[CONTRIBUTION FROM THE FRICK CHEMISTRY LABORATORY, PRINCETON UNIVERSITY]

The Role of Intragranular Fissures in the Occlusion and Evolution of Hydrogen by Palladium

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Among the most striking observations in the already extensive literature relating to the comportment of palladium with hydrogen, are those which concern the irreversibility of the occlusive process. Hydrogen is absorbed with less readiness than that with which it is again given off.

Thus, Lambert and Gates,[1] Gillespie and Hall[2] and Brüning and Sieverts[3] have observed that at constant temperature the pressure pertaining, during absorption, to a certain concentration of dissolved hydrogen, is greater than the steady pressure which establishes itself for this same concentration when the gas is being withdrawn. Since the latter, as the pressure which the system is itself able to maintain, may naturally be regarded as corresponding to the condition of equilibrium, the preceding statement is equivalent to saying that, in order to drive hydrogen into the metal, a pressure in excess of the equilibrium value is required. Absorption is therefore affected by something of the nature of a frictional resistance, to which evolution is much less subject.

This behavior is comprehensible in the light of the metallographic evidence recently obtained[4] that the primary distribution of hydrogen in palladium is along fissures in certain crystallographic planes of the grain; and that the fissures are in part closed, and the primary lacunal diffusion is throttled, by the distension of the surrounding metal as the secondary diffusion into the undisordered grains brings about expansion of the lattice. Ample evidence of this expansion exists in the results of Krüger and Gehm[5] and of several earlier investigators by x-ray methods.[6–10]

During absorption, therefore, the surrounding metal is steadily expanding, progressively closing the entry fissures, and producing the frictional resistance referred to above; during evolution, on the contrary, the lattice is contracting and the fissures are consequently enlarged, enabling the interior portions of the system to maintain equilibrium with the gas phase.

Another characteristic of the occlusive comportment of palladium, which has been repeatedly observed,[11–16] is its great variability. Absorption, and in lesser degree evolution, differ in velocity from specimen to specimen, and in the same specimen from time to time. This also is not difficult to understand if the number and openness of the crevices are the determining factors.

In the metallographic study,[4] it was also observed that, in rolled foils, the fissured planes that constitute the paths of primary diffusion, are rather widely spaced members of certain octahedral and dodecahedral sets, both of which form with the direction of rolling the angle of maximum shearing stress of 45 degrees; whence the conclusion is suggested that the fissured, active planes are those upon which slip has occurred during a previous plastic deformation of the metal.

It was therefore the principal purpose of the experiments below described to obtain evidence with regard to the effects of deformation, and hence of disturbance of planes of slip, upon the readiness with which hydrogen enters and leaves palladium. To make clear the bearing of this evidence it was necessary, however, to include several other factors, so that the experiments have extended to a general investigation of: (1) the velocity with which gaseous hydrogen is taken up, or, as it may be termed, the avidity of palladium; and (2) the readiness with which hydrogen is

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(2) L. J. Gillespie and F. P. Hall, THIS JOURNAL, **48**, 1207 (1926).

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(6) L. W. McKeehan, *Phys. Rev.*, **20**, 82 (1922).

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(11) T. Graham, *J. Chem. Soc.*, **20**, 235 (1867).

(12) A. Holt, E. C. Edgar and J. B. Firth, *Z. physik. Chem.*, **82**, 513–540 (1913).

(13) A. Coehn and K. Sperling, *Z. Physik*, **83**, 291–312 (1933).

(14) G. Tammann, *Z. Elektrochem.*, **35**, 21–28 (1929).

(15) G. Tammann and J. Schneider, *Z. anorg. Chem.*, **172**, 43–64 (1928).

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again evolved, or the stability of palladium–hydrogen. Both questions were in general studied upon the same specimen of palladium, in successive experiments conducted in the same apparatus.

Materials and Methods

The palladium employed was of two lots: vacuum fused metal from a commercial source, supplied as being 99.85% pure (Pd "A"); and metal specially purified at the Bureau of Standards[17] and rendered available by the courtesy of the Bureau (Pd "B"). The latter served only as a control, in the cases where its use is expressly mentioned. The palladium was received in the form of foils of different thickness, from which ribbons about 1 mm. wide and from 10 to 15 cm. long were cut to serve as objects of investigation.

The apparatus used in the absorption and evolution experiments included two similar tubes of clear fused silica, each 2 cm. in diameter and, respectively, 40 cm. and 60 cm. long, which served as the absorption vessels. These tubes were supported horizontally in two similar resistance furnaces, and were connected through liquid air traps with a single Pyrex system for evacuation and supply of hydrogen, so that the two samples of metal could be observed simultaneously under conditions which were the same with regard to hydrogen pressure and possible contamination.

The first of the two absorption tubes was connected to the Pyrex system by means of a ground joint some 15 cm. distant from the furnace, which was sealed with picein and water cooled. In this tube four platinum wire leads, two from each end of the palladium ribbon, were soldered at a point just within the joint to copper wires, which were brought out through the Pyrex, the seals being rendered vacuum tight by a backing of picein. The soldered connections were made with an alloy of 70% Au and 30% Sn, by weight, which we have found very satisfactory wherever a noble-metal solder of rather low melting point (near 300°), and of only moderate strength, is permissible. These connections were at a point where the temperature was constant, and very little different from that of the atmosphere, and the absence of disturbing electromotive forces was shown by the agreement between measurements made with commutated currents, as below described.

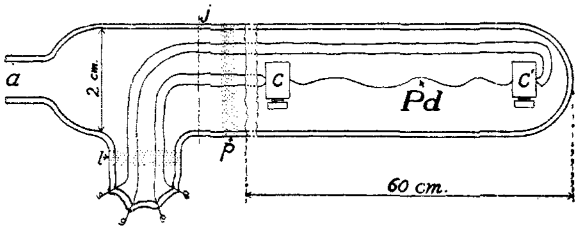

Fig. 1.—Absorption tube.

The second absorption tube, illustrated in Fig. 1, was constructed with a view to eliminating the sources of contamination which might conceivably exist in the picein seals of the other vessel, in order to make certain that any inertness of the palladium was not due to poisoning from this source. The tube of Fig. 1 was therefore joined to the Pyrex system by the graded seal at p; and the Pyrex was in turn joined by the graded seal l to a soft glass side tube, through which the platinum leads were taken out. The absorption chamber, as far as the liquid air traps, was thus of continuous glass. In order to replace the palladium, this tube was cut through the Pyrex at j, and again closed by fusion, the fusion being made with a small oxyhydrogen flame containing an excess of oxygen, in order that reducing flame gases might not enter the apparatus. It may be remarked that in the many comparison runs in which the two absorption tubes were connected either separately or together to the Pyrex system, no divergences were observed between the results obtained in the two tubes, so that the precaution of eliminating the picein joints was doubtless unnecessary.

