[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ADSORPTION AND ACTIVATION OF CARBON MONOXIDE AT PALLADIUM SURFACES

BY HUGH S. TAYLOR AND PAUL V. MCKINNEY

RECEIVED JUNE 16, 1931 PUBLISHED OCTOBER 5, 1931

Palladium has always been of interest because of the reaction of gases at its surface. In the field of contact reactions many references have been made to early work with this metal, particularly to the specificity of its reaction with hydrogen. There are several good summaries[1] of the literature concerning the nature of this specificity. The adsorption of hydrogen by palladium[2] is not qualitatively different from adsorption in general or from that reported here for carbon monoxide upon the same metal, but diffusion into the interior of the metal occurs simultaneously.

Before beginning the adsorption measurements of carbon monoxide, a series of reactions on the surface of palladium was studied. A brief résumé of the results in typical reactions is included in this introduction.

Acknowledgment is made to Mr. Charles Engelhard of Baker and Company, Inc., Newark, New Jersey, who supplied funds for the fellowship under which the first portion of this work was done and also the quantities of palladium used in the entire research.

Reduction of Nitrobenzene.—Probably the greatest use of palladium has been in the reduction of organic compounds. Its usefulness in this field is only exceeded by the commercial use of nickel since the war. Paal and Amberger[3] carried out an extended series of reductions by means of colloidal palladium in solution. The former[4] themselves refer to the fact that Kolbe[5] and Saytzeff[6] had reduced compounds of the type of nitrobenzene by passing the vapors mixed with a stream of hydrogen over heated palladium. However, the first reference to palladium as a carrier of hydrogen is by Böttger[7] in 1871. Recently Adams[8] has obtained better results by starting with the oxide, which is then reduced in the presence of the material to be hydrogenated. The best result obtained by Paal and Amberger was a 35% yield of aniline at 70° by colloidal palladium hydrosol. At room temperature their best result was only 4.5% aniline. There seems to be no doubt but that the catalyst materials used at present are of an entirely different order of activity than even those of Sabatier.

---

[1] Bose, *Z. physik. Chem.*, **34**, 701 (1900); McKeehan, *Phys. Rev.*, [II] **21**, 334 (1923); Howe, U. S. Geol. Survey Bull. 694, 454 pp. (1919).

[2] Holt, *Proc. Roy. Soc.* (London), **A90**, 226 (1914); Valentiner, *Ber. physik. Ges.*, **13**, 1003 (1911); Firth, *J. Chem. Soc.*, **117**, 171 (1920); **119**, 1120 (1921); Gutbier, Gebhardt and Ottenstein, *Ber.*, **46**, 1453 (1913); Sieverts, *Z. Metallkunde*, **21**, 37 (1929).

[3] Paal and Amberger, *Ber.*, **37**, 124 (1904).

[4] Paal and Amberger, *ibid.*, **38**, 1388 (1905).

[5] Kolbe, *J. prakt. Chem.*, [2] **4**, 418 (1871).

[6] Saytzeff, *ibid.*, [2] **6**, 128 (1872).

[7] Böttger, *Ber.*, **4**, 809 (1871).

[8] Shriner and Adams, THIS JOURNAL, **46**, 1683 (1924).

By using palladium black freshly reduced from the oxide, nitrobenzene has been quantitatively reduced to colorless aniline at room temperatures by hydrogen. For a given ratio of catalyst to nitrobenzene three hours were required for complete reaction. With alcohol as solvent only fifty minutes were necessary. An induction period was noted, thirty to forty-five minutes without solvents but only ten to fifteen minutes with solvents. This is the period during which the oxide is being reduced. By increasing the temperature in the absence of solvents, the induction period fell off, but above 50° the latter portion of the reaction became slower due to the coagulation of the colloidal catalyst at the higher temperatures.

The apparatus and method was that used by Adams. Table I affords a comparison of typical results on palladium and platinum. The reaction in the presence of alcohol as solvent was more rapid and reversed the order of activity of the two metals.

Table I

Reduction of Nitrobenzene in Absence of Solvent

Catalyst, g.			$C_6H_5NO_2$, mole	H_2 absorbed, mole	Time, Hrs.	Min.
PdO	No. 1	0.922	0.148	0.451	4	
PdO	No. 2	.273	.100	.313	3	
PtO_2		.277	.117	.354	6	
		Reduction with Alcohol as Solvent				
PdO	No. 1	0.600	0.124	0.361	2	30
PdO	No. 2	.200	.100	.343		50
PtO_2		.158	.068	.213		19

The effect of the various types of solvents studied is evident from Table II. Benzene in quantities as small as 3% in the alcohol slowed the reaction, while greater than 10% practically inhibited the reduction, the nitrobenzene having only absorbed one-half volume of hydrogen in six hours. The reduction with aniline as a solvent was even slower than without solvent present but continued to completion. With water the rate is linear over the largest portion of the curve and still quite slow. The reduction in the presence of the alcohols, methyl, ethyl and butyl, is rapid and they are all very similar. Butyl alcohol saturated with water is about twice slower than the dry reagent. Evidently the reduction of nitrobenzene is inhibited by the presence of reaction product, water, on the palladium. At room temperature with pyridine and amyl alcohol as solvents, reduction was incomplete in six hours. At 50° with pyridine the reaction became complete in two hours and forty minutes, while amyl alcohol required three hours and forty-five minutes at 90°.

