

the experimental data show no such minimum and maximum in this or other cases.

The data for 0° are given in Table II. These data cover a smaller range of concentration than for 25°, and therefore give a less severe test of the equations. The solubility is not great enough at 0° to make it possible to work with 0.5 molar solutions and the data below 0.001 molar were not obtained. These data are probably not quite so reliable as the data at 25°, because it is harder to control the temperature inside an oil bath at 0° than at 25°. The Kohlrausch method of extrapolating to infinite dilution using the data from 0.001 to 0.01 molar gives $\Lambda_0 = 353$ but this figure is undoubtedly much too low. The Jones and Dole equation for this case is $\Lambda = 420.40 - 4768.7 \sqrt{c}/(1 + 16.459 \sqrt{c}) + 33.87c$. The differences between the observed results and the results computed by this equation are given in column 3 of Table II. The deviations are much less than were found at 25°, but this is probably due to the fact that the data cover a smaller range of concentration and are therefore easier to fit to an equation. The deviations are probably somewhat greater than the experimental error.

By the use of the values of the relative viscosity given in the preceding paper we have computed the values of $\Delta\eta$ given in column 5 of Table II. With the viscosity correction applied the Jones and Dole equation becomes $\Delta\eta = 418.79 - 4635.89 \sqrt{c}/(1 + 16.0335 \sqrt{c}) + 68.40c$. As will be seen by a comparison of columns 3 and 6 the deviations are substantially reduced by the application of the viscosity correction especially in the more concentrated solutions.

The last column in Table II gives the ratio between the conductance at 25 and at 0°. As will be seen the temperature coefficient of the conductance decreases with increasing concentration.

Summary

1. The conductance of potassium ferrocyanide solutions has been determined at 25 and at 0° from great dilution up to nearly saturation.

2. The data have been used to test various equations which have been proposed to express the conductance as a function of the concentration.

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The Palladium-Hydrogen Equilibrium and New Palladium Hydrides¹

BY LOUIS J. GILLESPIE AND LIONEL S. GALSTAUN

The early work of Troost and Hautefeuille, Hoitsema, Sieverts, Lambert and Gates and others was reviewed in the paper of Gillespie and Hall. It may be remembered that Troost and Hautefeuille² claimed the existence of Pd₂H on the basis of evidence just short of that demanded by the phase rule, which was about to be announced by Gibbs, and that this claim was usually disallowed after the paper of Hoitsema,³ although Lambert and Gates⁴ pointed out that their descending isotherms show "breaks" at approximately the same composition (about Pd_{1.9}H) at

75, 103 and 120°. Gillespie and Hall⁵ worked with finely-divided palladium, allowed much time—often one to three days or longer—to elapse before recording pressures, and obtained for the first time a phase diagram for the system in obvious conformity with the phase rule. This diagram indicates the existence of Pd₂H capable of formation in definite proportions from about 80 to 180° or higher; at lower temperatures the phase contains a progressively greater excess of hydrogen.

In their first work at 0° they established the first break between the first rising isotherm and the relatively horizontal one as a sharp angle, which could be demonstrated reversibly at constant temperature. Large additions of hydrogen produced hysteresis effects. They discovered that if some hydrogen were withdrawn and the

(1) Part of this article is taken from the thesis presented by L. S. Galstaun in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology. The work at 270, 280 and 285°, upon which the finding of new hydrides mainly rests, was done since presentation of the thesis.

(2) Troost and Hautefeuille, *Compt. rend.*, **78**, 686 (1874); *Ann. chim. phys.*, [5] **2**, 273 (1874).

(3) Hoitsema, *Z. physik. Chem.*, **17**, 25 (1895).

(4) Lambert and Gates, *Proc. Roy. Soc. (London)*, **108A**, 456 (1925).

(5) Gillespie and Hall, *This Journal*, **48**, 1207 (1926).

system heated for a short time to 360° and exposed again to 0° , the pressure returned to the same level as that of the first break. They were able by the use of this "heat treatment" to follow along a truly horizontal isotherm. Now the pressure at the first break was proved by the classical method, and the results of the heat treatment must be correct—so long at least as the isotherm remains horizontal—as they maintained in an extended discussion. This method was then used for other temperatures, and for the second rising isotherms.

Some writers have since felt misgivings because of this use of heat treatment, yet no one has tried unsuccessfully to reproduce the results. No theoretical objection to the heating has been presented, except that Gillespie and Hall pointed out that the results refer to palladium that has recently been heated and that this must in any case be so, as heating *in vacuo* is a necessary preliminary to the experimentation. This being granted, it cannot be admitted further that there is any theoretical advantage in conducting the additions of hydrogen isothermally. A practical advantage is that of greater consistency of data at a given temperature.

Since the work of Brüning and Sieverts,⁶ who established the existence of a critical solution temperature at about 300° and found that equilibrium is very quickly reached above this even in the case of wire, it is possible to understand why the heat treatment was beneficial in the case of large additions of hydrogen.⁷ The heating to 360° must have brought about uniformity of composition throughout the mass. On cooling, the mass had to separate into two phases, but these phases could form equally well at all points in the mass, whereas a crust may form on direct isothermal addition. There is still of course a difficulty due to the necessary exchange of gas between solid and dead space, which would make the treatment nearly or quite useless for small additions.