The temperature of the experimental ribbon was recorded, for the first absorption tube, by a Pt, Pt–Rh thermocouple, which rested directly against the palladium at its middle point, the wires of the couple being brought out through the Pyrex in the manner already described for the resistance leads. A number of experiments, in which the indications of this inside couple were compared with those of another similar couple which rested against the outside of the absorption tube, having shown that at all temperatures above 100° the readings of the two accorded to within the expected error of 5°, no inside couple was provided in the second absorption tube of Fig. 1, and the temperatures given are those of the surface of the vessel, at a point midway of the length of the ribbon.

The Pyrex system connected to the absorption tubes at a included a mercury diffusion pump, a McLeod gage reading to 10^{-5} mm. of mercury, and a gasometer, as well as means for the purification of the entering hydrogen. The gas used was commercial cylinder hydrogen, made electrolytically, but in all instances was purified either by diffusion through a heated palladium diaphragm, or by passage in succession over long columns of freshly prepared, heated, platinized asbestos, and re-fused potassium hydroxide, and was finally admitted to the absorption chamber through a liquid air trap. In approximately half of the experiments the method of diffusion through palladium was used; and consistent agreement with the results obtained when the other method was employed gave adequate assurance that no contamination, having perceptible effect upon absorption, entered in any case.

The quantities of hydrogen absorbed by the palladium, and hence the rates of occlusion which have been taken as the measure of avidity, were determined by observing the electrical resistance of the ribbon. This method, based on the linear relation between the quantity of absorbed hydrogen and the resistance, which was first found to obtain by Fischer,[18] and has been confirmed by subsequent observers,[19,20] seems to be open to no objection when depended upon only for relative values, as in the present study, particularly since the metal used had been vacuum fused, and hence was practically free from the initial hydrogen content which constitutes the chief source of error in the method as sometimes applied.

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(20) B. Beckmann, *Ann. Physik*, **46**, 481–502 (1915).

For the observation of electrical resistance, the ribbon was connected at each end to two platinum wire leads, which were insulated by fine tubes of quartz, and were conducted out of the absorption tubes in the manner already described. The ribbon was joined to these leads by means of small screw connectors, c and c′ in Fig. 1, which had been cast and turned from an alloy of 77% Pt and 33% Au by weight. This alloy is sufficiently hard to form an excellent thread, and its vapor pressure is negligible at the temperatures under 1000° which were employed. Connection by fusion was inadvisable, both because of the high and uncertain temperatures to which parts of the palladium would have been subjected, and because of the danger of contamination.

Resistance measurements were made by the fall-of-potential method, using potentiometer and sensitive galvanometer, and were accurate to about 5 parts in 10,000. To avoid errors from thermoelectric and other chance sources, several control runs were carried out in which, for each value of resistance, readings were made with commutation of the measuring current. No parasitic e. m. f.'s of significant magnitude were observed.

Part I. The Avidity of Palladium

For reasons which become clearer as the results are discussed, our experiments upon avidity fall into sequence under the following topics:

1. Thermal influences:
   (a) the decay of avidity after annealing;
   (b) the effect of foregoing annealing alone.
2. Possible influence of grain size.
3. Influence of distortion (cold work):
   (a) by stretching;
   (b) by rolling.

The Decay of Avidity.—In order to study the effects of other factors, it seemed necessary first to ascertain, for the particular specimens of palladium under investigation, and the conditions of our experiments, the degree in which avidity is dependent upon the time which elapses between activation, by annealing, and exposure to the gas. The existence of such a dependence, at least under certain conditions, has been established by the work of Graham,[11] of Holt, Edgar and Firth,[12] and of other investigators.

Our general procedure in these experiments was to evacuate the absorption tube to a pressure of 10^{-5} mm. or below; to anneal the ribbon; to allow it to cool completely in the furnace; and then to admit hydrogen, allowing the gas to be absorbed at room temperature and at atmospheric pressure, and meantime observing at frequent intervals the electrical resistance of the ribbon. The usual period of cooling was some seven or eight hours, after annealing at 860°, and four to five hours from 450°; but by withdrawing the furnace from its position around the absorption tube, it was possible to cool to room temperature within half an hour.

For annealing temperatures much below and just above the recrystallization point of 400°, as well as for the much higher temperature of 860°, experiments were conducted in which the rates of cooling and the periods allowed to elapse between cooling and exposure to the gas were independently varied.

Figure 2 shows the results of four such runs, in each of which the temperature of heating was 450°, and rapid cooling to room temperature was effected within one half hour. The periods allowed to elapse after turning off the heat were, respectively, 0.5, 10, 24 and 39.5 hours. As may be seen, the rate of absorption was sensibly the same in each instance, and no decay of avidity was discernible within forty hours.

This result is typical of all of our observations after annealing at 450°, including one experiment conducted with palladium "B"; and a similar constancy of avidity during many hours after cooling was also found for an annealing temperature of 200°, although as is shown in the next section, the rate of absorption is smaller after treatment at this temperature. Ribbons annealed at 860° also appear to retain their avidity undiminished, although such a conclusion must be drawn with reserve, by reason of other uncertainties which are to be described.

These findings are, at first sight, in conflict with those of Holt, Edgar, and Firth,[12] who reported the following results:

Time, hrs.	0	0.75	16
Absorption, relative volumes	810	610	130

where the time is that elapsing between cooling and exposure to gas.

The difference proved, however, to be only one of rate, for although our metal retained its avidity unaltered for considerable periods, a decline was observable after a longer interval, as is evident from the following observations. A ribbon four times annealed in vacuum at between 400 and 410°, and each time subjected to hydrogen, but at intervals after cooling to room temperature which varied from 17 to 168 hours, showed in every instance an increase of resistance of 85% in twenty-four hours of absorption, the four resistance curves being practically identical. After again annealing at 400°, the ribbon was allowed to remain in a vacuum for twenty-one days before the admission of hydrogen, whereupon its resistance rose only 13% in twenty-four hours. On once more annealing, and this time letting in the hydrogen as soon as room temperature had been attained, a resistance increase of 62% in twenty-four hours was observed. Our palladium, therefore, exhibited the decay of avidity in question only after the lapse of several days, whereas in the studies above cited measurable decline occurred within a few minutes. The probable explanation of this divergency will be discussed in connection with the findings reported in a later section.

