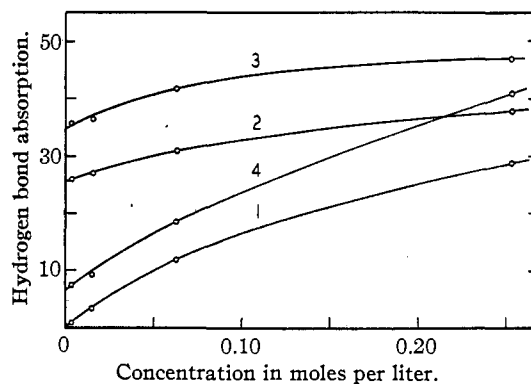


Fig. 7.—Heights of hydrogen bond peaks (1) 2-ethoxyethanol-1, (2) 3-ethoxypropanol-1, (3) 4-ethoxybutanol-1, (4) 5-ethoxypentanol-1.

2.8 μ . The results show that the ethoxyalcohols can associate through the formation of intermolecular hydrogen bonds. Also the substituted propanol and butanol can form stable rings, whereas ethoxyethanol shows no evidence of ring formation. The glycols likewise demonstrate hydrogen bonding, but the evidence for their precise behavior is not conclusive because of their limited solubility. The authors are indebted to Professors W. H. Rodebush and A. M. Buswell for many helpful suggestions and for their kind interest in the work.

URBANA, ILLINOIS

RECEIVED JULY 5, 1939

[CONTRIBUTION FROM THE SCHOOL OF PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

On the Degassing of Hydrogen-Charged Palladium

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For a long time experimenters have recognized that palladium sorbs very great quantities of hydrogen gas. Metals such as iron and nickel are known to sorb hydrogen and other gases in varying quantities, portions of which are held tenaciously even when the metals are heated to the melting point in vacuum. While there is considerable indirect evidence suggesting that palladium releases its sorbed gas quickly at comparatively low temperatures, apparently no direct measurements have been made of the degassing of palladium in vacuum.

In a recent investigation of the palladium-hydrogen equilibrium by Gillespie and Gal-

staun,² a series of pressure-composition isotherms over the range 80–313° is presented and several palladium hydrides postulated to explain the existence of certain discontinuities in the isotherms.

In the preparation of the palladium black with which these experiments were carried out, Gillespie and Galstaun reduced palladosammine chloride in hydrogen. The black was degassed of hydrogen at 500° in a stream of carbon dioxide and then cooled. It was further degassed in an evacuated Pyrex bulb by heating with a hand torch until the glass began to soften. The black was then transferred to the reaction bulb and hydrogen admitted in order to clean up adsorbed oxygen.

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(2) Gillespie and Galstaun, *THIS JOURNAL*, **58**, 2565 (1936).

Further degassing was carried out at the experimental temperatures³ (200–313°).

Question has been raised⁴ as to whether the procedure used by Gillespie and Galstaun was sufficient to remove all significant amounts of hydrogen from the palladium sample before the measurements were taken. The possibility of a small amount remaining in the palladium even under very strenuous degassing was suggested. Such a residual amount might cause serious error in the concentration values used by Gillespie and Galstaun and correction of the error would necessitate assumption of different hydrides from those mentioned.

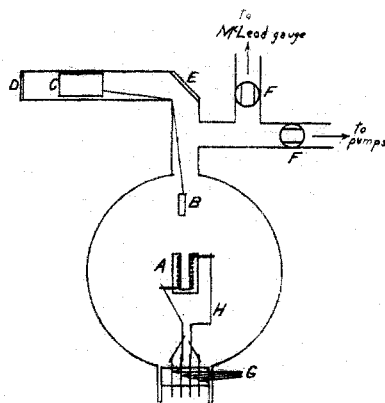


Fig. 1.

The work of Gutbier⁵ and Kemmerer⁶ on the determination of the atomic weight of palladium is open to similar objection, *viz.*, that neither of these investigators made certain that the palladium samples used were free of hydrogen. Kemmerer's technique differs from that of Gutbier in that Kemmerer allowed the hydrogen-treated sample to cool from 955° to room temperature in an atmosphere of nitrogen while the highest temperature at which degassing might have taken place in Gutbier's treatment was about 500°.