Busch and Schulz[9] have reduced various nitro compounds to obtain intermediate products by using less active preparations of palladium.

TABLE II

TIME OF REDUCTION OF 0.1 MOLE NITROBENZENE

0.2 G. of Palladium used

	Ethyl alcohol	Butyl alcohol	Butyl satd.	Amyl alc.		Pyridine		Aniline
				25°	90°	25°	50°	
Induction period	0:15 min.	0:12	0:25	1:00	0	0:40	0:5	0:40
25%	17	14	35	6:40	20	1:55	20	1:25
50%	20	17	39	15	50	3:20	40	2:05
75%	25	21	46	27	1:45		1:20	2:45
Complete	32	30	60	46	3:45		2:40	3:50

Without Solvent

	25°	40°	50°	60°	75°	80°	90°
Induction period	0:25	0:12	0:8	0:5	0:3	0:1	0:0
25%	45	29	21	17	19	14	12
50%	1:10	47	37	34	43	40	35
75%	1:55	1:15	1:03	1:04	1:24	1:25	1:15
Complete	3:20	2:10	2:00	2:05	2:50	2:50	2:20

Dehydrogenation of Ethylbenzene.—The high reactivity of palladium toward hydrogen indicates that it should be an excellent dehydrogenation agent. Since the reaction $C_6H_5C_2H_3 + H_2 = C_6H_5C_2H_5$ is exothermic by about 22 kg. calories, it was necessary to use high temperatures for the process. In the quartz reaction tube to be used in the catalytic study the thermal reaction was found to begin around 500°. One per cent. of styrene was produced at 550°. The rate of flow was 5 cc. of ethylbenzene per hour, which is equivalent to approximately one liter of vapor per hour. Palladium-black lowered the temperature at which styrene was observed to 300°. A fair yield was obtained at 400°. A 12-g. sample of catalyst produced no greater yield than the 8-g. sample. By passing air with the ethylbenzene vapor the dehydrogenation occurred at even lower temperatures and water was produced. Oxygen gas could not be used in place of air since it burned the hydrocarbon and even caused an explosion. With a furnace tube filled with palladized asbestos only 0.5 g. of palladium could be used. With this material over the temperature range 250 to 500° alternate runs were made with and without the use of air. Contrary to the results with palladium-black, the experiments with the palladized asbestos without the use of air gave only traces of styrene below 500°. With air admitted 15% styrene was obtained at 250°. The results are summarized in Table III.

[9] Busch and Schulz, *Ber.*, **62B**, 1458 (1929).

TABLE III

DEHYDROGENATION OF ETHYLBENZENE

Pd Black, g.	Temp., °C.	Styrene, %	Pd-Asbestos	Temp., °C.	Styrene, %
8	300	3		250	. .
	350	4	(air)	250	17.0
	400	21.9		275	. .
	400	22.0	(air)	275	10.8
	400	26.6	(air)	275	11.0
	400	34.2	(air)	275	19.6
(air)	250	15.5	(air)	275	14.7
			(air)	275	17.0
12	400	24.4	(air)	300	22.3
	400	15.5		300	. .
	400	23.6	(air)	350	8.5
(air)	250	8.0		350	. .
			(air)	400	16.4
			(air)	450	16.6
			(air)	500	25.3
				400	Trace

The Reduction of Carbon Monoxide to Methane.—There is a statement in "Catalysis in Organic Chemistry" by Sabatier and Reid,[10] "Carbon monoxide can be reduced in the cold, or better, at 400°, to *methane* in the presence of palladium sponge," and reference is made to work by Breteau.[11] The latter[12] refers to the fact that Sabatier and Senderens[13] failed to hydrogenate carbon monoxide and then stated that he obtained complete reduction by palladium sponge in the cold or at 100°. His material was prepared by the calcination of palladium ammino chloride in a muffle furnace at red heat.

The reaction $CO + 3H_2 = CH_4 + H_2O$ occurs very readily over nickel catalyst and to some extent on cobalt and iron but not on copper or platinum. Fischer, Tropsch and Dilthey[14] obtained a partial formation of methane working at higher temperatures. Their preparations can scarcely be called good catalysts since their yield was less than 34% on nickel at 300°. There is abundant evidence which has been repeated here that nickel causes 100% reduction to methane at 270°. The equilibrium in the reaction has been extensively studied with nickel catalysts by Neumann and Jacobs.[15]