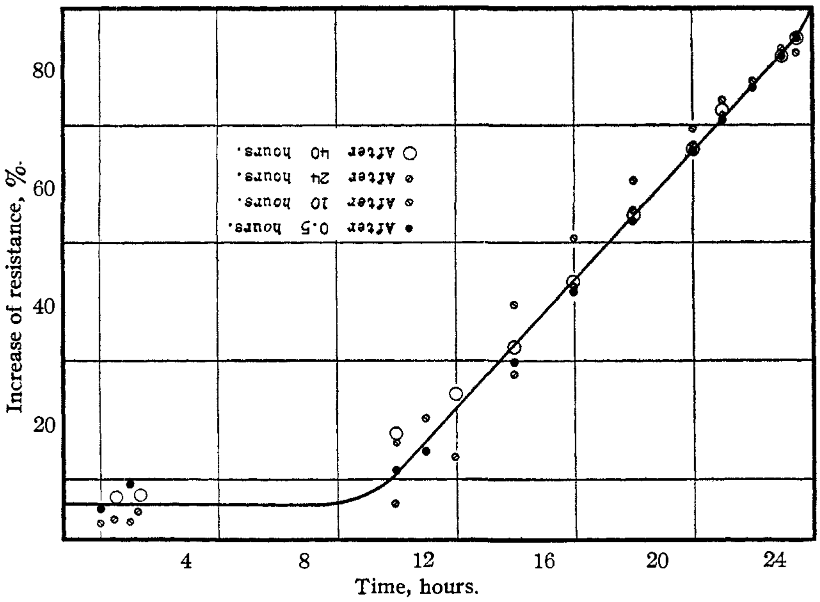

Fig. 2.—Constancy of avidity.

The Influence of Annealing Temperature.—Having thus established that, with the metal and conditions of our experiments, the time factor could be ignored, the influence of the previous annealing temperature upon the avidity could be examined without complication. In this respect the comportment of our metal showed, in general, good agreement with the results of Tammann and Schneider.[15]

Thus in four runs made with palladium "A," as received, in the cold rolled condition, the resistance increases in twenty-four hours ranged from 2.4 to 14.7%, or in the average 8.5%; and annealing below the recrystallization temperature of about 400° made no difference in this rate. These results may be summed up by saying that cold-rolled, gas-free palladium showed "an avidity of about 10%."

Upon annealing just above the recrystallization point, between 400 and 450°, the avidity rose to the highest values which we have obtained by *thermal treatment alone*. In 5 runs of this kind, the values obtained were from 76 to 87%, with an average of 84%; and two samples of palladium "B" showed avidities of 82.5%. Expressed as above, the avidity of palladium recrystallized from the cold-rolled state, and not overheated, is about 85%, with variations of some 5%.

Both of these findings accord entirely with those of Tammann and Schneider. Our results for higher annealing temperatures, in the neighborhood of 860°, also agree with those of the investigators named, in so far as they show an avidity considerably diminished by the higher heating. At these temperatures, however, we observed a marked variability. Thus, out of 35 ribbons annealed at 860°

28 showed avidities of from 2 to 27%; av. 12.5%
7 showed avidities of from 31 to 72%; av. 49.7%

while two ribbons of palladium "B" annealed at 960 and 860° showed increases of 8.7 and 10.5%, respectively. While the usual condition after such treatment is therefore one of considerable inertness, occasional ribbons are highly active. The possible causes of this variability are discussed in a later paragraph.

It should be mentioned that differences in the rates of heating and cooling had no evident effect upon the avidity of the ribbons annealed at 860°, wide variations occurring whatever the rate. There is, moreover, no sharp division between the active and inert groups, for while most ribbons showed either high or low values for the increase of resistance, a few scattered over the entire intermediate range, as can be seen in Fig. 7.

The Possible Effect of Grain Size.—Since mechanical and thermal treatments of various kinds affect the grain size, it seemed desirable to make certain whether this quantity is itself of influence upon the avidity.

The only method which we have found to yield large grains consistently is to anneal the metal at 800° or above, stretch to an elongation of about 5%, and then re-anneal at the same high temperature. To obtain a proper basis of comparison, the small-grained ribbons were produced either by heating the foil at 860°, without previous stretching, or by stretching insufficiently to cause grain growth, and then annealing at the temperature named. The behavior of all three types of ribbons proved to be the same. The small-grained ribbons gave counts of from 180 to 300 grains per square millimeter, and the large ones of from 0.4 to 20. Ten large-grained ribbons showed increases of resistance ranging from 2 to 66%, with an average of 28%; while a like number of small-grained ribbons, prepared in parallel experiments, ranged from 4 to 67%, and averaged 26%. Two large-grained samples prepared from palladium "B," showed increases of 17.6 and 23.5%.

The grain size is therefore not among the factors which influence avidity.

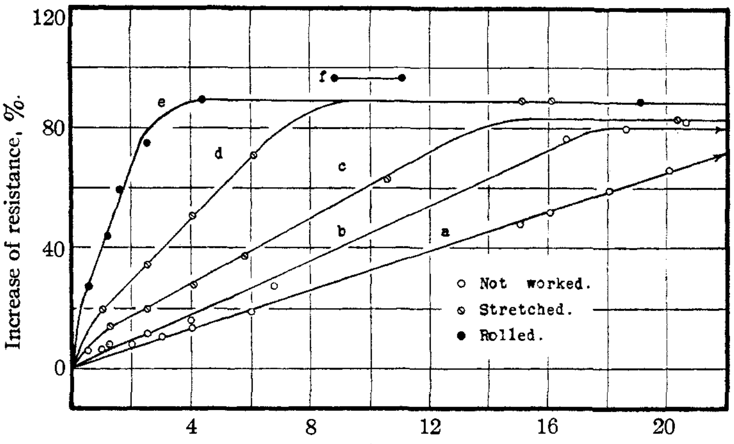

Fig. 3.—Influence of work on rates of absorption.

The Influence of Deformation.—The types of cold work applied were stretching and rolling. Stretching was in each instance carried to just below the point of rupture, which in ribbons annealed at 450° is near 3% elongation, and in those heated to 860° lies close to 5%. The rolling of the ribbons was done upon a glass plate, either under a glass rod of 5 mm. diameter, or under a 1 cm. rod of stainless steel. The ribbons of 0.025 mm. thickness, which were used in all of these experiments, could be rolled to 0.015 mm., or a reduction of 40%, without danger of tearing.