Linde and Borelius⁸ obtained very exact X-ray data that show at 100, 150 and 200° the presence of two mutually saturated solid solutions. The lattice constant of that richer in hydrogen is about the same at all three temperatures, and they suggested without further evidence that perhaps Gillespie and Hall were mistaken in supposing the

richer phase to contain, at temperatures below 80° , an excess of hydrogen over the composition of Pd_3H . This appears impossible, however, as the proof of the excess seems to be perfect, according to the discussion above. Linde and Borelius found the lattice constant practically the same at the two higher temperatures for the hydrogen-weak phase. This is quite consistent with the original data plotted in the Fig. 3 of Gillespie and Hall (though not consistent with the broken line that interprets the compositions of this phase). This fact indicates the existence of Pd_3H , which will be discussed later in connection with new data.

Brüning and Sieverts⁶ have studied the pressures, compositions and electrical resistance of palladium wire containing hydrogen. In their work at 210 to 310° the compositions were estimated from the resistances with the aid of extrapolated relations determined at lower temperatures. Thus no great accuracy can be claimed for the calculated compositions, particularly in some cases where the relations involved an angle whose magnitude must change with the degree of hysteresis (see their Fig. 9), since the hysteresis vanishes at the highest temperatures. Nevertheless they found with certainty that there is a critical solution temperature between 290 and 310° , estimated at about 300° .

In their work at 160, 180 and 200° they measured the compositions directly. Hysteresis was very marked when two solid phases were obviously present. They forebore to compare their results with those of Gillespie and Hall at the two lower temperatures on the grounds that the latter used finely divided palladium heated to 400° in a vacuum and did not carry out the measurements isothermally. But along the first rising isotherm there was no hysteresis; their results with wire should not differ from the results in this Laboratory. Figure 1 shows one of their two series at 180° , their points being joined with broken lines, and the final results of Gillespie and Hall being shown by a solid line. The agreement along the first rising isotherm is not bad; in the case of their other series at 180° it is better; at 160° , as also shown in Fig. 1, it is very good; and at 200° the agreement is equally good, when in this case the data presented below are used for comparison. Although Gillespie and Hall believed they reached the second rising isotherm, it is doubtful whether Brüning and Sieverts did so, except prob-

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

(7) We cannot say it was really beneficial for small additions.

(8) Linde and Borelius, *Ann. Physik*, [4] **84**, 747 (1927).

ably at 160° . Only in this case is there a hint of agreement along the second rising isotherm, and here their break is estimated at the atomic ratio $H: Pd = 0.49$ —nearly at Pd_2H . Figure 1 indicates very clearly that the experiments at 180° were not carried along with sufficient addition of hydrogen to convert the whole of the wire into the second solid phase. For, if from the point A hydrogen had been subtracted instead of added a false break at a ratio of 0.4 or less would probably have been obtained; whereas if from B hydrogen had been added again instead of withdrawn it appears entirely possible that another hysteresis loop might have been observed, followed by a break at a ratio greater than 0.49. Figure 1 shows that at 160° the rising and falling isotherms at the top of the figure nearly coincide, and therefore complete conversion, or nearly so, may have been obtained at the point D. Even here, all that can be concluded is that the second break lies somewhere within the area of hysteresis, probably at a level higher than the line EC. In short, Fig. 1 indicates a complete confirmation of the 160° isotherm of Gillespie and Hall within the error of hysteresis. In the other three cases not enough hydrogen was ever added to produce rising and falling isotherms at the top of the diagrams in approximate coincidence and the results do not really speak against the existence of Pd_2H .

This matter has been discussed at length because, interpreting the phase relationships for this system, Brüning and Sieverts allow the picture in their Fig. 13 to be obscured by the inclusion of the unexplained early results of Hoitsema and some irrelevant data⁹ concerning palladium charged with hydrogen by electrolysis and draw their temperature-composition line in disregard to data of Lambert and Gates and of Gillespie and Hall (particularly at 80°) and of the existence of Pd_2H .

It seems significant that when they draw the locus of the resistance of mutually saturated solid phases as function of the pressure in their Fig. 11 they avoid the second break-points plotted at 180° and 200° to prevent an unnatural change of curvature. We think the corresponding points should

(9) We do not call these data irrelevant simply because hydrogen was added by a special method (electrolysis), but because the line in question is supposed by phase theory to be the locus of compositions of mutually saturated solid phases. There appears not the slightest reason to suppose that the substance prepared by electrolysis is a pure phase in equilibrium with the so-called first, hydrogen-poor phase. It is probably not even in internal equilibrium.

be similarly avoided in the composition-pressure locus of their Figs. 12 and 13.¹⁰

Ipatieff and Tronow¹¹ have measured some rising isotherms at various temperatures and at pressures up to about 25 atm. Hysteresis was not discussed but was evidently great. Thus at 150° the pressure could be reduced from 3.5 atm. (at the atomic ratio 0.79) to 1 atm. without changing the amount of hydrogen absorbed by more than about 1 part in 250. The object of the authors was not to study the phase diagram and they do not refer to recent work on it.