The carefully purified and dried gases were passed at a flow rate of 30 cc. per minute over palladium reduced from the oxide at 110°. The proportion of carbon monoxide to hydrogen, 1:5, was that found most effective in the reduction over nickel. Preliminary experiments of one hour were made at 25, 50 and each 50° higher. The exit gas from the catalyst tube passed through a phosphorus pentoxide weighing bulb and a tube containing a promoted nickel catalyst, and finally another weighing bulb. By maintaining the nickel tube at 270° the carbon monoxide remaining after passing over palladium was completely reduced. At 150 and 200° an increase of three and five milligrams, respectively, in the weight of the first weighing bulb, occurred. At 250° an increase of 7 mg. in fifteen minutes was obtained. Since previous work had shown that palladium black sinters rapidly above this temperature, the procedure was changed. Duplicate runs of only fifteen minutes each were made and the volume of excess gas was observed to determine if any unusual decomposition was occurring. The results are given in Table IV. Methane formation began at 250° and reached a maximum of 90% at 300°. As had been expected the catalyst sintered badly, and the second run at this temperature gave a much lower yield. In the subsequent adsorption measurements it will be shown that unsupported palladium sinters readily at 280°. The average values of Table IV have been used to calculate the velocity constant and an approximate value for the activation

---

[10] Sabatier and Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1923, p. 186.

[11] Breteau, "Étude sur les meth. d'hydrogenation," 1911, p. 22.

[12] Breteau, *Bull. soc. chim.*, [4] 9, 729 (1911).

[13] Sabatier and Senderens, *Ann. chim. phys.*, [8] 4, 424 (1905).

[14] Fischer, Tropsch and Dilthey, *Brennstoff-Chem.*, 6, 265 (1925).

[15] Neumann and Jacobs, *Z. Elektrochem.*, 30, 557 (1924).

TABLE IV

REDUCTION OF CARBON MONOXIDE TO METHANE

Expt.	Temp., °C.	CO, cc.	H_2, cc.	Exit gas, cc.	Time, min.	Amt. H_2O	Reaction % calcd. from H_2O	k
4	230	5	28			0.0010		
6	250	5	25	27	17	.0090		
					(15)	(.0080)	14.6	
7	250	5	25	27	15	.0070		
8	270	5	25	22	15	.0155	28.0	
9	270	5	25	23	15	.0145	26.6	
10	280	5	23	22	15	.0177	32.0	
11	280	5	23	21	15	.0163	30.0	
12	300	5	25	17	15	.0490	90.0	
13	300	5	25	17	15	.0250		
14	320	5	23	17	15	.0260		
				Averages used in Calculation				
6–7	250	5			15	0.0075 H_2O	13.8	0.0055
8–9	270	5			15	.0150	27.6	.0111
10–11	280	5			15	.0170	31.0	.0125
12	300	5			15	.0490	90.0	.0355

ACTIVATION ENERGY

Temp. interval, °C.	E, calculated, g.-cal.
250–270	19,320
270–300	24,000
250–300	24,750

energy of the reaction $CO + 3H_2 = CH_4 + H_2O$. An average value of 23 kg. calories is obtained.

Reduction of Palladium Oxide.—In the course of this work an attempt was made to reduce a sample of palladium oxide by carbon monoxide. In general the reduction of oxides, for example, copper and nickel, is even more readily accomplished by carbon monoxide than by hydrogen. However, no carbon dioxide could be detected and no reduction observed between room temperature and 125°. Hydrogen, in the ratio of 1:3 of carbon monoxide was admitted very carefully at 25° because of the extreme speed with which it reduces palladium oxide even at 0°. No formation of water or carbon dioxide could be detected in two hours. With equal quantities of hydrogen and carbon monoxide and finally a ratio of 4:1, no reduction was obtained. It was thought that perhaps this might be due to the lack of an interface (see Pease and Taylor[16]) or to the fact that dry gas was being used. Since, with the apparatus used, water vapor could not be admitted, reduction was started by hydrogen at room temperature. There was a period of about twenty minutes during which no reaction occurred, apparently involving desorption of carbon monoxide. Then, with great suddenness, all the hydrogen in the system reacted and much water was formed. The hydrogen flow was stopped and carbon monoxide admitted but no carbon dioxide was formed, even at 120°. That there was oxide remaining was proved by subsequent reduction by hydrogen with the formation of water; again the reaction, after an induction period, was so rapid as to produce a temporary vacuum in the catalyst vessel. The hydrogen flow was about 10 cc. per minute. Carbon monoxide is a powerful inhibitor to the reduction of palladium oxide by hydrogen.

Decomposition of Carbon Monoxide.—It is of interest that carbon monoxide is not decomposed to carbon dioxide by palladium. During this study a portion of the catalyst was used to attempt this reaction $2CO = C + CO_2$, which Sabatier has shown occurs on nickel, cobalt and iron. Cobalt[17] is less effective unless there is already some carbide present. With palladium reduced from the oxide, no carbon dioxide was detected in the temperature range 25 to 300°, even with two-hour runs, and no carbon was deposited. Furthermore, no evidence of carbonyl formation was obtained, which is in agreement with work of Mond,[18] who investigated the metal carbonyls at high pressures and high temperatures. We may note also that Sabatier[19] obtained no decomposition of ethylene on palladium and Wohler[20] could detect no carbide formation. In these essentials palladium acts more like copper and platinum than like nickel, cobalt or iron; compare with discussion by Taylor[21] of specificity in reaction and adsorption.