The effects of both stretching and rolling upon ribbons annealed at 450°, are illustrated in Fig. 3. The curves a and b refer to two ribbons which were exposed to hydrogen immediately after being annealed, without intermediate treatment, and show avidities of the same order of magnitude, although they also display the accidental differences to the causes of which we shall come later in this section. Curves c and d are for ribbons which, after cooling, were stretched before being permitted to absorb the gas. Both exhibit unmistakable increases of avidity. That they differ markedly from each other is doubtless the result of unequal working of different portions. Curve e is that of a rolled ribbon, and the two points at f relate to another similarly treated; while one such sample had an avidity of the order shown by curve c. The effect upon avidity, produced by this method of deformation, is therefore somewhat variable, but is very great in some instances, reducing the time required for saturation to less than one-fifth of that taken by the unworked specimens.

From the results displayed in Fig. 3 it may therefore be said that the avidity of palladium which has been heated to only slightly above the recrystallization temperature, and is accordingly in the most active state inducible by thermal treatment alone, is further increased by fairly severe cold work, to an extent which depends upon the type and degree of deformation, and which may under the proper conditions be large.

The influence of deformation after annealing at 860° is quite different. Thus five ribbons, after stretching, displayed increases of resistance of from 4 to 18%, with an average of 10.6%; and a sample of palladium "B" gave 6.5%; while as we have seen, ribbons similarly heated, but not stretched, usually show increases of about the same order, or in the average 12.5%, and a few exceptional specimens, unstretched, have avidities of the order of 50%.

Rolling, on the other hand, brings about an in-increase in avidity even in ribbons annealed at 860°. Thus six ribbons treated in this manner showed resistance increases of from 19 to 54%, with an average of 34.3%, or an avidity nearly three times as great as that of the usual unworked metal, although still in the average inferior to the 50% of occasional unworked specimens.

In all of the experiments just described, the metal was subjected to work within twenty-four hours after it had been cooled from the annealing temperature. Upon rolling, and then at once exposing to hydrogen, two ribbons which had been annealed at 810°, nine months previously, and had meantime been preserved in a desiccator, resistance increases of only 7 and 11% were obtained. In another instance a ribbon was annealed at 450° and kept in vacuum for twenty-one days, whereupon it was rolled and exposed to hydrogen, showing the following rate of occlusion:

Time, hours	13.00	21.25	30.75	46.25
Increase of resistance, %	48.5	67.4	79.1	82.6

The contrast of these values with those of the curves shown in Fig. 3 is very sharp, and even though the time interval between annealing and exposure to gas may have been sufficient to cause some decay of avidity, it is yet certain that the rolling did not restore this entirely, as would result if deformation alone were required to activate the metal. It hence appears that deformation must follow closely upon annealing, in order to cause an increase of avidity. Like the avidity itself, the susceptibility to activation by mechanical deformation seems gradually to decline.

Avidity and Slip-Plane Fissures.—The preceding observations on the factors which influence the avidity of palladium for hydrogen may be summarized as follows.

1. They confirm the gradual decline of avidity, after annealing, noted by previous observers, but show that the rate of this decline varies greatly for different samples of metal.

2. They confirm also the findings of Tammann and Schneider[15] that the greatest avidity producible by purely thermal treatments is induced by annealing just above the recrystallization temperature, and is *usually* again diminished by heating to still higher temperatures; but yield the supplementary information that the higher heating sometimes produces extremely active metal. It should be recognized that our experiments do not make it certain whether these results are a consequence of the heating or of the subsequent cooling.

3. They show that the avidity of the metal is independent of its grain size, and is accordingly not directly connected with grain boundaries, or intergranular crevices.

4. They establish the facts that plastic deformation increases the avidity of recently annealed palladium, whether the annealing has occurred at the temperature of greatest thermal activation, just above the recrystallization point, or at a much higher temperature; but that this susceptibility to activation by cold working, like the thermally induced activity itself, diminishes as the time allowed to elapse after annealing is increased.

The influence, upon avidity, of a disturbance of the slip-planes, which was anticipated in accordance with the role which slip-plane fissures have previously[4] been found to play in occlusion, has therefore been shown to exist, and under suitable conditions to enhance the avidity by as much as several hundred per cent.; but the additional finding that the influence of deformation is effective only with freshly annealed metal necessitates some amplification of conceptions with regard to opening and closing of fissures.

In the first place it is to be noted that slip, and consequent disturbance of the slip-planes and their environment, with partial fissuring along planes of ready cleavage, is doubtless produced not only by cold working, but also by the extreme dislocations which accompany recrystallization. Both of the treatments by which avidity has been found to be induced, recrystallization and cold working, are therefore to be classed as types of deformation.

There are, moreover, many well-known evidences that the effects produced by the deformation of metals diminish, and often wholly disappear, with lapse of time. It will suffice to mention the phenomenon of elastic after-effect.[21] This power of metals to recover implies a spontaneous restitution of disturbed conditions along the planes of slip, and hence a gradual closing of the slip-plane fissures.

We may accordingly regard the increase of avidity, by recrystallization, as probably brought about by the fissuring of slip-planes as a result of stresses developed during the rearrangement; and the decline of avidity in the course of time

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(21) See especially H. v. Wartenberg, *Ber.*, **20**, 113–122 (1918).

as due to the healing of these minute rifts. That the rate at which this healing occurs differs from one specimen of metal to another is not improbably a consequence of variations in chemical composition, for it is well recognized that very small admixtures may produce marked differences in the hardness and plasticity of a metal, and that the effect depends upon whether the admixture is present in solid solution or otherwise.

The great increase of avidity which is produced by annealing just above recrystallization temperatures requires no further comment; and the diminution of avidity when the recrystallized metal is heated to higher temperatures is also readily interpreted as the consequence of accelerated processes of recovery, with closing of the fissures caused by the recrystallization. But that this diminution sometimes fails to occur, the metal in these instances retaining a high degree of avidity after cooling, appears to depend upon accidental factors as to which no definite evidence is yet at hand. Possibly the closing up which usually takes place is induced by something as uncontrollable as a chance jar, a supposition for which there is support in the effect which the mere transference of a ribbon from one apparatus to another is shown, in a later paragraph, to exercise upon the stability of palladium–hydrogen.

The facts listed under 4 of this section may be restated by saying that slip produced by cold working increases the avidity of the metal only when the latter is already in the active, fissured condition, caused by thermal treatment. Evidently slip at room temperature is not alone capable of producing fissures where none already exist, but suffices to enlarge those previously opened. Whether the formation of the fissures is always the result of recrystallization, or is also caused by thermal expansion and contraction, or by deformation at somewhat elevated temperatures, are questions to which it will probably not be easy to obtain an answer, since the several processes are intricately involved, one with another.