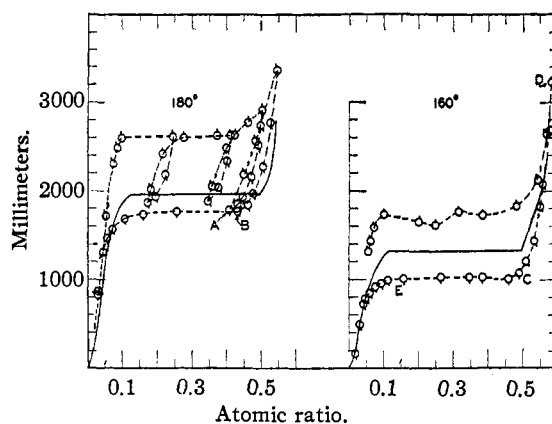


Fig. 1.—Comparison of previous data.

Tromp and De Loor¹² criticize the interpretation of Gillespie and Hall, but the criticism is really not specially directed against them, being a general attack on orthodox interpretations of phase diagrams, and is based on a misunderstanding of the mass action law.¹³

Hüttig¹⁴ has given a general review of hydrides.

Valensi¹⁵ has given a general discussion of the action of gases on metals and has pointed out the similarity of the chromium-nitrogen diagram studied by him—with its compound CrN and critical solution temperature—to the palladium-hydrogen system.

(10) Their reference to the material of Gillespie and Hall as *gesinterter Mohr* is not understood by us. Our palladium black will undergo great volume contraction and sinter when heated in air or oxygen, but nothing like this happens when it is heated much over 400° *in vacuo*, in carbon dioxide or in hydrogen, and sintered material has not been used by us for absorption experiments.

(11) Ipatieff and Tronow, *J. Phys. Chem.*, **38**, 823 (1934).

(12) Tromp and De Loor, *J. Chem. Met. Mining Soc. S. Africa*, **35**, 169 (1934).

(13) The mass action law for *homogeneous* systems admits of no discontinuities. This is taken to deny certain orthodox discontinuities in the diagrams representing *heterogeneous* systems.

(14) Hüttig, *Z. angew. Chem.*, **39**, 67 (1926).

(15) Gabriel Valensi, Thesis, Paris, 1929.

Experimental

Apparatus.—The apparatus for the generation, measurement and confinement of hydrogen is shown schematically, not to scale, in Fig. 2. Hydrogen is made by electrolysis of 10% NaOH containing some barium hydroxide between nickel electrodes, the generator being run continually to keep out air. It can be passed through a heated platinized-asbestos tube M, but in the present experiments it has

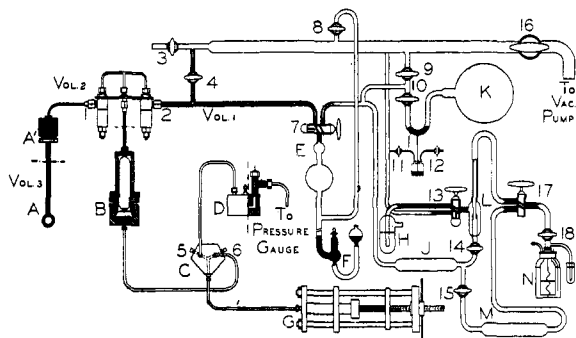


Fig. 2.—Apparatus.

been passed through a thin palladium tube, L heated to about 300°. Some is rejected through H, the rest is passed through two phosphorus pentoxide tubes, one of which is shown at J, and hence to the storage bulb K or the gas buret E. From this a measured portion can be passed into the steel-protected glass bulb B by means of a mercury compressor G. By closing the stopcock 2 and opening 1 the gas can then be compressed into the heavy Pyrex reaction bulb A until the mercury stands in the glass capillary tube at the level of the dotted line above B.

The stopcocks 1 and 2 are of steel, worked from below, and are provided with mercury seals to keep gas from the waxed packing gland. The volumes 1, 2 and 3 were determined by expanding dry hydrogen from the gas buret in a series of experiments, volume 3, extending to the dotted line, having first been determined by weighing water. Stopcock 1, when opened, is open always to the same extent, likewise stopcock 2. In this case the change of volume on closing is 0.02 cc. The volumes 1, 2 and 3 contain 2.4383, 1.5834 and 0.8906 cc., respectively, the last without palladium. 0.96670 g. of palladium was added to the bulb and the capillary resealed without appreciable change of volume. Assuming the density of palladium to be 11.78, we find the free volume 3 to be 0.8085 cc. This is assumed to be at the temperature of the palladium in the thermostat, as the level of demarcation was suitably chosen after exploration with a thermocouple.

The riser block D contains the junction between mercury on the left and oil on the right. The oil line leads to a dead-weight pressure gage. The junction can be maintained at a known level at the end of a steel needle, by means of a vacuum tube circuit which requires only a grid current across the junction. Corrections were made for all oil and mercury columns and the barometric pressure exerted on the gage and the pressures are reported in international atmospheres.

The glass-to-steel joint A' is shown in detail in Fig. 3. A small steel baffle A, slightly greased, is used to catch and

detect any chance droplet of mercury from the stopcocks, but none was found at the end of the experiments.

The thermostat is of steel, provided with an efficient stirrer and wells of steel for the reception of two platinum thermometers, a knife-blade heater and the reaction bulb. Steady heating is provided by an external coil, operated through a Raytheon voltage regulator of 250 watts, working at full load by means of an adjustable shunt load. One of the platinum thermometers is used for measuring the temperature, having been carefully calibrated and compared with other good thermometers. The other is part of a bridge circuit, the galvanometer in which actuates a selenium cell controlling, in a "phase-shift" circuit, a thyatron tube which furnishes the auxiliary current for the knife-blade heater. The thyatron furnishes about 15 to 20% of the total heat. The bath is a mixture of sodium, lithium and potassium nitrates. Under favorable circumstances of room temperature, regulation to better than 0.001° is obtained at the experimental temperatures.

