

### Summary

1. The quantum yield of carbon monoxide formation from diethyl ketone in the wave length region 1850–2000 Å. is quite high and seems to approach unity as the pressure is lowered.

2. With an assumed quantum yield of 0.095 at 3000 Å. for carbon monoxide formation from acetone it has been shown that the yield from ethyl methyl ketone is only slightly higher and that that of diethyl ketone is about one.

3. These facts indicate either a high intrinsic

instability of propionyl radicals or very probable reactions involving them which lead to carbon monoxide.

4. Ethyl methyl ketone probably dissociates almost but not quite solely to give ethyl radicals in the near ultraviolet. At short wave lengths methyl and ethyl radicals are produced in nearly equal amounts from the primary process.

5. Most of the ethyl radicals form butane, but a small fraction yield ethane and ethylene.

ROCHESTER, NEW YORK

RECEIVED JUNE 19, 1939

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 426]

## The Palladium-Deuterium Equilibrium

BY LOUIS J. GILLESPIE AND WILLIAM RICHARD DOWNS

The purpose of this investigation has been to study the absorption of deuterium by palladium black in the region of temperature and pressure in which hydrogen and palladium have been found by Brüning and Sieverts<sup>1</sup> and by Gillespie and Galstaun<sup>2</sup> to exhibit a critical solution temperature, and inclusive of the region at 200° and above in which hydrogen and palladium exhibit a tendency toward compound formation—in short, to obtain part of the phase diagram for deuterium and palladium analogous to that of Gillespie and Galstaun for hydrogen and palladium.

Sieverts and Zapf<sup>3</sup> studied the solubility of hydrogen and of deuterium in a palladium wire. The ratio of the solubility of deuterium to that of hydrogen was 0.67 at 300° and increased to 0.91 at 1000°.

Sieverts and Danz<sup>4</sup> studied the absorption of deuterium by palladium black from 20 to 350° at various low pressures (less than 2 atm.). Isotherms at 80 and 100° gave evidence of two solid phases, but in all cases, even for the corresponding curves for hydrogen, there was considerable hysteresis. Sieverts and Danz<sup>5</sup> have also studied the electrical resistance and magnetic susceptibility of palladium wire charged with deuterium.

Since the early work of Oxley<sup>6</sup> the magnetic susceptibility of palladium charged with hydrogen has also been studied by Aharoni and

Simon,<sup>7</sup> Svensson,<sup>8</sup> and Michel and Gallissot.<sup>9</sup> The latter have also studied the variations of the lattice parameter, the Brinell hardness and the electrical resistance as hydrogen is added to the metal.

There are recent X-ray studies of the system palladium-hydrogen by Kruger and Gehm<sup>10</sup> and by Owen and Jones.<sup>11</sup> The latter, as well as Michel and Gallissot, found in agreement with the early experience of Wolf<sup>12</sup> that simple degassing of palladium that has been well charged with hydrogen—to the formation of the second (beta) solid solution—does not entirely restore the original physical constants of the palladium, but that high temperature annealing (*e. g.*, 450° for one-half hour<sup>11</sup>) is necessary and sufficient.

This finding is of two-fold interest in connection with the equilibrium of either hydrogen or deuterium with palladium. In the first place, one need not expect the whole of an isotherm containing a horizontal portion to be reversible, since the palladium would appear not to be the same for the first rising portion when traced upward from zero concentration as when later traced downward after formation of the beta phase and its subsequent decomposition. This effect seems, however, to be rather theoretical than actual. In the second place, one might expect that any reluctance to form the beta phase, if once over-

(1) Brüning and Sieverts, *Z. physik. Chem.*, **163A**, 409 (1933).

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

(3) Sieverts and Zapf, *Z. physik. Chem.*, **174A**, 359 (1935).

(4) Sieverts and Danz, *ibid.*, **38B**, 46 (1937).

(5) Sieverts and Danz, *ibid.*, **38B**, 61 (1937).

(6) Oxley, *Proc. Roy. Soc. (London)*, **101A**, 264 (1922).

(7) Aharoni and Simon, *Z. physik. Chem.*, **4B**, 175 (1929).

(8) Svensson, *Ann. Physik*, **18**, 299 (1933).

(9) Michel and Gallissot, *Compt. rend.*, **208**, 434 (1939).

(10) Kruger and Gehm, *Ann. Physik*, **16**, 174 (1933).

(11) Owen and Jones, *Proc. Phys. Soc.*, **49**, 587, 603 (1937).

(12) Wolf, *Z. physik. Chem.*, **87**, 588 (1914).