The purpose of this investigation is to make some quantitative determination of the degassing of hydrogen-charged palladium at various temperatures up to the melting point of palladium and to determine whether a considerable amount

of hydrogen is retained at low temperatures (200–600°).

The experimental work is divided into two sections, the first of which deals with the degassing of palladium over the temperature range 650–1553°; the second covers the degassing experiments at temperatures 180–440°.

Experimental. I

Apparatus.—Figure 1 shows a schematic representation of the degassing apparatus which consists essentially of a small high-temperature furnace in a closed system with auxiliary mechanism for evacuation of system, introduction of the palladium sample and measurement of pressure changes. A refers to the crucible, B to the metallic palladium sample suspended by a thin tungsten wire from a soft-iron cylindrical shell C. The shell may be moved by magnets outside the system and the palladium lowered into the furnace at will. D is a plane piece of Pyrex sealed onto the tube; E is an aluminized mirror sealed in and inclined so that the interior of the crucible may be seen by viewing through D. F and F are mercury seal stopcocks. G indicates four 60 mil tungsten leads sealed into the bulb. H shows the 40 mil nickel wires used to support the crucible and conduct current to the tungsten furnace winding. All interior connections are spot-welded. 110 v. d. c. through a suitable system of control rheostats was used to heat the furnace. A current of 9.5 amp. was sufficient to attain the highest temperatures used—about 1600°.

The furnace itself consists of a 20 mil tungsten winding embedded in zirconium oxide shaped in crucible form. Crucible dimensions do not exceed 2 cm. each way. Zirconium chloride added to the oxide paste served as a binder until the whole had been fired by a hand torch.

Samples and Charging.—In these experiments metallic palladium rod was used instead of palladium black. The electrolytic charging method was found to be the only efficient method of charging the solid samples.

Dilute sulfuric acid (5% by weight) was used as the electrolyte in the charging cell. The sample of palladium was made the cathode of the cell and held by a platinum electrode sealed through glass under an inverted 50-cc. buret filled with the electrolyte. The hydrogen given off at the cathode either entered the palladium sample or came off in gaseous form and was collected in the buret. By passing a known charge through the cell and observing the amount of gas collected, the amount of hydrogen sorbed by the palladium could be deduced. In reducing the amount of gas collected to N. T. P. correction was made for the vapor pressure of the solution which was assumed sufficiently dilute to be considered the same as pure water. No correction was made for the amounts of hydrogen in solution in the electrolyte; these were so small as to be negligible (0.00016 g. of hydrogen dissolves in 100 g. of water at 20° and 1 atm. hydrogen pressure).

The palladium sample was charged past equilibrium by this electrolytic method, but on standing lost gas until approximate equilibrium was reached. After several chargings a nearly constant H/Pd ratio was obtained and at this ratio the sample was considered completely charged.

(3) This use of hydrogen to clean up adsorbed oxygen was not mentioned specifically in Gillespie and Galstaun's paper, but Dr. Gillespie in written communication with Dr. W. R. Ham (of The Pennsylvania State College) stated that the clean-up technique was used and has been described by him in a previous paper: Gillespie and Hall, *THIS JOURNAL*, **48**, 1207 (1928).

(4) Dr. W. R. Ham raised this question in the unpublished correspondence with Dr. Gillespie.

(5) Gutbier, *J. prakt. Chem.*, N. F., **79**, 235 (1909).

(6) Kemmerer, *THIS JOURNAL*, **30**, 1701 (1908).

Degassing.—For degassing, the charged sample was cut in half and one part left under the buret while the other was sealed into the degassing chamber. In this way a check was had on the amount of gas given up by the sample in the sealed chamber during the time prior to actual degassing.

The general technique of degassing was as follows. The furnace was heated to the highest temperature to be used in the degassing process and the system thoroughly degassed. Then the furnace was cooled to approximately 650°, system closed off and palladium introduced to furnace. Large amounts of hydrogen were liberated, but pressure change was not measured until furnace and gas had been cooled down to room temperature. The system was then evacuated thoroughly, closed off and furnace and sample again degassed at 650° to determine the amount of hydrogen sorbed when furnace and sample were cooled in the atmosphere of liberated hydrogen. This correction proved to be slightly more than 1%.