The dead space at room temperatures is protected by the use of aluminum foil and the temperature measured.

Materials.—The hydrogen was purified by diffusion through a hot palladium tube as described above. In some preliminary work at 310° such hydrogen was found to give the same isotherm as hydrogen passed over platinized asbestos (and in either case, over phosphorus pentoxide).

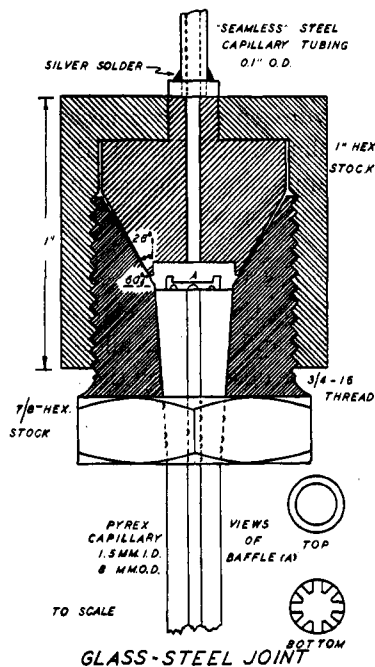


Fig. 3.—Detail of glass to metal joint.

Ammonium chloropalladate was obtained through the kindness of the National Bureau of Standards. It was stated to be free of other metals, particularly platinum-like metals, though not of alkali metals. From this the yellow palladosammine chloride was prepared, reprecipitated twice from ammoniacal solution with hydrochloric acid, thoroughly washed in conductivity water and dried at 100°. A weighed sample was reduced in a stream of hydrogen at 150°, the temperature then slowly raised to a

maximum of 500° and a stream of carbon dioxide substituted for the hydrogen. After ten minutes at 500° it was then slowly cooled in the stream of carbon dioxide and weighed. Vacuum corrections were applied. Palladium found, 50.353 and 50.344%; calculated by 1935 atomic weights 50.407%.

Palladium reduced in this way was placed in a Pyrex bulb, and the bulb was evacuated and heated with a hand torch until it partly collapsed. This was an effort to remove any trace of ammonium chloride. The material was allowed to cool in a vacuum, weighed and transferred to the reaction bulb.

In this type of experiment the palladium is easily contaminated with mercury through accident. Furthermore, mercury may be transferred with hydrogen to the palladium, or may distil to it during evacuation. We have not introduced a liquid air-bath to prevent this because of the damaging increase of dead-space corrections and increased liability of accident to the glass apparatus. A palladium mercuride occurs naturally in British Guiana, containing 54.4 to 65.2% Hg.¹⁶ An excess of mercury can react with palladium, especially readily if the palladium contains hydrogen and if heated. After driving off mercury with a fairly strong Bunsen flame we have found to remain 58.2 and 59.1%, most of which could be removed by the strongest Bunsen flame on a small crucible. The formula Pd₄Hg₃ corresponds to 58.5% Hg. Our preparation was hard, sank in the excess of mercury and appeared to have a very low solubility in it. The natural mercuride is hard and denser than its elements.

If the hydrogen which actually entered the palladium during our experiments had been saturated with mercury at 1 atmosphere total pressure, the palladium would have contained about 0.01% of mercury at the end of the experiments. Even ten times as much would not—we have reason to suppose—influence the pressures seriously, though it might hinder equilibrium.

After the last pressure measurement the palladium was exhausted at 290°, cooled in a vacuum and exposed to air. It was then weighed in a porcelain boat with a suitable tare. Then it was conditioned at about 370° in hydrogen, followed by carbon dioxide for half an hour and finally cooled in carbon dioxide, conditioned in the balance case and weighed again with undisturbed weights and rider. The loss of weight was only 0.03 mg. on 942 mg. of sample. Such heating will not remove small amounts of mercury. The boat was placed in a narrow quartz tube and strongly heated with a Meeker burner to bright red heat in a current of carbon dioxide, the palladium conditioned with hydrogen and carbon dioxide, cooled in carbon dioxide and weighed as before. The loss of weight was about 2 mg. The palladium was then heated again in the quartz tube in a current of oxygen, followed by hydrogen and carbon dioxide as before. The further loss of weight was about 0.3 mg. The total loss of weight was 0.26% of the weight of the palladium. Previous experience with the elimination of known quantities of mercury showed that this procedure is sufficient.

The loss in weight in this case cannot be due mainly to mercury, as this should have been collected in a narrow

water-cooled part of the quartz tube, and none could be found by inspection with the low-power microscope. As the tube at this place appeared etched, about 2 mg. of mercury was intentionally distilled and collected in this part, without cleaning it. Under the low power, the mercury made a striking display, no substantial fraction of which could have been missed in the analysis. In the analysis the gas was passed into a test-tube of water for cooling, and this gave a test with Nessler's reagent.

We conclude that part of the loss of weight was due to elimination of ammonium chloride, and that the amount of mercury in the palladium was much less than 0.2%.