Although not conducted with that end in view, the experiments of which the results are shown in Figs. 2 and 3 also make plain that, at constant atmospheric temperature and pressure, the quantity of hydrogen occluded by palladium is a linear function of time. Since some of the results of Tammann and Schneider,[15] while obtained at constant volume and slightly varying pressure, indicate a similar relation in the cases of iron–hydrogen and nickel–hydrogen, it seems probable that this constancy of rate is a characteristic of the occlusive process.

This linearity also accords with the distributive mechanism above discussed. For when entry of hydrogen takes place against the frictional resistance offered by the slip-rifts, in any except the fully opened state which they show in palladium above the break-point discussed in the next section, the entry must be of a lower order of velocity than the subsequent distribution through the many fissures of the interior, and as a result the pressure must drop practically to zero immediately within the external rifts. This extremely rapid distribution is a result of the number and extent of the active dodecahedral planes which cross the entry crevices, whether of the (111) or (110) sets, at short intervals within the surface, rather than to any increased diffusion velocity in these interior fissures. The entire process of occlusion is therefore comparable to diffusion through a dense porous plug into a space from which the gas is instantly removed. Thus, although the metallographic evidence[4] has shown that the process of diffusion through the undisordered lattice is slower than that of distribution through the fissures, it is not this solution of hydrogen in the lattice which determines the over-all rate of occlusion. This rate, in consequence of the mass effect of the internal fissures, is controlled by the earlier and slower of the two processes, (a) diffusion through the external slip-rifts, (b) subsequent distribution through the numerous internal fissures of similar kind. Under these circumstances a constant diffusion gradient establishes itself between the exterior and the region within, a region in which the pressure may be regarded as having the value zero, until the saturation of the interior is almost complete.

The primary process of occlusion may therefore be expressed by the simple relation $dq/dt = kp$, or (1) $q = q_0 + kpt$, where q is the occluded quantity at the time t, and k is a constant which is fixed by the number and the frictional resistance of the entry rifts. Empirical data with regard to the effect of pressure upon rates of occlusion, implied in equation (1), are as yet lacking. For constant pressure, however, the relation takes the still simpler form (2) $q = q_0 + Kt$, to which the graphs of Figs. 2 and 3 are seen to conform throughout the major part of the occlusion.

The results of the experiments upon avidity may therefore be regarded as evidence that gaseous hydrogen, as was previously shown to be the case for electrolytic hydrogen, enters and disseminates itself in palladium through minute intragranular fissures; that these fissures are situated upon the planes of slip; that they are neverthless not initially produced by cold work but originate only at somewhat elevated temperatures, chiefly, and perhaps solely, during recrystallization; and that, when once formed, and not yet closed again by the "recovery" of the metal, they can be enlarged and made more effective in occlusion, by cold working.

Part II. The Stability of Palladium-Hydrogen

The isobars of the system palladium-hydrogen, typified by Fig. 4, like the isotherms[1,2,3] from which they are derivable, show hysteresis. When electrical resistance is observed, as a measure of concentration, the variation of resistance with temperature yields Fig. 5, in which the branch e, b corresponding to the drop of the isobar in Fig. 4, is also subject to hysteresis.[9] In what follows we are concerned with factors, other than the direction of change of temperature, which alter t_1 of Fig. 4, relating to the point e of Fig. 5, the break-point, at which palladium-hydrogen becomes unstable with rising temperature. The resistance observations constituted the continuations of the individual experiments upon avidity already described, the usual procedure being to heat the charged palladium ribbon, either in vacuum or in hydrogen, at the rate of 6° per minute, noting its resistance at short intervals.

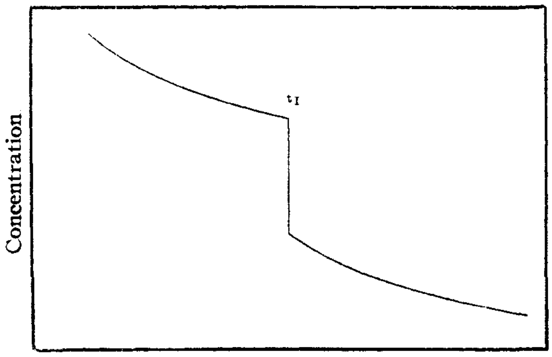

Fig. 4.—Ideal isobar.

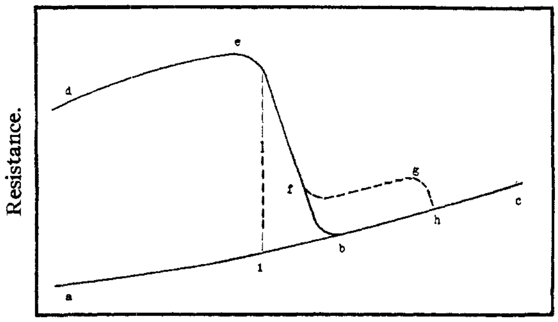

Fig. 5.—Typical break points.

For pure palladium, the curve of resistance as a function of temperature is convex toward the temperature axis (curve a, b, c, Fig. 5). For palladium-hydrogen, in conformity with the general behavior of alloys of the solid solution type, the resistance at any given temperature is greater, and the temperature coefficient is less, than for the pure metal; and since the temperature variation of the coefficient is also normal ($d^2R/dt^2 < 0$), in contrast to the exceptional case of pure palladium ($d^2R/dt^2 > 0$), the curve of the resistance of Pd-H is of the general form shown by the section d,e until the temperature is reached which, for the prevailing conditions, corresponds to t_1 of Fig. 4. Here the hydrogen begins to escape rapidly from the metal and the resistance makes its transition from the Pd-H curve, d, e, to the Pd curve, a,b,c, along the branch e, b. From the temperature corresponding to b, at which the hydrogen has been fully expelled, the resistance then follows the Pd curve b,h,c. As was shown earlier,[22] the rising temperature causes no noticeable increase in the loss of hydrogen from Pd-H, over the very small rate observable at ordinary temperatures, until the breakdown begins. The curve d, e is therefore very little different from that pertaining to Pd-H of the composition at which heating began. The true temperature of breakdown is that of the point e, as may be shown by holding the temperature constant, as soon as the first decline of resistance has been noted, in which case the hydrogen is lost completely at this temperature, the resistance falling vertically along e, i, and thereafter rising, as the temperature is again increased, along the curve of pure Pd, i, b, h, c. The slope of the branch e, b, as usually observed, is therefore dependent upon the rate of heating. For the rate of 6° per minute, and palladium

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[22] E. A. Harding and D. P. Smith, THIS JOURNAL, **40**, 1508 (1918).

rendered highly permeable by recrystallization at 450°, the comportment is that shown by the curves of Fig. 6, which represent four successive runs with the same ribbon. Between runs the ribbon was in each case again annealed at 450°, to the complete expulsion of hydrogen, and saturated with the gas at room temperature and atmospheric pressure; after which the vessel was exhausted to a pressure of 10^{-5} mm., before heating was renewed. The results are typical for other experiments made under similar conditions.