---

[16] Pease and Taylor, THIS JOURNAL, **43**, 2180 (1921); **44**, 1638 (1922).

[17] Bahr and Jessen, *Ber.*, **63B**, 2226 (1930).

[18] Mond, Hirtz and Cowap, *Proc. Chem. Soc.*, **26**, 67 (1910).

[19] Sabatier, *Compt. rend.*, **124**, 616 (1897).

[20] Wohler, *J. Chem. Soc.*, **31**, 437 (1877).

Adsorption of Carbon Monoxide.—There has been little direct study of the adsorption of carbon monoxide by palladium. In 1898, De Hemptinne[22] noted a smaller adsorption at −78° than at 15°, and the poisoning effect of this on the adsorption of hydrogen to −20°. About the same time Harbeck and Lunge[23] noted the effect of carbon monoxide in preventing reactions of hydrogen on palladium and platinum. Nickel has been shown by the work of Taylor and Burns[24] and Gauger and Taylor[25] to adsorb carbon monoxide very strongly in the range of temperature below that in which it decomposes carbon monoxide.

With palladium Taylor and Burns obtained the same amount of adsorption at 25 and 110° on a sample of palladium sponge reduced from the chloride. The latter also observed that on platinum which does not catalyze the reduction of carbon monoxide, the adsorption is greater at 110° than at 25°.

Recently Garner and Kingman[26] observed a desorption process followed in the same system by an adsorption in the case of both hydrogen and carbon monoxide on zinc oxide at very low pressures. They considered this phenomenon as proof of two types of adsorption, physical and chemical, an idea Benton[27] had discussed with regard to oxide catalysts and Benton and White[28] then extended in the case of hydrogen on nickel. Taylor[29] in the theory of activated adsorption has presented a thorough theoretical explanation not only of this phenomenon but also of adsorption in general as the basis for contact catalysis. In the case of palladium the same process of desorption followed by an activated adsorption with increased temperature has been studied in detail for carbon monoxide. The isotherms have been determined from 86 to 553°K. and rates of adsorption measured. These phenomena are shown to be intimately connected with the catalytic activity.

Experimental Method

Apparatus.—The apparatus and method used in the study of the adsorption of carbon monoxide on palladium was essentially that of Taylor and Burns, and certain details are shown in Fig. 1.

---

[21] Taylor, *J. Franklin Inst.*, **194**, 1 (1922).

[22] De Hemptinne, *Bull. Acad. Roy. Belg.*, [3] **36**, 155 (1898).

[23] Harbeck and Lunge, *Z. anorg. Chem.*, **16**, 26 (1898).

[24] Taylor and Burns, This Journal, **43**, 1273 (1921).

[25] Gauger and Taylor, *ibid.*, **45**, 920 (1923).

[26] Garner and Kingman, *Nature*, **126**, 352 (1930).

[27] Benton, This Journal, **45**, 887, 902 (1923).

[28] Benton and White, *ibid.*, **52**, 2325 (1930).

[29] Taylor, *ibid.*, **53**, 578 (1931).

A represents the catalyst bulb with a thermometer well and surrounded by a boiler vessel. To prevent any contamination of the catalyst by mercury vapor or stopcock grease the trap B was provided and kept continually cooled by solid carbon dioxide and ether, from the sealing of the catalyst bulb in position to the end of the study. A constant volume manometer C, McLeod gage M and Toepler pump connected by a stopcock at E all entered the trap to connect with the catalyst bulb. The stopcock E was sealed by a thread of mercury when not in use. A large stopcock of special construction at F served for the introduction of measured volumes of gas from the burets and to connect with the mercury-vapor and oil or Sprengel pumps. In the latter portion of the work the McLeod gage was connected through another large stopcock similar to F, permitting a reduction of the nitrogen volume of the system by an amount equal to the volume of the gage (240 cc.), and a consequent increase in the accuracy of the measurements of adsorbed gas. The latter volume was in every case determined as a difference between the volume of gas admitted and the nitrogen volume of the system. A novel procedure in this case was to mount the Sprengel pump as a fore-pump to the mercury-vapor pump, making it possible to collect the entire volume of gas removed from the catalyst even to the lowest pressure. This method was much more rapid than in the use of the Sprengel alone.

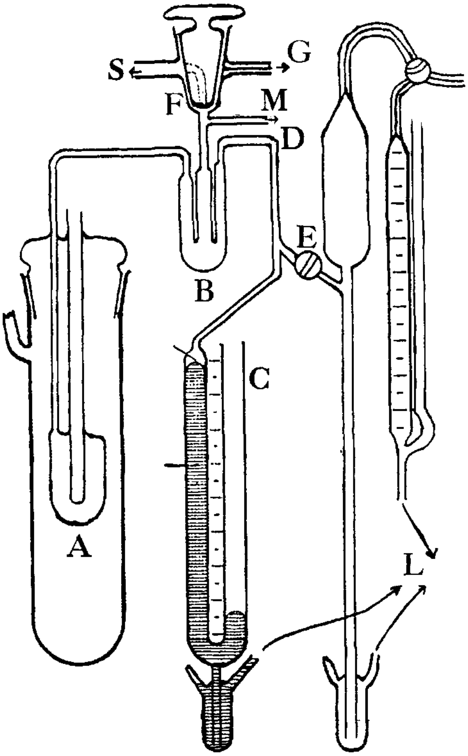

Fig. 1.—Apparatus: G, gas burets; L, leveling bulbs; M, McLeod gage; S, Sprengel and mercury pumps.