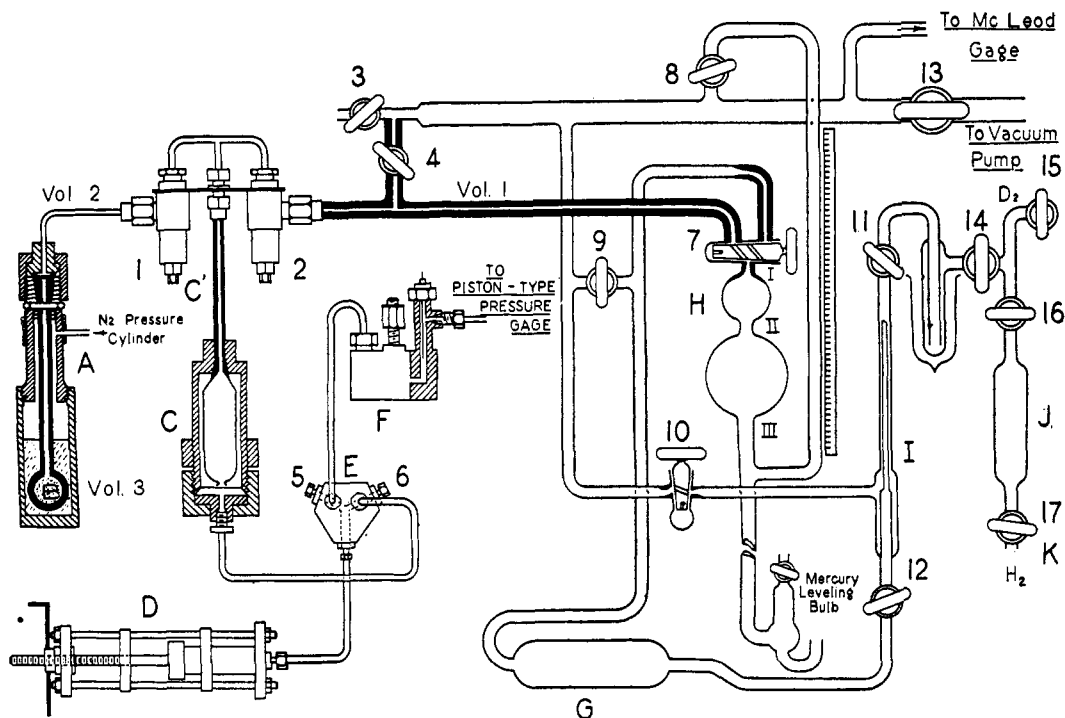


Fig. 1.—General apparatus.

come, might disappear on repetition of the experiment, since the alteration in the physical state of the metal may serve as well as the presence of "nuclei" (or perhaps actually constitute such), about which the new phase may freely form. This expectation has been borne out in the present work with deuterium.

Lacher<sup>13</sup> has derived with the aid of statistical theory an approximate equation to represent the results of Gillespie and Galstaun for palladium and hydrogen. If we remember the arbitrary nature of the fundamental assumption that was made, which did not permit representation of compound formation, we may consider the semi-quantitative success of the representation very gratifying.

**Apparatus and Procedure.**—The apparatus of Gillespie and Galstaun was used, after redetermination of the dead-space volumes and recalibration of the pressure gage, and the same procedure for the measurements was used. The only modifications were as follows. After we found that the critical solution pressure was to prove much higher than that for hydrogen we installed a steel jacket around the Pyrex reaction bulb and part of its capillary lead, within which jacket a compensating pressure of nitrogen can be maintained. For fear of excessive heat loss along the jacket and consequent unknown stem-correction we have used melted Wood's metal within the jacket to transfer heat to the reaction bulb. Measurements with

hydrogen and palladium, with and without the jacket, showed that the stem-correction was zero or the same in both cases. The design is such that without the jacket the stem-correction should be the same as for the platinum thermometer. This jacket and the associated apparatus are shown in Fig. 1. A change was made in the procedure for freeing the palladium black from ammonium chloride, and this will be discussed later.

Deuterium is prepared by electrolysis of a dilute solution of anhydrous potassium sulfate in heavy water in the apparatus shown in Fig. 2. By adjustment of the mercury in the bulb B the volume of bulbs A and B can be made exactly half the volume of the deuterium bulb E, so that electrolysis can take place without attention to the levels in the U-tube at D. Ice was used in a Dewar flask about the U-tube for cooling during electrolysis.