Unlike the drop in the isobar, at t_1 in Fig. 4, which represents only the passage from the beta to the alpha phase of Krüger and Gehm,[5] the curve branch e, b of Fig. 5 corresponds to the complete loss of hydrogen. That this loss is in fact complete, on annealing in nitrogen, was shown in an earlier study.[22] Similar evidence, for annealings in vacuum, was obtained in the present instance from the following procedures. A ribbon of vacuum fused and annealed palladium, free from hydrogen, upon being gradually heated in vacuum, yielded the resistance curve a, b, h, c of Fig. 5. After charging with hydrogen *in situ*, the ribbon was again heated in vacuum, giving the curve d, e, f, b, h, c, of which the part beyond the break-point, b, h, c, coincided with that obtained before. The ribbon having been saturated again, its resistance curve was taken in hydrogen of one atmosphere pressure. A break-point somewhat displaced toward higher temperatures was now observed, and from this point on the values lay upon the higher curve f, g, which pertains to the alpha phase. Upon evacuating, the resistances quickly dropped to those of the curve h, c, of empty palladium. It is plain that the breakdown of the beta phase, with accompanying contraction of the lattice, had so widely opened the fissures that the effective pressure throughout the metal was that of the external gas; and hence, upon subjection to vacuum, the alpha phase also gave up its hydrogen.

To make clear the import of the empirical results which follow, the nature of the break-point, or the (usually displaced) temperature t_1 of Fig. 4, which corresponds to the point e of Fig. 5, must be somewhat more closely examined.

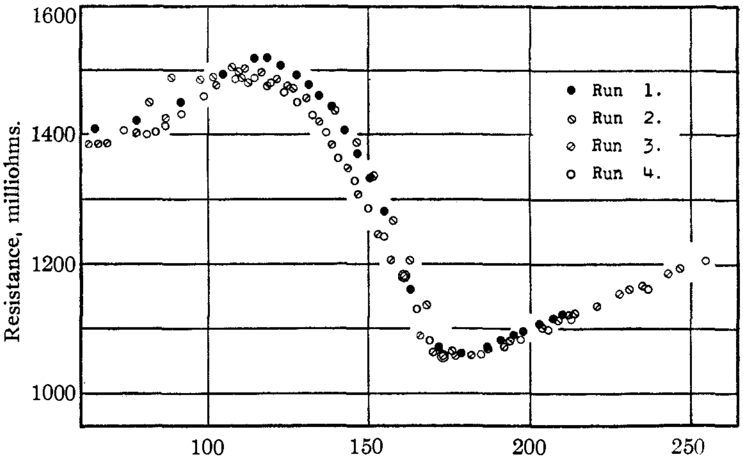

Fig. 6.—Experimental break points.

In terms of the conception under discussion, the slip-plane fissures existing in any sample of palladium which actively occludes, are in the course of the occlusion throttled by the distension of the surrounding lattice. Hence, even when the charged metal is subjected to vacuum, the equilibrium pressure of hydrogen, p_t, which belongs to Pd–H at the temperature of the system, t, maintains itself in the interior. The contracted fissures may therefore be regarded as presenting to the effusion of hydrogen a hindrance measurable in terms of the pressure reached at the break-point, p_b, which suffices to expand the throttled fissures and restore equilibrium between the interior and the gas phase. This critical pressure, p_b, is therefore: $p_b = p_t - p_g$, where p_g is the pressure of the external gas. When a charged ribbon is heated in vacuum, p_g is zero, and as long as $p_t < p_b$, the throttled fissures prevent the escape of gas from the metal. As soon, however, as p_t becomes equal to p_b, at the break-point, this hindrance is overcome; whereupon rapid escape is possible and proceeds until equilibrium is reached, becoming progressively more rapid with the contraction of the lattice.

The results obtained with reference to the influence of external pressure upon the break-points are in accord with this interpretation. Thus the break-point in vacuum, for ribbons recrystallized at 450°, has repeatedly been found to be near 130°; whereas three such ribbons, when heated from room temperature with an initial pressure of one atmosphere of hydrogen, which in the closed system rose to 800 mm. at 170°, gave break-points of 173, 165 and 169°.

The isotherms recently given by Brüning and Sieverts (*loc. cit.*, Fig. 16), for falling pressures, may be regarded as giving the equilibrium pressures, p_t, for various values of t, within the range in question; and being very nearly linear, permit interpolations which yield the data of Table I.

TABLE I

t, °C.	120	130	140	150	160	170	180	200
p_t, mm.	380	510	660	820	1030	1330	1830	3100

As may be seen, temperatures of 130 and 170° correspond, respectively, to pressures of 510 and 1330 mm., a difference of 820 mm., as compared with the pressure of 800 mm. which we have found to displace the break-point through the same interval. In view of the difficulty of the exact determination of the break-point, because of the rounding off of the curve at e, the agreement is satisfactory, and appears not only to support the interpretation which has been given of the nature of the break-point, but to show that p_b is little affected by temperature within the above limits.

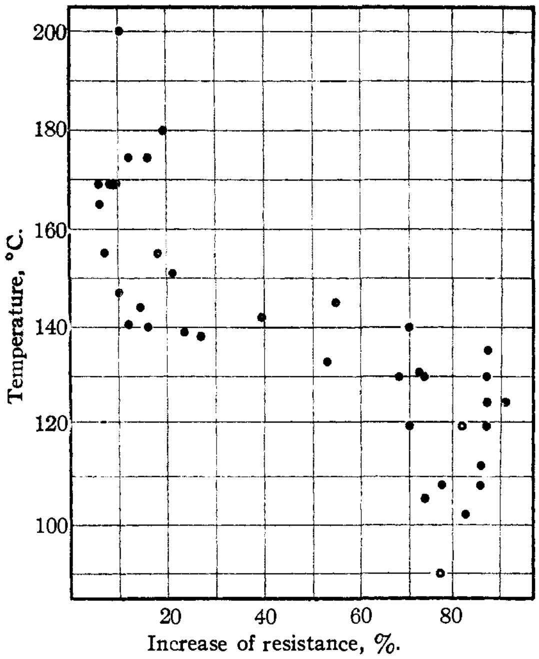

Fig. 7.—Dependence of break points upon avidity.