Preparation of Catalyst.—Palladium oxide was prepared from the chloride by the method of Roger Adams.[8] For the adsorption measurements 100 g. of the chloride was fused with sodium nitrate in a large sillimanite casserole in a muffle furnace. The melt was dissolved and filtered on a large fritted glass filter plate and washed for three days both with suction and intermittent periods of soaking for hours in distilled water. It is thought that the more extensive washing of this catalyst produced a purer oxide with less adsorbed material, probably sodium nitrate, acting as support. This fact was shown by the more ready sintering and less reactivity toward methane formation above the sintering temperature, 280° in this case.

Forty grams of this oxide dried over phosphorus pentoxide was transferred to the adsorption bulb and reduced by electrolytic hydrogen at room temperature and then at 110°, until no further moisture was detected in the exit gas. During the period of rapid reduction an equivalent mixture of hydrogen and nitrogen gases was used. Even with this precaution and an ice-bath around the catalyst bulb, the thermometer in the well registered 15°. However, it is not likely that the reaction zone ever exceeded 110°.

As in the reduction of copper oxide by Pease and Taylor[16] the reaction was observed to start at spots within the mass of the catalyst near the surface, extend outward until a layer across the tube was reducing and then proceed downward through the charge with a definite reaction layer present. In this case, as in the reduction of copper oxide, the process was easily observable, for the color of the oxide was velvety blue-black, the reaction zone showed a distinct gray metallic appearance, and the reduced mass distinctly a brown-black not far from the color of precipitated bismuth sulfide. This was either due to large volumes of adsorbed water, or dissolved hydrogen. On warming, hydrogen was evolved and, near 100°, large volumes of water; at the same time, the color and physical nature of the catalyst changed from a brown and powdery appearance to the gray and metallic form noted in the reaction zone during reduction. This process was accompanied by a small amount of sintering with portions of the catalyst appearing in the form of small granules. These catalysts which have been prepared at 110° are probably of the same type Sabatier and the earlier workers spoke of as palladium sponge. The palladium blacks prepared by reduction with formaldehyde keep their finely divided state in solution due to this adsorbed hydrogen or water but also sinter above 100°.

Purification of Gases.—Electrolytic hydrogen from an alkali cell with nickel electrodes was dried by calcium chloride, freed of oxygen over palladized asbestos and dried by phosphorus pentoxide.

Tank nitrogen was freed of oxygen by passage over copper wool at 375°, from carbon dioxide by potassium hydroxide and was dried by phosphorus pentoxide.

Carbon monoxide was generated by dropping formic acid into concentrated sulfuric acid. Oxygen was removed by a copper furnace as with nitrogen, and carbon dioxide by askarite and the gas was finally dried as before. The purity of the carbon monoxide was proved by gas analysis in a combustion pipet over mercury. The volumes are all corrected to standard condition and temperatures are stated in the absolute scale.

Temperature Baths.—The adsorption isotherms and most other measurements were made in constant temperature baths. Liquid air gave a temperature of 86°K., carbon dioxide–ether 195°, water–ice 273°, toluene 383°, chlorobenzene 405°, aniline 457° and α-naphthol 553°K.

Procedure.—The general procedure has been to obtain adsorption isotherms by the process of adsorption and then by desorption. The velocity of adsorption was often quite slow depending upon the temperature of observation and the actual activation energy necessary. The process of adsorption gives a lower limit and desorption an upper limit for the isotherm. Often twenty-four hours were allowed for the determination of a single point of the isotherm; in some cases such observations approached equilibrium and in others they fell far short.

The adsorbed gas was removed by the Toepler pump, varying amounts of time being permitted after each stroke to observe the attainment of equilibrium. The desorption by the Toepler pump was continued to less than 1 mm. pressure in most cases. The final gas was pumped off by the mercury-vapor pump. In the later experiments with the Sprengel pump in the system the desorbed gas was collected to the full vacuum of the vapor pump, *i. e.*, 10^{-5} mm., over a period of twelve hours. This does not represent complete degassing or an equilibrium pressure since the system after degassing at 383° to 4×10^{-5} mm. pressure showed an increase to 5.3×10^{-4} mm. on standing for five hours.

The rate of adsorption was followed on the constant volume manometer by observation of the pressure change after admission of the gas. The difference between the volume of carbon monoxide admitted to the catalyst and the volume of nitrogen required to fill the vessel under the same conditions is taken to be the volume of gas adsorbed. The agreement of the variation of the observed nitrogen volume change with temperature and pressure with that calculated by the gas laws, and the fact that no drift in pressure of the nitrogen could be observed at any temperature are sufficient proof of the negligible adsorption of that gas. Taylor and Burns[24] also found no adsorption of nitrogen by palladium.