Heavy water guaranteed 99.9% pure was obtained from

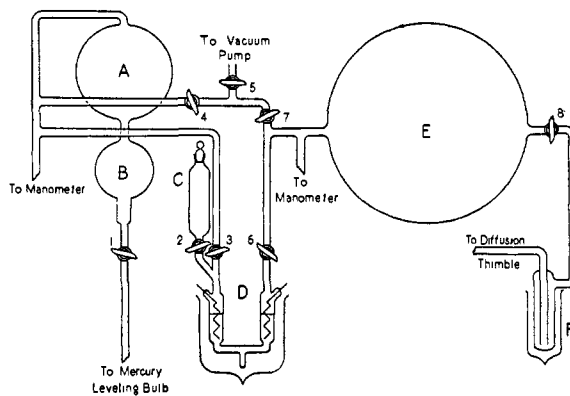


Fig. 2.—Deuterium generator.

(13) Lacher, *Proc. Roy. Soc. (London)*, **A161**, 525 (1937).

the California Isotope Company in sealed ampoules. The water was exposed to air only long enough to break off the tip and introduce the liquid into the tube C. The cell was evacuated before introducing any heavy water, and rinsed out before final filling.

Deuterium was not passed over phosphorus pentoxide, but passed through the hot (300°) palladium diffusion thimble (I of Fig. 1) after freezing out the oxide at F with liquid nitrogen.

Precautions were taken at all times to avoid contamination of the deuterium with hydrogen, all parts of the apparatus being well pumped and repeatedly rinsed with deuterium. That this was successful is indicated by the reproducible character of the curves and especially by the horizontal character of the flat portions.

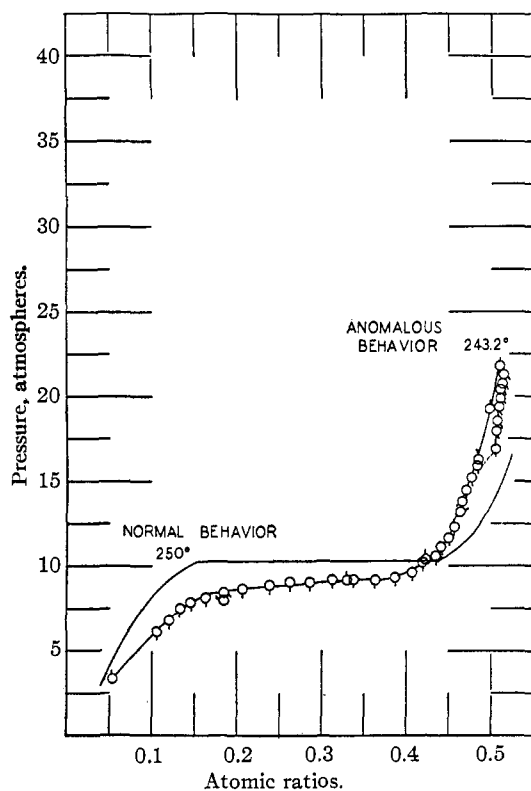


Fig. 3.—Anomalous and normal behavior of hydrogen with palladium black.

The palladium was prepared from ammonium chloropalladate obtained through the kindness of the National Bureau of Standards. This salt was converted into the chloride, then into palladosammine chloride, which was reprecipitated repeatedly from ammoniacal solution, well washed, dried, and converted to metal in a boat in a stream of hydrogen at about 150°. The hydrogen was replaced with carbon dioxide before cooling and then the metal allowed to cool in carbon dioxide. At the temperatures at which 1 atm. of hydrogen was in contact with the metal no beta phase could have been formed, a consideration that proves to be of importance.

For the first experiment the ammonium chloride, formed with the metal upon reduction of the pallados-

ammine chloride, was largely removed by substantially the same procedure used by Gillespie and Galstaun (heating *in vacuo*).

For all the other experiments the ammonium chloride was better removed by thorough washing with hot distilled water until disappearance of chloride ion, after washing for several minutes in boiling 3 *N* ammonium hydroxide to dissolve any unreduced ammine. After being dried at 105°, the metal was then heated between 360 and 380° for an hour or more under vacuum and allowed to cool in a vacuum before weighing. Two portions of metal prepared in this second way were available. After joining the reaction bulb to the apparatus and just before starting an experiment with hydrogen or deuterium, the sample was conditioned by admitting the gas at about 2 atm. at bath temperature and then exhausting, this procedure being repeated several times.