After evacuation at 650° the system was again closed off and temperature raised to 1550° in order to melt the palladium. Pressure change over the range was recorded.

Experimental. II

Apparatus.—Figure 2 shows a schematic diagram of the degassing apparatus used for the low temperature measurements. A refers to a heavy nickel tube about 14" (35.5 cm.) long with inside diameter 3/8" (1 cm.) and outside diameter 13/16" (2.1 cm.) situated in the nichrome wound electric furnace D. B refers to water coolers brazed onto the ends of the nickel tube to cool the de Khotinsky joints E where the nickel tube is sealed to the glass tubing which makes up the remainder of the system. C is the chromel-alumel thermocouple used to measure furnace temperatures. Its leads pass out through de Khotinsky joints F. I represents the charged sample of palladium which is attached by a stiff nichrome wire to a small piece of soft iron which may be moved by means of magnets from the outside. G and H indicate mercury seal stopcocks and K denotes the mercury manometer on which pressure changes may be read. For this series of experiments stopcock G was closed and manometer alone was used.

Samples and Charging.—A thin palladium tube about 3 mm. in diameter and 3 cm. long was used. The tube was charged by the electrolytic method exactly as described in the first section except that no particular effort was made to reach the final equilibrium charge each time. After several electrolyses the sample would spontaneously degas to a certain extent and when this occurred the tube was considered sufficiently charged.

Degassing.—The charged sample was attached to the nichrome wire and sealed into the system. The furnace was heated to the experimental temperature desired and system allowed to degas for several hours at this temperature. Then stopcock H was closed and the palladium sample introduced to the furnace. At this point time and manometer readings were recorded. Usually the degassing of the sample started within one minute from the time of introduction into the furnace and continued for a considerable period of time, especially at the lower temperatures. When the manometer reading remained constant for several minutes the degassing was taken to be complete;

the sample was withdrawn and the furnace shut off so that the system could come to room temperature. When the system was cool, manometer, temperature and barometric pressure readings were taken. These together with the volume of the system allowed calculation of the amount of gas liberated by the palladium.

It was thought for a time that the low-temperature degassing might not be complete or that the furnace and palladium might re-sorb considerable quantities of hydrogen and to detect these the system was evacuated cold, closed off and heated several hundred degrees higher than the experimental temperature, whereupon the sample was readmitted and degassed further. It was found that the hydrogen given off during this process was about 3% of the total at the lowest temperature and negligible at the three higher ones.

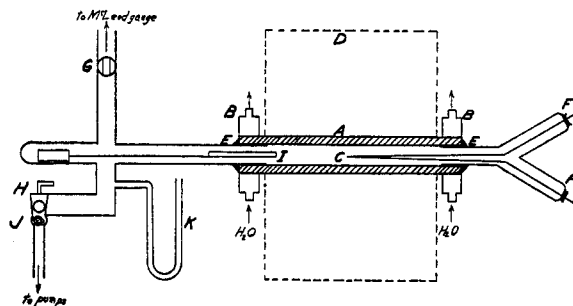


Fig. 2.

Experimental Data and Results

TABLE I

CHARGING DATA

Wt. of sample, 0.690 g.; H₁, cc. of hydrogen collected in buret during electrolysis (reduced to N. T. P.); H₂, cc. of hydrogen given up on standing (reduced to N. T. P.).

No.	Current, mils	Time, min.	H ₁ , cc.	Initial H/Pd	H ₂ , cc.	Final H/Pd
I	0.150	89.5	51.5	0.577	0	0.577
II	.150	60.8	50.8	.753	2.6	.718
III	.150	55.5	51.8	.800	5.3	.727
IV	.150	54.7	51.8	.800	6.9	.705
V	0	0	0	.705	0.5	.698

TABLE II

DEGASSING DATA

Wt. of sample, 0.336 g.; vol. of system, 1300 cc.; H indicates cc. hydrogen at N. T. P.

Temp., °C.	Pressure change "	H, cc.	H/Pd
650	15,600	24.6	0.700
650	156	0.25	.007
650	43	0.07	.002
1553	17	neg.	..