Following two series of measurements a break in the system permitted air to leak into the catalyst. The catalyst was reduced again by hydrogen, dried and degassed at 383°K.[30] The excellent agreement obtained in both the amount and the rate of adsorption after this occurrence is sufficient proof of the continued activity of the catalyst, an observation Mond[31] and all later workers with palladium have made.

The presence of activated adsorption and the necessity of energy of activation in the process of adsorption of carbon monoxide on palladium were further proved by an alternative experimental procedure. Following an adsorption measurement at 195°, a volume of gas was admitted to the evacuated catalyst sufficient to produce a pressure greater than 50 mm. With this constant volume of carbon monoxide in the system equilibrium was established, and then the temperature was changed and the appearance of activated adsorption with each increased temperature followed by the change in pressure in the system. The abnormal desorption followed by readsorption on elevation of the temperature, noted in the introduction as evidence of such activated adsorption, was firmly established.

Discussion of Data

Isotherms.—The larger portion of the adsorption study of the system carbon monoxide and palladium is represented by the isotherms of Fig. 2. The complete system of isotherms is given on the one chart and represents as nearly as possible measurements upon a catalyst of identical history. Previous experience in catalysis, especially the work of Russell and Taylor[32] and many others, indicates that heat treatment markedly affects metallic catalysts. The present sample of palladium was reduced and evacuated at 383°K. Therefore all measurements at or below this temperature were completed before the catalyst was heated to a higher temperature. After each isotherm the catalyst was evacuated at 383°K. In the later experiments the temperature of evacuation was that of the adsorption process which was to follow.

---

[30] The reduced material was degassed at 383° until when left open to the McLeod gage for twelve hours no increase in pressure was observed.

[31] Mond, Ramsay and Shields, *Phil. Trans. Roy. Soc.*, **186**, 657 (1895).

[32] Russell and Taylor, *J. Phys. Chem.*, **29**, 1325 (1925).

The adsorption values are marked by × and a broken line in Fig. 2, the desorption values by ○ and the solid line. The greatest difference between desorption and adsorption isotherms occurs at 273°K. At liquid air temperatures the two are almost identical, probably representing true equilibrium values of the low temperature form of adsorption which occurred as rapidly as temperature equilibrium was established. At 383° and higher temperatures the desorption and adsorption isotherms show very little divergence. The second type of specific adsorption has, at the higher temperature, a more rapid approach to equilibrium values.

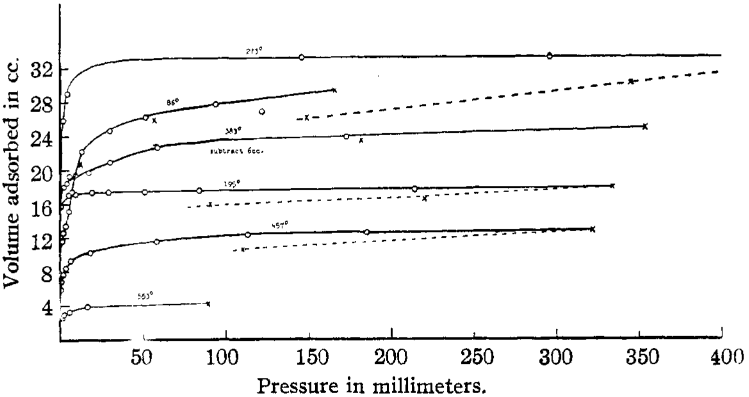

Fig. 2.—Adsorption isotherms of carbon monoxide on palladium. In order to separate the curves, 6 cc. has been added to each value in the plotting of the isotherm for 383°K.

The adsorption at liquid air temperatures differs but little in the total amount adsorbed from that occurring at 273°K., but the rapid attainment of equilibrium, the large variation of the amount adsorbed with pressure, over the entire range studied, and the fact that it was easily evacuated to a small fraction remaining on the surface all indicate an entirely different type of adsorption process. This will be spoken of as the low temperature type of adsorption; the terms molecular and physical adsorption have also been used.

The isotherm for 195°K. represents a normal decrease in the low temperature adsorption process due to the increase in temperature and yet it is followed at higher temperatures by an increase in adsorption. Very convincing evidence will be given in a subsequent section to show that the adsorption at this temperature is partially of the activated type. The character of the isotherm would also indicate that this is true, since the gas is much less easily desorbed than that of the 86° isotherm.

Normally most of the carbon monoxide adsorbed at 86° should have evaporated with the temperature increase to 273°. However, a large increase in adsorption occurs which is not explainable on the simple theory. This latter process requiring an activation energy is referred to as activated adsorption. The wide separation between the adsorption and desorption isotherms at this temperature, representing a slow adsorption process, is an indication of the necessity of such an activation energy. Reference to the amount of this energy in the case of carbon monoxide on palladium will be made later.