It is hence permissible to consider the break-point as a rough measure of the pressure p_b, and an indication of the degree to which the fissures are throttled in palladium which has been subjected to various treatments. In so doing, however, it is important to bear in mind that this measure of the facility of evolution is wholly different in kind from the avidity, or *rate* of absorption, which has been employed in Part I to represent the ease of ingress. The two "facilities" are therefore not directly comparable, and in particular do not bear to each other the relation of opposed velocities.

The Relation between Stability and Avidity.—The connection between these quantities is clearly evident when the results of all the 42 experiments, in which determinations of the two were made in succession, are assembled, as in Fig. 7. Here the break-points are plotted against the avidities, defined as before as the percentage increase of resistance during twenty-four hours exposure to hydrogen at atmospheric temperature and pressure. These experiments covered a range of annealing temperatures from 400 to 900°, and included instances in which the metal was cold worked after the first annealing and then heated again above the recrystallization temperature, with the production of coarse-grained metal, as well as experiments involving very different rates of heating and cooling. In spite of these wide diversities, it may be seen that palladium which exhibits small avidity invariably yields palladium–hydrogen of high stability, and *vice versa*, the maintenance of this regularity being particularly impressive in the case of ribbons annealed at 860°, for which the avidities vary, in the apparently accidental fashion already discussed, between the extreme limits of the diagram. Although the results scatter too widely to permit of quantitative deductions, they may be taken to establish definitely that the facility of egress varies in parallel to the facility of ingress of hydrogen. Attention should be called to the fact that this regularity holds only for unworked metal.

Deformation and the Break-Point.—The influence of cold work is divided conveniently into effects upon ribbons annealed at 450°, and upon those heated to 860°; and in each case the effects of severe and of mild working must be distinguished.

With metal annealed at 450°, severe cold working, by stretching or rolling in the manner already described, whether applied before or after exposure to hydrogen, appears to have no effect whatever upon the break-point. Thus four runs, under different conditions, gave break-points ranging from 118 to 140°, with an average of 130°, results which fall within the limits usually observed with unworked palladium. Mild working, on the other hand, such as is involved in any handling of these thin ribbons, raises the break-point. Thus three ribbons, each of which had been exposed to hydrogen after annealing, and without intervening treatment, upon being transferred from one of the absorption tubes to the other, showed break-points of 150, 150 and 153°, which are some 20° higher than those exhibited by metal which has been either severely worked, or not worked at all.

With metal annealed at 860°, our results as to the possible effects of severe working are not conclusive, because of the undetermined factor which influences the effects of heating to these higher temperatures, as has already been explained in Part I. The observations were the following. Two ribbons annealed at 860°, and then cold rolled before exposure to hydrogen, gave resistance increases of 50 and 54%. The first was again rolled, and the hydrogen expelled, the break occurring at 185°. The second ribbon, after charging, was heated in vacuum without other treatment, and showed a break-point of 176°. These values appear to indicate that severe working raises the break-point. But a third ribbon, which had been rolled after annealing, gave a resistance increase of 34% and a break-point of only 157°, which is little above the average for metal similarly annealed and not worked.

The effect of mild working is, on the contrary, quite definite, and like that observed after annealing at 450°. Thus, three ribbons which showed resistance increases of 60, 66 and 67%, after annealing at 860°, having been subjected only to the working involved in transfer from one absorption tube to the other, gave breaks at 185, 185 and 182°; whereas ribbons similarly treated, save that they were not transferred, all showed break-points below 140°, whenever their resistance increases were above 60%.

It might be supposed that this effect is not the result of the working, but of exposure to air. As against this interpretation, it is to be recalled that the ribbons annealed at 450°, and similarly exposed to air, showed no elevation of the break-point. Nevertheless, in order to put the matter beyond doubt, a single ribbon was submitted to the following treatments, with the results shown: (1) annealed at 860°; cooled in vacuum; exposed to hydrogen, the resistance increasing 44%; transferred to the other absorption tube, and gas expelled by heating in vacuum—*break at 183°*. (2) Maximum temperature reached in expulsion, 335°, insufficient to cause recrystallization; cooled in vacuum; hydrogen admitted, the resistance increasing 72%; gas expelled as before, but *in situ—break at 131°*. (3) Maximum temperature reached, 350°; cooled in vacuum; exposed to hydrogen, the resistance increasing 73%; hydrogen pumped off at room temperature and air admitted for one half hour; evacuated and hydrogen expelled as before—*break at 130°*. (4) Maximum temperature reached, 300°; cooled in vacuum; exposed to hydrogen, the resistance increasing 73%; opened apparatus and subjected ribbon to working comparable to that which it receives in being transferred from one tube to the other; expelled hydrogen as before—*break at 160°*.

This series of experiments was then repeated with entirely similar results. It is hence clear that the elevation of the break-point which attends the transfer of a ribbon from one absorption tube to another is not the result of exposure to air, but of the slight cold working involved.

So far, at least, as concerns the types and degrees of deformation considered, it appears that, when they have any influence upon stability, the effect is to increase it. Recalling that in Part I deformation was shown also to increase avidity, it hence appears that, unlike the influence of thermal treatment alone, which has been shown (*cf.* Fig. 7) to have the same effect upon facility both of ingress and of egress, the effect of deformation is to increase the ease with which hydrogen enters palladium, but to diminish the readiness with which the gas is again given off.

An observation at variance with this was recorded by Hanawalt,[10] who found that the stability of his palladium–hydrogen was diminished by rolling the charged metal. In view of this discrepancy, and of the differences above noted, between the effects of work of varying degrees of severity, it is apparent that the effects of deformation upon stability are of too involved a character to be interpreted fully without a more extended investigation. For the present it can be said only that such effects unquestionably exist, and that their existence is evidence that the slip-planes play a part in the absorption and evolution of hydrogen.

The Influence of Method of Charging.—Of the factors which come within the scope of this study, the one having the greatest effect upon the stability of palladium–hydrogen is the method by which the metal is charged. As has been shown, ribbons which have taken up large quantities of hydrogen from the gas phase, and have not been subject to special treatments, invariably give a break-point of approximately 130°. If the metal has been charged cathodically, however, the break occurs near 200°. As may be seen from the experiments, of which the results are displayed in Table II, this is true both for cold-worked and recrystallized ribbons, and for current densities of a wide range.

TABLE II

Expt.	Condition of metal	C. d. amp./sq. dm.	Break, t, °C.
1	Rolled	2	220
2	Rolled	2	202
3	Recrystd.	2	190
4	Recrystd.	2	208
5	Rolled	0.02	198
6	Rolled	.02	198
7	Rolled	.008	215

It is to be noted that the greater stability of electrolytically charged palladium–hydrogen has previously been observed by Linde and Borelius,[9] using methods similar to ours; and in an x-ray study of Hanawalt.[10]

For comparison, the effect was also tried of charging with the heavy isotope of hydrogen. Two ribbons charged electrolytically at a current density of 2 amp./sq. dm., from 95% heavy water containing sodium hydroxide as electrolyte, showed break-points of 205 and 190°. Apparently, therefore, the stabilities of the systems hydrogen–palladium and deuterium–palladium are alike, unless, perhaps, only the light isotope is occluded, even from water of the composition employed.