Measurements of Equilibrium Pressure.—We considered the pressure worthy of record as equilibrium pressure when it remained constant for one-half hour. Weighings of the pressure were made to 1 g., corresponding to about 1 mm., though in most cases not reported so precisely in the table. At the higher temperatures equilibrium was evidently reached very quickly, and this was confirmed by coincidence of the rising and falling isotherms. In the two-solid-phase region hysteresis was increasingly evident as the temperature was lowered, until it was very serious at 200°. The "heat treatment" of Gillespie and Hall was not used at all in this work, as it was very inconvenient with the new apparatus. The mercury compressor allowed of a withdrawal of hydrogen followed by return of the same amount to the palladium plus dead space. This seems to be of some assistance in gaining proper equilibrium, but proof of this is lacking, and in the interpretation of the measurements no particular weight has been given to data secured in this way. Such points are shown in the diagrams by circles without tails—they should in most cases be regarded as additions. Additions are shown by tails pointing upward; subtractions, by tails pointing downward.

Calculation of Concentrations.—The hydrogen admitted to the apparatus during an experiment is partly in the palladium and partly in the dead space. Frequently only one-fourth of it was in the palladium. The dead space is in two parts, one at bath temperature and one at room temperature. The density of palladium with adsorbed hydrogen is not well known, and perhaps cannot be. Measurements of Wolf¹⁷ on palladium wire show marked hysteresis and lack of reproducibility. However, they lead us to believe that the error we make in assuming constant density is not serious. We have given above enough apparatus constants to allow of easy correction of our concentrations, if better density data become available. The error of neglecting the thermal and pressure expansion of the glass reaction bulb should be much smaller. At the higher pressures it is necessary to correct for the non-ideality of hydrogen and this correction has been made throughout. It amounted to an increase of 0.0086 in the atomic ratio at 32 atm. and 310° and was a strong function of the pressure and a weak function of the temperature.

The concentration is reported throughout as the atomic ratio: atoms hydrogen per atom palladium.

Experimental Results.—The data are presented in Table I in the order in which they were taken, except for some measurements at 0°, made

(16) Harrison and Bourne, *Off. Gazette, Brit. Guiana*, No. 71, Feb. 27, 1925; *C. A.*, **19**, 3075 (1925).

(17) Wolf, *Z. physik. Chem.*, **87**, 575 (1914).

between those at 200° and those at 280°. When the mercury compressor was used as described above to withdraw and return hydrogen the ratio is followed by an asterisk. In the last few cases the entries do not begin with zero pressure. This means that the preceding experiment was continued at a new temperature without exhaustion.

TABLE I
Equilibrium Pressures in Atmospheres and Corresponding Atomic Ratios (r)

313.02°		310°		295°	
p	r	p	r	p	r
0	0	9.47	0.0606	19.805	0.2856
5.78	0.0398	5.51	.0417	19.818	.2961
10.86	.0621			19.811	.2934
15.60	.0914			19.846	.3101
19.59	.1253	0.31	0.0123	19.95	.3308
22.44	.1690	4.76	.0384	20.20	.3532
24.43	.2179	10.08	.0660	22.42	.4194
25.16	.2818	15.05	.0993	27.90	.4721
25.85	.3303	18.84	.1427	25.10	.4526
27.01	.3669	20.51	.1804	22.69	.4243
30.44	.4196	21.01	.2316	20.75	.3804
27.65	.3814	21.20	.2845	19.868	.3214
25.91	.3362	21.62	.3391	19.867	.3179
24.98	.2719	22.83	.3863	19.805	.2978
23.67	.1946	0	0	19.792	.2793
22.54	.1679	4.23	0.0359	19.794	.2716
19.41	.1253	9.33	.0614	19.791	.2746
16.63	.1031	14.15	.0960	19.767	.2627
13.47	.0833	18.45	.1368	19.777	.2629
10.69	.0679	20.84	.2121	19.753	.2503
8.39	.0576	21.12	.2617	19.455	.2034
6.32	.0500	21.15	.2738		
		310°		290°	
		0	0	0	0
		0.296	0.0078	0.464	0.0105
		.538	.0106	5.96	.0466
		.740	.0125	11.22	.0777
		.891	.0138	15.57	.1217
		0	0	17.10	.1477
		0.30	0.0078	18.18	.1873
		3.72	.0306	18.20	.1915
		7.89	.0511	18.39	.2092
		11.81	.0706	18.38	.2096
		16.77	.1020	18.45	.2256
		20.67	.1409	18.49	.2444
		23.02	.1925	18.51	.2609
		24.06	.2720	18.53	.2790
		25.29	.3506	18.53	.2933
		28.58	.4146	18.54	.3198
		31.87	.4449	18.57	.3363
				18.57	.3376
				18.79	.3594
				19.03	.3739
				19.61	.3995
				21.89	.4415
				21.80	.4392
				26.30	.4792
				30.58	.5040
				25.23	.4749
				21.86	.4434