Total 0.709

TABLE III

Degassing temp., °C.	Degassing time	H/Pd Apparent	H/Pd Correction	H/Pd Charge	% Variation
181	14 hrs.	0.619	0.017	0.618	3
225	50 min.	.676665	2
297	3 min.	.665671	1
438	1 min.	.646672	4

Discussion

Table I gives the charging data and calculations. From Table I we see that the first electrolysis was sufficient to bring the ratio of hydrogen to palladium atoms to 0.577. This charge was evidently well below equilibrium because no hydrogen was lost on standing. Further electrolysis succeeded in raising the charge as high as 0.800, but on standing hydrogen was lost spontaneously until the ratio fell to about 0.700. This loss of hydrogen was easy to follow visually, for on breaking the current bubbles of hydrogen continued to come from the sample until the equilibrium charge was reached.

Row V shows the amount of hydrogen lost over a two-day period after the fourth electrolysis, and 0.698 represents the stable charge ratio of the sample at room temperature. Observations on the control sample show no further loss of hydrogen during the remainder of the time prior to actual degassing.

This final, stable charge is in good agreement with results of von Samson-Himmelstern⁷ who found, on electrolytically charging palladium at 20°, stable charge values from 0.70 to 0.80. Of his seven determinations, four lie between 0.70 and 0.72.

The 30° isotherm of Gillespie and Hall⁸ shows that at an external hydrogen pressure of 500 mm. about 72.5 cc. of hydrogen is sorbed by each gram of palladium. This amount is equivalent to an atomic ratio of about 0.69. From the curvature of the isotherm it seems likely that a moderate increase in external pressure would have brought the equilibrium charge up to 0.70.

Table II shows the degassing data and calculated results. At 650° an initial large change in pressure is recorded. The succeeding pressure changes represent the amount of gas taken up by the furnace and sample upon cooling in the liberated hydrogen.

The apparent concentration of hydrogen in palladium as shown by the 650° degassing is 0.709. This value is in close agreement with that of the known initial charge, 0.698. The variation here is about 1.6%, which is within the experimental error.

The degassing at 1553°, the melting point of palladium, gave rise to a very small pressure change and indicated that a negligible amount of hydrogen was given off.

Table III shows the results of degassing a charged sample at four temperatures lower than

650°. Of these four trials the first at 181° was the only one in which any appreciable amount of hydrogen came off during the second degassing. The 0.619 apparent H/Pd came off over a period of fourteen hours at 181° and the 0.017 correction came off in less than a minute at about 300°. Thus the total charge indicated for this trial was about 0.636 H/Pd.

The variations between the H/Pd ratio as shown by degassing and the H/Pd ratio calculated from electrolytic charging data are from 1 to 4%. These variations are erratic and are due to experimental error.

Within the uncertainty of the experiment these data show that massive hydrogen-charged palladium degasses completely and rapidly in vacuum at temperatures as low as 300°. Below this temperature degassing occurs, but takes place over much greater lengths of time and at temperatures below 200° is probably not complete.

While these data apply strictly to massive palladium, similar results obtain without doubt for palladium black. Massive palladium is notoriously more difficult to use in equilibrium experiments because of the slowness with which it takes up or gives off hydrogen. One would expect the degassing of palladium black to be somewhat more rapid than that of massive palladium, but otherwise essentially the same.

Summary

A stable charge of hydrogen in palladium is obtained by the electrolytic method such that the ratio H/Pd is equal to 0.698. This value agrees well with the existing experimental data on the subject.

It is shown within the limits of experimental error that all of the important amounts of hydrogen in a charged sample of massive palladium are driven off by degassing in vacuum at temperatures as low as 300°. Below this temperature degassing occurs but at much slower rates and with less probability of completion.

Further degassing up to the melting point shows negligible liberation of hydrogen.

No correction for unremoved hydrogen in the atomic weight of palladium as determined by Gutbier⁵ and Kemmerer⁶ is indicated. The assumption of Gillespie and Galstaun² that their samples of palladium black were sufficiently well degassed by treatment at 650° and over the range 200–300° is correct.

(7) Von Samson-Himmelstern, *Z. anorg. Chem.*, **186**, 337 (1930).

(8) L. J. Gillespie and F. P. Hall, *THIS JOURNAL*, **48**, 1212 (1926).