In the calculation of the average compositions of the solid phases, corrections were applied for the deviation of deuterium from the ideal gas law, under the assumption that the equation of state for deuterium is the same as for hydrogen. It should be noted that the sensitiveness of the calculations of composition to small errors of volume, to the allocation of dead space between bath and room temperature along the capillary lead from the reaction bulb, and to uncertainty of the density of the palladium (assumed to be 11.774) increases with the pressure. Therefore the compositions at the highest pressures may not be so exact as those at 20 atm.

**Experiments.**—Before proceeding to the study of deuterium it was thought well to check with hydrogen some of the results of Gillespie and Galstaun. The first experiment was with palladium prepared substantially as by them, but which stood without exclusion of air for nine months after preparation and before the experiment. The results at 243.2° are shown in Fig. 3, labelled *Anomalous Behavior*, together with the curve of Gillespie and Galstaun at a nearby temperature, 250°, labelled *Normal*. Tails on the circles distinguish points obtained by addition of hydrogen (tails pointing up) from those obtained by withdrawal. It is evident that the hysteresis is slight and the curve within the hysteresis region is lacking in a truly horizontal portion. Gillespie and Galstaun saw such a result but once, and the palladium was then found to be heavily contaminated with mercury (10% or more). Therefore this preparation was examined for mercury by very strong heating in a boat, but none could be detected. The loss of weight on heating, due in part or whole to expulsion of ammonium chloride, was 0.23%, about the same as for the preparation used for the final results of Gillespie and Galstaun. This preparation was not studied further.

Because of the experience of Holt, Edgar and Firth<sup>14</sup> with active and inactive palladium it seems possible that the nine months of storage (and not in an atmosphere of hydrogen) allowed an "inactivation." Our next experiments showed the propriety of the labelling.

For all subsequent experiments the palladium was freed from chloride by washing, as described above, and was recently prepared from the palladosammine chloride.

With such material, hydrogen isotherms were deter-

(14) Holt, Edgar and Firth, *Z. physik. Chem.*, **82**, 513 (1913).

mined at 250 and 280°. The manipulation was isothermal, no "heat treatment" being used at any time in this work. The results are shown by the centers of the circles in Fig. 4. The lines are those by Gillespie and Galstaun. The check is good. The first rising portion of the 250° curve lies underneath the old curve, but a plot of  $\log p$  against  $1/T$  indicates that the new points are more consistent with the earlier results at other temperatures than are the old 250° points. No particular effort was made to fix the exact compositions at the ends of the horizontals, but the confirmation of the earlier results is good so far as it goes; indeed, it seems better for these compositions than for the pressures.

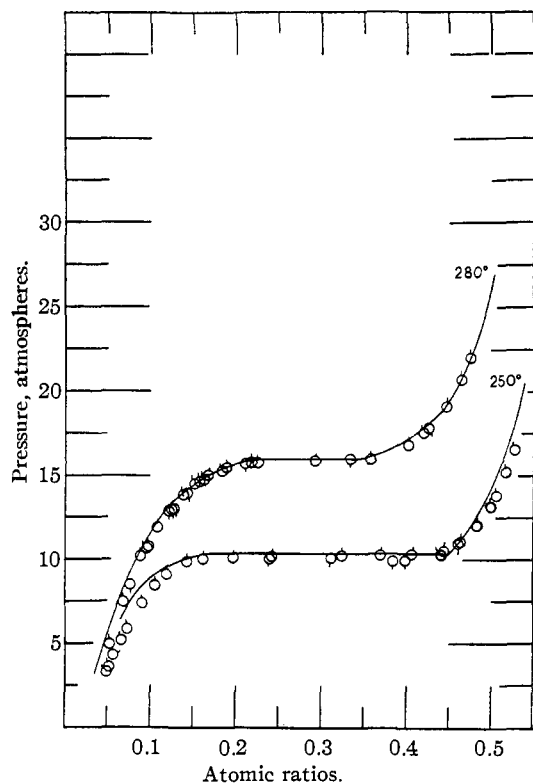


Fig. 4.—Comparison of new hydrogen data (circles) with old (lines).

Figure 4 gives a check of all apparatus constants except the volume of the gas buret and the delta value of the platinum thermometer (the ice-point agreed with the earlier value and also did the settings of the thermostatic control). It proves that the queer result at 243.2° is in fact anomalous.

In the next experiment we determined deuterium isotherms at 200 and 250°. Figure 5 shows the points for deuterium at these temperatures, with the best lines. At 250° circles of two sizes show two experiments. For comparison, the curve for hydrogen of Gillespie and Galstaun is added, as well as their points at 200° (but not at 250°), so that the spread of the points in the horizontal region can be compared. The spread is greater for  $D_2$  at 200° than for  $H_2$ . The spread decreases with rising temperature in both cases.