290°		250°		280°	
p	r	p	r	p	r
19.32	0.3894	8.63	0.0992*	16.30	0.3625
18.76	.3605	6.27	.0615	16.38	.3646*
18.75	.3570			200°	
18.57	.3390	0	0	16.72	.3853
18.52	.3247	0.35	0.0140	18.82	.4379
18.52	.3180	3.22	.0608	21.84	.4704
18.51	.2983	4.40	.1068	26.44	.5024
18.52	.2960	4.36	.1074	20.35	.4586
18.50	.2765	4.44	.1286	16.89	.3961
18.52	.2771*	4.47	.1549	16.36	.3702
18.51	.2699	4.52	.2583	16.36	.3700
18.51	.2639	4.53	.3465	16.12	.3406
18.50	.2586	4.58	.4299	16.11	.3312
18.49	.2538	4.55	.4553	16.10	.3261
18.49	.2527	4.40	.4723	16.14	.3269*
18.45	.2328	4.51	.4706*		
		250°		270°	
		4.58	.4773	14.01	0.3633
		0	0	13.93	.3540
		8.88	0.0958	13.88	.3299
		10.27	.1446	13.94	.3379
		10.36	.1555	13.95	.3438
		10.39	.1624	12.55	.5794
		10.41	.1778	11.33	.5820
		10.36	.1793	8.43	.5648
		10.44	.1965	5.76	.5357
		10.48	.2377	5.04	.5206
		10.38	.2002*	4.67	.5119
		10.44	.2127	4.41	.5032
		10.40	.2140*	4.31	.4992
		10.49	.2891	4.49	.4962*
		10.38	.2915*	3.95	.4434
		10.55	.3580	4.46	.4338*
		10.49	.3591*	3.81	.3116
		10.55	.4257	4.43	.3003*
		12.61	.4805	3.76	.2344
		12.58	.4835	4.39	.2229*
		15.97	.5138	4.35	.1456
		20.62	.5385	3.80	.0782
		20.51	.5396		
		16.83	.5215	280°	
		16.82	.5214*	0	0
		14.27	.5031	3.05	0.0327
		14.23	.5031	6.42	.0552
		11.72	.4686	8.19	.0684
		11.75	.4691*	11.06	.0931
		10.78	.4435	13.75	.1271
		11.06	.4513	15.61	.1784
		10.19	.4171	15.87	.1985
		10.44	.4128*	15.98	.2127
		10.44	.4294	16.02	.2191
		10.62	.4383	16.01	.2263
		10.56	.4356	16.09	.2435
		10.44	.4306	16.13	.2597
		10.39	.3684	16.13	.2748
		10.27	.2756	16.20	.3489
		10.39	.2737*	0	0
		10.25	.1869	5.18	0.0458
		10.28	.1852*	9.94	.0803
		10.07	.1675	13.62	.1223
		10.27	.1650*	16.05	.2178
		8.63	.0996	16.04	.2340
				16.11	.2503
				290°	
				18.33	0.2436
				18.33	.2436*

At 0° no attempt was made to investigate the whole curve, or to find again the first break, but we have tried to find the pressure of the horizontal isotherm more accurately than did Gillespie and Hall, who found the average 3.95 mm. by the use of capillary tubes and a meter stick. In this case we have used wide tubes and a good cathetometer. We find that the equilibrium pressure cannot be greater than about 3.56 mm. "Heat treatment" was not used, but the palladium was heated *in vacuo* at 360° before the experiments. The material absorbed hydrogen over a wide range of composition at much lower pressures than in the former investigation, as did the material used by Gillespie and Ambrose.¹⁸ For instance, when the atomic ratio was increased from 0.047 to 0.408 the pressure fell in twelve and a half hours to only 4.03 mm. This is probably a result of the better elimination of ammonium chloride. On withdrawing hydrogen, however, even from the ratio 0.07, the material showed hysteresis, the pressure falling to 3.0 mm. with a decrease of only 0.002 in the ratio.

The last entry of Table I is for a check on the condition of the palladium in comparison with the earlier 290° isotherm. It is not plotted in the diagrams. This result is about 1% lower than the curve at 290°. If plotted in Fig. 5 the center of its circle would lie on the circumference of one of the circles shown. This result points to some small change in the material. The palladium was found to be packed together after the experiments. The mass could be broken up almost entirely by shaking the container so that most of it was removed through the capillary tube. Care was taken to include all of the packed material for the test for mercury.

Discussion

The data cannot be properly judged by a single diagram of constant scale. Hence the experimental points in the neighborhood of the heterogeneous region are plotted in Fig. 4 with different pressure scales for the different isotherms. Even here, the magnification is not quite sufficient to make evident the horizontal portion at 295°, and one must examine the numbers. The scale at 300° is the same as at 295°, though displaced, and the difference between these isotherms, one above the critical point, and one just below it, is very clear. The isotherm at 285° is the last one ob-

tained. It is not so consistent as the others—indeed, taken by itself, it suggests a continuous curve. In order to locate the breaks as well as possible in this and some other cases, we have sought to take advantage of the fact that the pressure level of the horizontal portion is very well defined at some temperatures. A plot was made of $\log p$ against $1/T$ for the horizontal por-