The data of Table V for the isotherms at 273 and 86°, respectively, refer to the corresponding curves in Fig. 2. The coincidence between adsorption and desorption at 86° and the divergence of these at 273° is especially to be noted.[33]

The sequence of the isotherms at 383, 457 and 553° is logical and represents a decreasing adsorption as found in all previous work and expected from the Le Chatelier theorem for an exothermic process, and also from the Langmuir theory of adsorption as an evaporation–condensation phenomenon. The data at 457 and 553° are not comparable with those at 383° and lower owing to the sintering of the mass at the higher temperatures.

TABLE V

ADSORPTION ISOTHERM AT 273 °K.

Adsorption			Desorption		
Time of observation, hours	Pressure, mm.	*V* cc. ads.	Time of observation, hours	Pressure, mm.	*V* cc. ads.
23	149	25.1	14	296	33.3
8.5	345	30.2	6.5	146	33.2
24	474	32.0	40	4.5	29.0
12	605	33.6	29	1.8	25.9
				Desorption 383°	
			12	0.27	8.5
		Adsorption Isotherm at 86 °K.			
2	12	20.75	5 min.	122	26.8
7.5	57	25.8	5	94	27.7
12	166	29.3	5	52	26.2
			5	30	24.6
			10	13	22.1
			10	7	17.4
			5	5	15.1
			5	3	13.4
			5	1.6	12.6
			10	1	11.6
			3 hours (Sprengel)		5.9

---

[33] The complete data for these isotherms are given in the original copy of thesis by one of us (P. V. McK.) filed in the Princeton University Library.

Isobaric Adsorption.—The direct study of the isotherms presented in the previous section has emphasized the complex nature of the adsorption process. The resulting variation in the amount of adsorption at different temperatures has been given as first evidence of an activated adsorption. From the same data the amount of carbon monoxide adsorbed by palladium at a constant pressure is plotted in Fig. 3. The values are taken directly from the isotherms of Fig. 2. The character of the curve is related to a change from a low temperature type of adsorption to an activated adsorption at the higher temperature. In the present method of presentation the relation of the two types of adsorption is even more apparent.

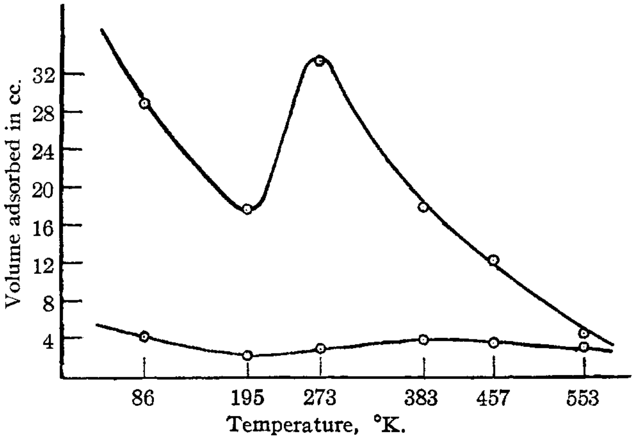

Fig. 3.—Isobaric adsorption (150 mm.).

(a) **Normal Surface.**—The isobaric adsorption on the unsintered catalyst is plotted for a pressure of 150 mm. The decrease in low temperature adsorption from liquid air to 195°K. and the very rapid increase between that and 273°K. is very striking. Certainly, owing to the ready reversibility of adsorption of the major portion of the gas present on the surface at 86°K., marked evaporation of such gas must occur with increase in temperature. Nevertheless, above 195°K. the amount of carbon monoxide adsorbed by palladium increases extremely rapidly with increased temperature to a maximum around 273°K. for the normal unsintered catalyst. The subsequent decrease at higher temperatures follows the normal course for an adsorption phenomenon but the adsorption must be essentially distinct from that in the 86–195°K. interval.

All isobars for pressures greater than 10 mm. would be identical in shape and practically occupy the same position as that at 150 mm., with the single correction that the height of the curve to the left at 86°K. would continually decrease for isobars of lower pressures. Below 10 mm. the minimum would finally disappear since the equilibrium pressure of the physical or low temperature adsorption falls off quite rapidly. The curve then would merely show a maximum for the activated adsorption near 273°K. For all types of measurements performed the adsorption at 195°K. was lower than that at 273°K. This maximum at 273° is also to be observed in the chart of the effect of temperature upon adsorption, Fig. 4, which is discussed in the next section. The chemical or activated adsorption appears in the case of carbon monoxide on palladium at very low temperatures, reaches a maximum around room temperature and above that decreases with temperature.

(b) **Sintered Surface.**—A similar isobar is plotted in the same figure for the adsorption at 35 mm. pressure obtained on a catalyst badly sintered by experimental study at 553°. These results also indicate a variation in the type of adsorption process. On the sintered catalyst the adsorption maximum appears to be around 383°. Such a shift of the temperature region in which activation of the adsorbed carbon monoxide by palladium occurs is compatible with the theory of activated adsorption. In the case of chemical reactions at surfaces a variety of evidence is available that the most active surface atoms of the catalyst are destroyed by the sintering process. The present results prove that the same decrease in activity of the surface occurs in the case of activated adsorption by palladium.