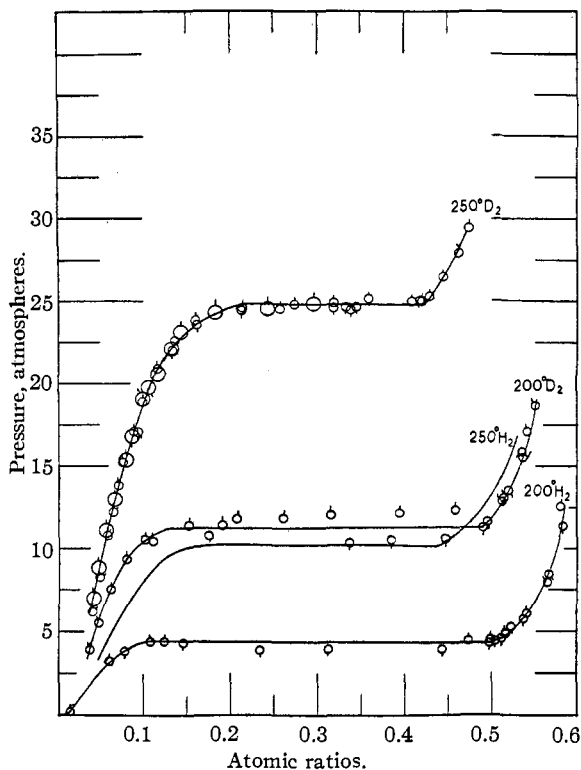


Fig. 5.— $H_2$ :Pd and  $D_2$ :Pd at 200 and 250° (normal behavior).

It was at this point that the jacket was installed to protect the reaction bulb and the second portion of the palladium was also placed in the bulb, a portion that had not been exposed to hydrogen so as to form beta phase. The resulting curve is shown at the left of Fig. 6, labelled *Virgin Pd, Sample B*. All the points represent additions. They are so far from the curve previously obtained and here labelled *Normal Curve* that the deuterium was removed, fresh deuterium added to a pressure of about 6 atm. (at 250°) and the system evacuated. This pressure is only one-quarter of that required for beta phase formation under equilibrium conditions, but had some effect on the palladium. This is shown in the same Fig. 6 by the curve labelled *Virgin Pd, Sample B'*. The hysteresis is considerable and the loop does not enclose the normal curve shown without points. If the additions had been extended to high enough pressures the loop might well have enclosed the normal curve or perhaps coincided with it in part.

In the next experiment the deuterium was removed and replaced with hydrogen, and the points of a hydrogen isotherm at 250° determined as shown in Fig. 7 along with the line of the earlier experiment (of Fig. 4). The agreement of the points with the line shows that the metal was like that used before. After removal of hydrogen and flushing with deuterium, the points for a deuterium isotherm were determined as shown in the same Fig. 7 along with the line previously determined (of Fig. 4).

These experiments showed us that there is a reluctance toward formation of the deuterium beta phase, which has

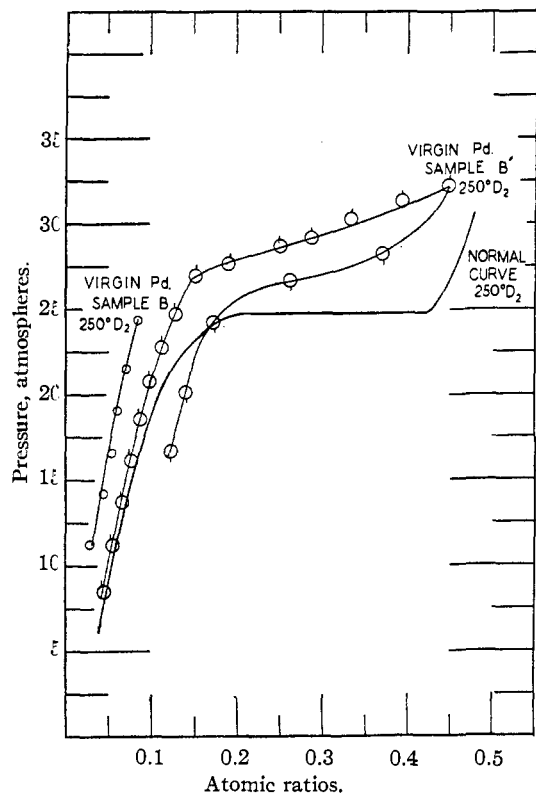


Fig. 6.—Deuterium in virgin Pd and in Pd previously used for hydrogen ("normal curve").

seldom been observed by us in the case of hydrogen, but is serious in the case of deuterium. We think that the loop of Fig. 6 indicates the formation of some beta phase at moderate pressures of deuterium (in material within which no beta phase of hydrogen had ever been produced), but that in this case beta phase was not formed in all portions of the metal.