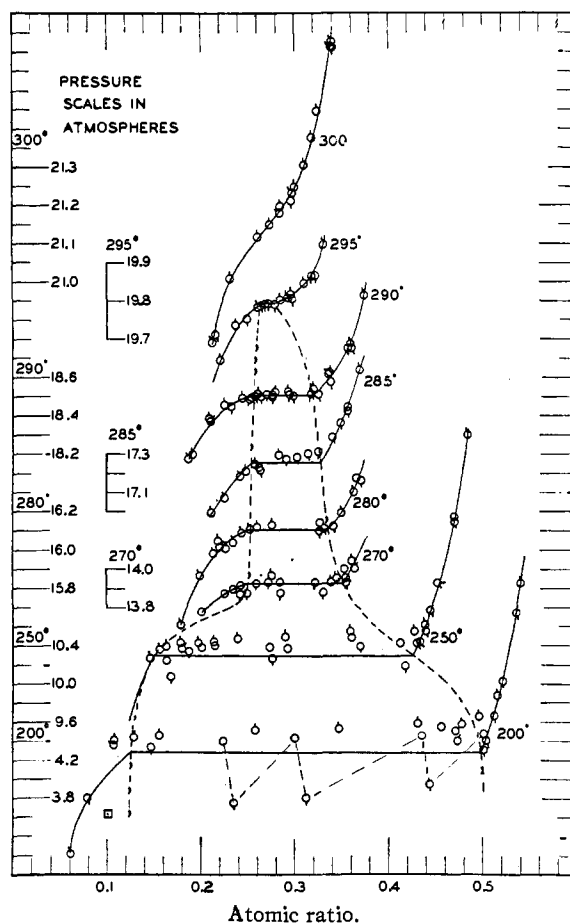


Fig. 4.—Detail of breaks. The square denotes a point in the 250° isotherm. All other points belong on the nearest curve.

tions, and the doubtful levels were chosen so that all the pressures lie within 0.2% of the pressure given by the equation

$$\log p = 4.6018 - 1877.82/T$$

At the seven temperatures increasing from 200 to 295° the pressures chosen differ from those given by this equation by the respective percentages: 0, +0.24, -0.11, 0, -0.06, 0, 0. This equation prescribes a pressure of 4.05 mm. at 0°, which is too high. It agrees with the experimental value 3.56 mm. about as well as any linear equation can, the true equation being that of a curve. On this

(18) Gillespie and Ambrose, *J. Phys. Chem.*, **35**, 3105 (1931).

plot the results of Gillespie and Hall at the higher temperatures, particularly 180° , appear too low.

The breaks may be sharper than we have drawn them, but it would seem that the heat of absorption per mole of hydrogen is nearly the same at a given temperature, whether the palladium is nearly saturated or whether it is already a two-phase mixture and hydrogen is being used for compound formation. One would therefore expect it legitimate to use a continuous function for smoothing in the manner just described.

The main results of the measurements are shown in summary in Fig. 5, a diagram of uniform scale. Although the exact location of the breaks is very difficult, requiring a smoothing in two variables,

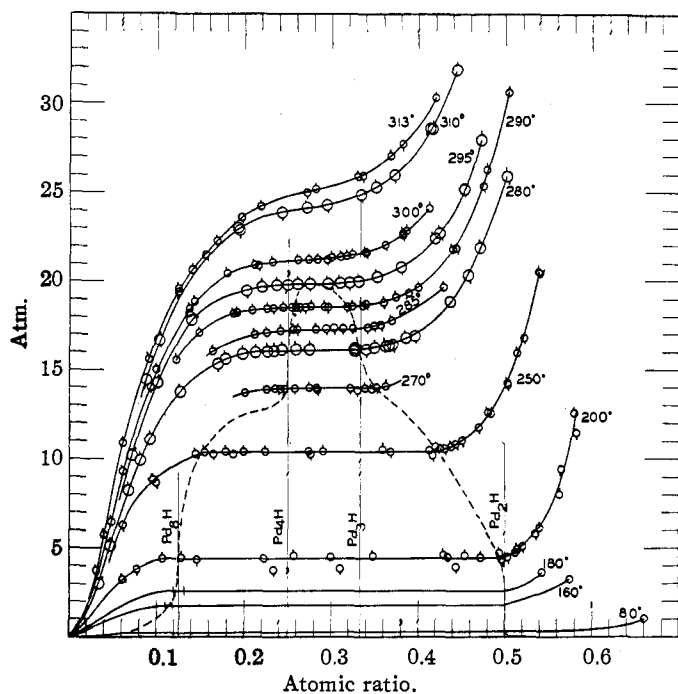


Fig. 5.—Pressure-concentration diagram of palladium-hydrogen system.

yet we think it certain that the boundary of the two-solid-phase region is substantially as shown in Figs. 4 and 5 and that the boundary has steep tangents at ratios 0.125, 0.250, 0.333 and 0.5, corresponding to the compounds Pd_5H , Pd_4H , Pd_3H and Pd_2H . The existence of the first and last of these depends in part on the results of Gillespie and Hall, which are likewise shown in Fig. 5, and is supported in both cases by the X-ray diagram of Linde and Borelius.⁸ The short vertical lines across the isotherms at 160 and 180° show the limits allowed by the original data.

We have drawn the tangent much steeper at Pd_4H than at Pd_3H , but such comparisons depend upon the smoothing and are perhaps not fully justified. We think it possible that the tangents are vertical in all cases except Pd_3H , which would mean that the corresponding compounds follow the law of definite proportions. In such a case as shown for Pd_3H there is evidence of chemical individuality, even if the law of definite proportions seems to hold only at a point—*i. e.*, not at all from a practical standpoint. The curve for it is like the curve for FeO in the Fe-H-O system shown by Eastman and Evans,¹⁹ and Pd_3H seems to have as great a claim for existence as FeO .