With regard to the seeming greater stability of palladium–hydrogen, when formed electrolytically, it must be observed that in the experiments just described, and evidently also in those of Linde and Borelius, and of Hanawalt, the metal after being charged was transferred to another apparatus for observation. As has been shown earlier, the mild work attendant upon such handling increases stability. It is hence possible that the different comportment of the cathodically charged metal is merely the result of this effect of intervening deformation. But the differences seem too large to be accounted for in this way; moreover, as metallographic evidence makes plain,[4] cathodic hydrogen affects the behavior of palladium toward etching agents in a manner entirely different from that in which it is affected by the gas. It is therefore not improbable that the slip-fissures and their environments are disturbed in different ways or degrees by the two methods of charging. The question is in need of further examination.

Conclusion

The principal results of the experiments just described are the facts: (a) that the effects of heating and cooling palladium, up to the highest temperatures studied, near 900°, together with the recrystallization which is often incident, and the gradual recovery which the metal undergoes after cooling, always influence in the same direction both the ease with which the metal absorbs gaseous hydrogen and the readiness with which the gas is again given off; and (b) that plastic deformation of the metal, in general, influences both of the processes named, although often in opposite senses.

The former of these findings indicates that the entry of hydrogen, and its subsequent escape, are in the main controlled by a physical, rather than a chemical, factor since a factor of the latter type, if determinative, must influence the two processes in opposite directions.

The second finding makes it clear that the two processes are affected by any disturbance of the slip-planes upon which deformation occurs, and in conjunction with metallographic evidence previously obtained that the primary distribution of hydrogen through the metal is along widely spaced planes, of sets oriented in the directions of the maximum shearing stresses of a foregoing deformation, affords proof that the planes concerned are actually the planes of slip.

The results as a whole therefore support the conclusion already reached, that the diffusion of hydrogen into palladium occurs rapidly along minute fissures in the slip-planes, and only as the result of a slower secondary process, extends to the undisordered lattice, while the mechanism of evolution is the reverse of that just depicted.

There are to be found in the literature many indications that the occlusion of hydrogen by the metals which exhibit large absorptions is of the same type as that shown by palladium. Schmidt[23]

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(23) O. Schmidt, *Z. physik. Chem.*, **A165**, 133–146 (1933).

includes palladium as one of the outstanding examples of the importance of porosity in the absorption of hydrogen, especially in connection with catalytic problems. Reference should also be made to the recent observations of Alexejew, Afanassjew and Ostroumow,[24] who have investigated the effect of tension on the permeability of iron to electrolytic hydrogen, and from their results have drawn conclusions not dissimilar to those reached in earlier studies of the electrical conduction of palladium–hydrogen, iron–hydrogen, etc.,[22,25] to the effect that the highly absorbent metals display both lacunal and lattice occlusion. The evidence here presented, together with that of our preceding metallographic study,[4] demonstrates, however, that the lacunae concerned are not *inter*granular, as we were previously inclined to suppose, but are situated within the grains, upon the planes of slip.

Summary

Experiments by resistometric methods are described upon the facilities with which pure palladium foils absorb and evolve hydrogen, and the ways in which these facilities are influenced by factors which affect the physical state of the metal.

The factors studied include: time of decay; annealing temperature; rate of cooling; grain size; effect of air; deformation and its degree.

The effects of electrolytic charging and of charging from the gas are compared.

The results confirm and extend those of several earlier observers, and in addition yield the following facts.

Any variations in the metal not caused by mechanical deformation always affect the facilities of absorption and of evolution in the same sense.

Deformation affects, in general, both facilities, whether in like or in opposite senses being sometimes dependent upon its severity.

The rate of occlusion at atmospheric temperature and pressure is independent of time, for both worked and unworked metal.

The results are shown to confirm conclusions previously reached, that diffusion occurs primarily along slip-plane fissures, and only secondarily through the undisordered lattice.

FRICK CHEMICAL LABORATORY
PRINCETON, N. J.
RECEIVED JUNE 12, 1934

[24] D. Alexejew, P. Afanassjew and W. Ostroumow, *Z. Elektrochem.*, **40**, 92–98 (1934).

[25] D. P. Smith, *Z. Physik*, **69**, 253 (1931).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

A Thermodynamic Study of Liquid Potassium Amalgams[1]

BY MARION H. ARMBRUSTER[2] AND JAMES L. CRENSHAW

Introduction

The present study was undertaken to investigate the conditions under which the potassium amalgam electrode gives the most reproducible results in aqueous solutions. In a recent paper, Spencer[3] has compared the values for the activity coefficients of potassium chloride obtained by freezing point methods with those obtained by electromotive force measurements and has come to the conclusion that the amalgam electrode is not reliable. There is considerable evidence that electromotive force and freezing point methods agree,[4,5] but since the amalgams do react with aqueous solutions and are admittedly unreliable in dilute solutions, it seemed worth while to make a study of the conditions under which the only appreciable reaction is a reversible transfer of potassium from the amalgam to the solution.

The purpose of the present paper is to determine the effect of the following factors on the reproducibility of the potassium amalgam electrode: (1) the concentration of the amalgam; (2) the concentration of the potassium ion in the aqueous solution; (3) the form of dropping electrode and the rate of flow; and (4) temperature. If in a cell made up as follows

K (c_2) (amalgam)/KCl (solution)/K (c_1) (amalgam)[6,7]

the electrodes are reversible, the only reaction

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[1] This article is based upon the dissertation presented to the Faculty of the Graduate School of Bryn Mawr College by Marion H. Armbruster in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The complete dissertation is on file in the Bryn Mawr College Library.

[2] Helen Schaeffer Huff Memorial Research Fellow.

[3] Spencer, THIS JOURNAL, **54**, 4490 (1932).

[4] Young, *Chem. Rev.*, **13**, 103 (1933).

[5] Smith, THIS JOURNAL, **55**, 3279 (1933).

[6] Cells similar to this have been studied by Bent and Gilfillan, THIS JOURNAL, **55**, 3989 (1933), using non-aqueous solutions and by

[7] Shibata, *J. Chem. Soc. Japan*, **52**, 352, 365 (1931), using a concentrated potassium hydroxide solution, but the influence of the various factors mentioned above was not investigated.