Once beta phase is formed throughout the metal by the use of hydrogen, an effect persists after evacuation. In the X-ray experiments distortion of the diffraction pictures remains and here the material seems to retain enough structure to serve as nuclei for subsequent beta phase formation. We have not hesitated therefore to proceed to extend the study of the deuterium-palladium diagram by the use of palladium thus conditioned with hydrogen.

Our complete phase diagram of the system Pd:D<sub>2</sub> is shown in Fig. 8. The anomalous results quoted above are not included, and no further anomalous results were seen. There is a critical solution temperature at about 276°. The corresponding pressure is 35 atm. to within 0.5 atm., and the composition is about 0.25 atom of D per atom of Pd.

Sieverts and Danz<sup>4</sup> suggested from the course of some low pressure measurements that the critical solution temperature might possibly be lower than for hydrogen, but they did not show that one exists for deuterium.

The pressures along the horizontals for deuterium are given in the following table, as observed directly without

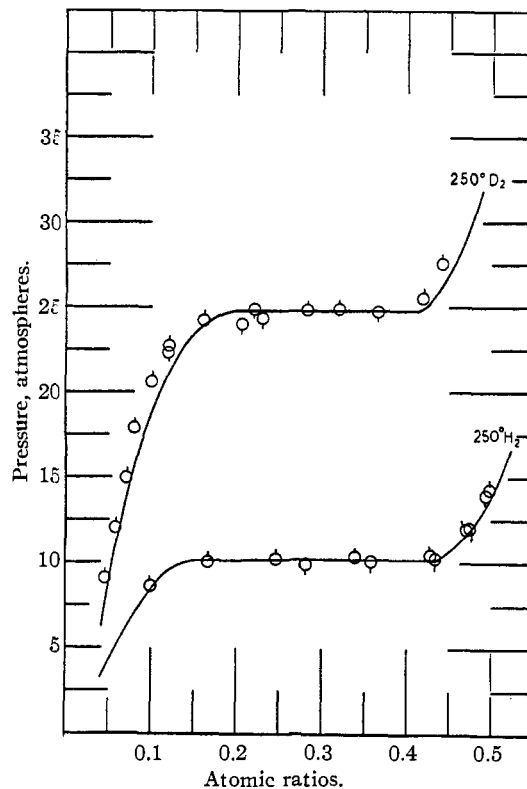


Fig. 7.—Normal H<sub>2</sub> curve followed by normal D<sub>2</sub> curve in the sample of Fig. 6.

regard to temperature consistency, and as calculated from the equation

$$\log_{10} p_{\text{atm.}} = 4.6330 - 1696.11/(t + 273.13) \quad (1)$$

TABLE I  
PRESSURES ALONG THE HORIZONTALS FOR D<sub>2</sub> AND Pd  
IN ATM.

Temp., t°	200	250	260	270
Obsd.	11.4	24.5	28.25	32.5
Calcd.	11.7	24.5	28.3	32.4

The calculated pressures agree with the points of each isotherm as well as the directly observed, and should be regarded as the final best values.

From Eq. (1) and the simple Clapeyron equation (with ideal gas assumptions) the heat evolved when 1 mole of deuterium is added to palladium to convert the alpha (first) to the beta (second) solid solution is calculated to be 7760 cal. The corresponding result for hydrogen is 8590 cal. from the previous work.<sup>2</sup> This heat is therefore 10% less for deuterium. Its value is more uncertain, being determined from only four points between 200 and 270°.

As in the case of hydrogen, the fictive heat effect upon adding 1 mole of gas to palladium is least along the first rising portions of the iso-

therms, greater along the horizontals, and greatest along the second rising portions of the isotherms. The fictive heat above the critical point at the critical composition seems to be greater for deuterium than the heat along the horizontals.

Ten weeks after the completion of the isotherms shown in Fig. 8 another isotherm was determined at 260° and also a few points at 280°. These last results did not check exactly with the previous. The pressure of the horizontal at 260° was correct as judged by Eq. (1) and as shown in Table I, but the compositions were lower at both temperatures by about 0.01 in the atomic ratio. This suggests an error in the reading of the gas buret at the beginning of this last experiment, but in any case the check is sufficient to exclude the possibility that the results of Fig. 8 (in which the 260° isotherm is not included) suffer from aging of the palladium, and the results speak definitely against a tendency toward compound formation in the neighborhood of Pd<sub>3</sub>D.