It may be noted that the tangent cannot be assumed vertical at Pd_7H or Pd_9H . The next compound in the obvious series would be Pd_{10}H . This was not observed by Gillespie and Hall, and their data in the neighborhood of 80° are not sufficient to give any information about its possible existence.

The critical solution temperature is estimated by us to be 295.3° , the corresponding pressure 19.87 atm. and the atomic ratio, 0.270.

No compound PdH has ever been shown, nor any phase diagram presented that gives evidence of it. Palladium has been heavily loaded with hydrogen by electrolysis by Fischer²⁰ to an atomic ratio of 0.84. On standing, hydrogen was lost until the ratio was 0.81. Paal and Gerum²¹ report a single experiment in which hydrogen was absorbed by palladium black suspended in water and shaken until the ratio reached 0.98, indicating PdH . But when their absorptions are plotted against the time, a curve is obtained which suggests that further absorption might have been observed in a longer time. Thus there is no evidence here of the existence of PdH even if one grants the enormous absorption, which appears quite inconsistent with the results of electrolysis. This process ought to be capable of saturating palladium under virtually very great pressure—indeed, von Samson-

(19) Eastman and Evans, *THIS JOURNAL*, **46**, 888 (1924). In this case the temperature is replaced with per cent. of H_2 in the gas phase as variable, the temperature and partial pressure of water being held constant in the 3-component system, but the curves are analogous.

(20) Fischer, *Ann. phys.*, [4] **20**, 503 (1906).

(21) Paal and Gerum, *Ber.*, **41**, 818 (1908).

Himmelstern²² has found an increase of pressure from 1 to 968 atm. to increase the atomic ratio found on electrolysis by a negligible amount (from 0.7 to not more than 0.707).

Summary

Seven isotherms, from 200 to 313°, have been traced on the pressure-composition diagram for palladium and hydrogen, in most cases from zero pressure through the heterogeneous region and well into the second homogeneous solid phase. The diagram, including the previous results at lower temperatures of Gillespie and Hall, indicates that the compounds Pd₂H, Pd₃H, Pd₄H and Pd₅H have chemical individuality, even though in the second case, and possibly others, the tangent to the boundary curve is not vertical, the curve then resembling the analogous curve for FeO in the Fe-H-O system. In all cases the

(22) Von Samson-Himmelstern, *Z. anorg. Chem.*, **166**, 337 (1930).

compound is to be regarded as a solid solution that has a stoichiometrical composition over a limited range of temperature. The finding of Brüning and Sieverts of a critical solution temperature for the solid phases near 300° is confirmed, and the critical constants are found to be: temperature, 295.3°; pressure, 19.87 atm. and atomic ratio H: Pd, 0.270.

In the discussion the validity is denied of (1) certain evidence against the existence of Pd₂H, and (2) certain evidence in favor of the existence of PdH.

Mention is made of palladium mercuride, probably Pd₄Hg₃, of very low decomposition pressure. The palladium investigated was found at the conclusion of the experiments to contain a presumably harmless amount of mercury, much less than 0.2%.

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The Extraction of Ferric Chloride from Hydrochloric Acid Solutions by Isopropyl Ether

BY RICHARD W. DODSON, GERARD J. FORNEY AND ERNEST H. SWIFT

Introduction

The extraction of ferric chloride from solutions approximately 6 formal in hydrochloric acid by ethyl ether has been studied repeatedly,¹⁻⁵ but, although such an extraction process offers obvious advantages over precipitation methods, this separation has not been used as widely in general qualitative and quantitative procedures as would seem justified. This has been due to several factors: the efficiency of the extraction process is critically dependent on the hydrochloric acid concentration; the solubility of ether in the acid is of such magnitude that the volume of the aqueous phase is increased by as much as 25%, making the concentration of the acid after an extraction uncertain or requiring the use of acid previously saturated with the ether; it has been feared that peroxide or alcohol which are frequently present in ether would reduce the iron to the ferrous state,

in which form it is not extracted; finally, the volatility of ethyl ether makes the quantitative technique of the extraction somewhat difficult at room temperatures, and especially for student use, involves a serious fire hazard. Because of these facts, it has seemed worth while to investigate the use of other, less volatile ethers for this separation, and this paper presents the results of experiments with isopropyl ether. This ether is readily available, and the present cost of the best technical grade is somewhat less than that of ethyl ether of a comparable grade.

The Experimental Method

Materials.—Concentrated hydrochloric acid, c. p. grade, was standardized against sodium carbonate. Ferric chloride solutions were prepared and standardized, by permanganate, using the Zimmermann-Reinhardt method, or by thiosulfate, using the iodometric method.⁶ In every case the ferric chloride used was shown to be free from ferrous salt by testing with ferricyanide. Except when testing the suitability of the technical product for routine analyses, the isopropyl ether used was prepared from a technical grade by fractional distillation, the fraction

- (1) Skey, *Chem. News*, **36**, 48 (1880).
- (2) Rothe, *Mitt. könig. tech. Ver.*, **10**, 32 (1892); *Chem. News*, **66**, 182 (1892); *Stahl und Eisen*, **12**, 1052 (1892).
- (3) Langmuir, *THIS JOURNAL*, **22**, 102 (1900).
- (4) Kern, *ibid.*, **23**, 689 (1901).
- (5) Speller, *Chem. News*, **83**, 124 (1901).

- (6) E. H. Swift, *THIS JOURNAL*, **51**, 2682 (1929).