The locus of the compositions of the coexistent solid phases, alpha and beta, as shown by the broken line in Fig. 8, discloses no tendency toward compound formation—indeed, seems to exclude the possibility of compound stability. The results shown are not completely convincing as regards a hypothetical Pd<sub>3</sub>D, but the 260° isotherm completes our conviction that no compounds are in evidence above 200°, our lowest temperature.

A final analysis was made of the last palladium sample studied, introduced with the jacket as mentioned above, and no mercury could be detected. The loss of weight after very severe heating in a stream of nitrogen was only 0.03%, within the experimental error.

On a large diagram of Fig. 8 new horizontals were drawn at the pressures given by Eq. (1) and with their aid the compositions of the alpha and beta phases determined at the ends of the horizontals. The values are given in Table II.

TABLE II

COMPOSITIONS OF COEXISTENT ALPHA AND BETA PHASES				
Temperature, t°	200	250	260 <sup>15</sup>	270
Atomic ratio D/Pd, alpha phase	0.130	0.173	0.195	0.215
Atomic ratio D/Pd, beta phase	0.495	0.418	0.365	0.310

The ratio of  $p_D$ , the pressure along a horizontal for deuterium at any temperature, to  $p_H$ , the

(15) Estimated by applying the correction of 0.01 to the results of the 260° isotherm.

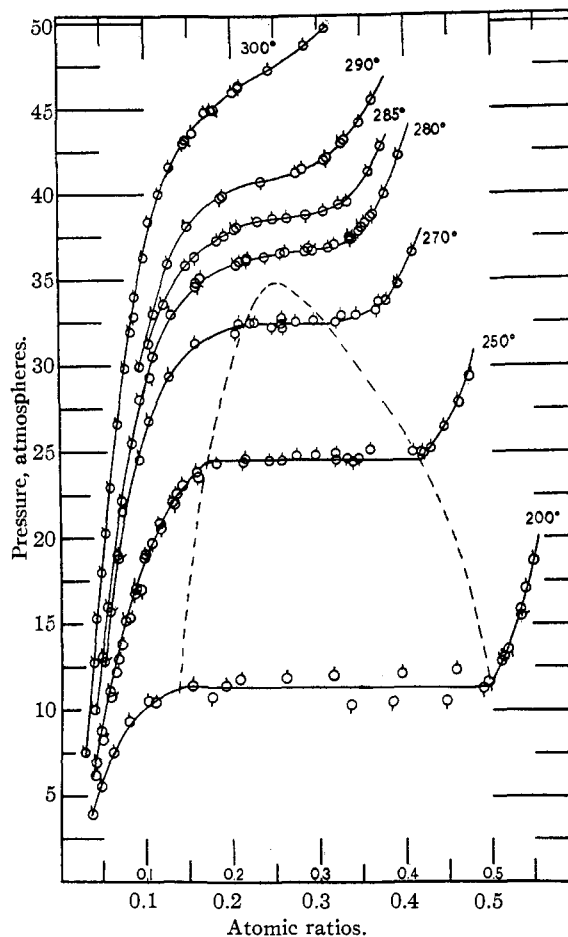


Fig. 8.—Phase diagram of deuterium and palladium.

pressure along the horizontal for hydrogen at the same temperature, is given by Eq. (2) up to the critical point for deuterium.

$$\log_{10} (p_D/p_H) = 0.0312 + 181.71/(t + 273.13) \quad (2)$$

In our publications we have never presented our reasons (some of which are based on indirect evidence) for believing that our degassing technique has been sufficient to ensure that our compositions really start at zero as is assumed in all our phase diagrams. Mercury diffusion pumps have always been used—the metal was in the finely divided black form—the temperature of degassing in the early work<sup>16</sup> was never less than 360° and in the later work<sup>2</sup> and the present work never less than 200° (the lowest bath temperature). Recent special degassing experiments by Bennett<sup>17</sup> on massive palladium richly charged

(16) Gillespie and Hall, THIS JOURNAL, 48, 1207 (1926).

(17) F. D. Bennett, *ibid.*, to be published. We wish to thank Mr. Bennett and Professor W. R. Ham, through whose courtesy we were able to see the paper in advance of publication.

with hydrogen by electrolysis show no difficulty at 300° (which is above the critical solution temperature) and not too much at 200°. This work seems to close the question and to make it unnecessary to discuss the indirect evidence.

### Summary

The isotherms of Gillespie and Galstaun for palladium and hydrogen at 250 and 280° have been confirmed.

A series of isotherms for deuterium and palladium black has been obtained from 200 to 300°, including a critical solution point. A difficulty due to reluctance to formation of the second solid phase was overcome by first forming the beta phase of hydrogen-palladium by pretreatment with hydrogen.

After such pretreatment the isotherms of deuterium are thoroughly reproducible, and after prolonged treatment of palladium with deuterium the hydrogen isotherms are again reproducible.

For a given temperature and pressure, the absorption of deuterium is less than that of hydrogen, but at all the temperatures studied there is not much difference in the maximum absorption of the two gases at the highest practicable pres-

ures after the second solid phase has been formed. Horizontal lines appear in the deuterium isotherms at pressures about 2.3 to 2.5 times the pressures of the corresponding hydrogen horizontals.

The critical solution temperature for deuterium and palladium is found to be 276°, the critical pressure 35 atm., and the critical composition 0.25 atom D per atom Pd.

The heat of solution per mole of deuterium increases regularly with increasing deuterium content and is 7760 cal. per mole for the conversion of the first to the second solid phase.

The phase diagram is given. The locus of the compositions of coexistent solid solutions is smooth and continuous without rising steeply at any simple atomic ratio. This indicates that no palladium deuterides exist in the region above 200°. As the composition of the second solid phase is practically that of Pd<sub>2</sub>D at 200° (like the H<sub>2</sub> system), further work at lower temperatures will be required to determine the possible existence of this compound.

The palladium black was prepared by reduction of palladosammine chloride and studied at once.  
CAMBRIDGE, MASS. RECEIVED JULY 10, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

## The Reduction of Metal Oxides in Liquid Ammonia. I. Preliminary Communication

BY GEORGE W. WATT<sup>1</sup> AND W. CONARD FERNELIUS

Recent studies have shown that bismuth oxyiodide is reduced completely by solutions of sodium and potassium in liquid ammonia.<sup>2</sup> The removal of oxygen from the oxyiodide appears to involve the formation of alkali monoxide and its subsequent ammonolysis to alkali hydroxide and alkali amide. These experiments suggest that some oxides, like almost all halides,<sup>3</sup> may be reduced by liquid ammonia solutions of the alkali metals.

There have been recorded in the chemical literature certain observations which suggest that mercurous oxide,<sup>4</sup> zinc oxide,<sup>5</sup> ferric oxide,<sup>6</sup> and

cobaltous-cobaltic oxide<sup>6b</sup> may be reduced under similar conditions. In none of these cases, however, has it been proved that oxygen may be removed *quantitatively* from a heavy metal oxide by means of these reducing agents.

### Experimental<sup>7</sup>

**Bismuth Trioxide.**—One-half gram of bismuth trioxide in the presence of 15 cc. of liquid ammonia<sup>8</sup> was treated with a solution containing 0.25 g. (six equivalents) of potassium in a like volume of ammonia. The characteristic blue color of the potassium solution was discharged immediately and the yellow trioxide was reduced to a gray

(1) Present address: Department of Chemistry, The University of Texas, Austin, Texas.

(2) Watt and Fernelius, *THIS JOURNAL*, **61**, 1692-4 (1939).

(3) For primary references see Fernelius and Watt, *Chem. Rev.*, **20**, 211-13, 226-32 (1937).

(4) Weyl, *Ann. Physik*, **121**, 601 (1864); **123**, 350 (1864); **131**, 524 (1867).

(5) Weyl, *ibid.*, **123**, 353 (1864).

(6) (a) Bergstrom, *THIS JOURNAL*, **53**, 3037 (1931); (b) Burgess and Kahler, *ibid.*, **60**, 191 (1938).

(7) The experimental methods employed were those developed by Franklin and co-workers. All reactions were carried out in Faraday tubes at or near room temperature. For details see: Franklin, "The Nitrogen System of Compounds," Reinhold Publishing Corporation, New York, N. Y., 1935, pp. 317-30; Johnson and Fernelius, *J. Chem. Educ.*, **6**, 447-50 (1929).

(8) All of the oxides studied appeared to be insoluble in and unreactive toward liquid ammonia. However, there appears to be some evidence to indicate that cuprous and cupric oxides are slightly soluble; see Franklin and Kraus, *Am. Chem. J.*, **20**, 827 (1898).