Adsorption and Temperature.—Additional evidence of the two types of adsorption was obtained by an interesting variation in the experimental procedure. A limited volume of gas was introduced into the system and sufficient time allowed for adsorption equilibrium. The temperature was changed and the variation in the volume of gas adsorbed was followed on the constant volume manometer by the change in pressure produced in the system.

(a) **Normal Surface.**—The equilibrium pressure was 1.8 mm. with 25.9 cc. of carbon monoxide adsorbed, Table VI. As the temperature was increased to 383° an evolution of nearly one-half of the adsorbed gas occurred as was measured by a pressure rise in the system to a maximum of 37 mm. The slower process of activated adsorption accompanied this desorption so that by the time the temperature of the system became constant, adsorption had occurred and the pressure dropped 1 mm. This process continued, the pressure being 33 mm. at the end of five hours and 27 mm. after thirty-six hours.

The upper chart of Fig. 4 is the result of measurements upon 24.3 cc. of gas in the system. The carbon monoxide was admitted at 195°K. and twenty hours allowed for equilibrium. The amount of gas adsorbed at this time, 17.4 cc. at 59 mm. pressure, agreed exactly with the data of the adsorption isotherm. The temperature of the system was then systematically varied. With each increase in temperature, desorption occurred quite rapidly with temperature change. This was accompanied by a slower but definite adsorption. Above 383° the additional activated adsorption was slight, since here a condition obtained in which the velocity of such adsorption was reasonably great.

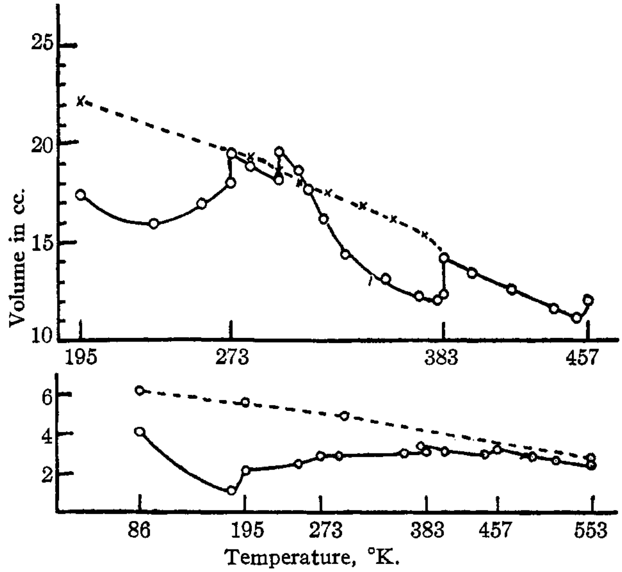

Fig. 4.—Change of adsorption with temperature.

If now, in the case of an equilibrium at elevated temperature cooling occurs, no desorption of activated molecules takes place, but adsorption of the unactivated type may occur on free portions of the surface. This adsorption increases regularly as the temperature is lowered, thus yielding an adsorption at 195°K. larger than any obtained by saturation of the clean surface at this temperature. The increase in adsorption at low temperatures above former equilibrium values is equal to the amount of activated adsorption that has occurred while the surface was at the higher temperatures. A succeeding increase of temperature merely produces an evaporation of this gas which was taken up in passing from the higher to the lower temperatures.

(b) Sintered Surface.—The lower chart of Fig. 4, is very significant; it is a plot of the data for the same effect of temperature upon the adsorption but with a catalyst which by heating at 553° has become less active. In this case the large physical adsorption at liquid air temperatures has almost completely evaporated from the surface at 195°K. Furthermore, due to the decreased activity of the catalyst, activated adsorption is much reduced and only reaches a maximum at 383°, a shift of 100° from the position of maximum of the original active catalyst.

TABLE VI

ADSORPTION WITH TEMPERATURE VARIATION, 273–383°

Time Hours Min.	Temp., °K.	Pressure, mm.	Volume adsorbed, cc.
...	373	1.8	25.9
20	313	11	22.7
38	341	24	17.2
45	360	31	14.5
50	374	35	13.0
55	381	37	12.2
1:00	382	37	12.2
1:05	382	36.5	12.4
1:10	383	36.5	12.4
1:30	383	36.0	12.7
2:35	383	35	13.0
5:00	383	33	13.6
6:15	383	30	15.0
8:00	383	29.5	15.1
9:30	383	28.5	15.4
19:35	383	28.0	15.9
48:00	383	27.0	16.3

TABLE VII

EFFECT OF TEMPERATURE VARIATION UPON ADSORPTION, 195–273°

Time Hours Min.	Temp., °K.	Pressure, mm.	Volume adsorbed, cc.
..	195	59	17.4
10	*ca.* 258	74.5	16.0
15	272	69	17.0
20	273	65.5	17.7
25	273	63	18.0
30	273	61	18.15
35	273	59.5	18.3
45	273	58.0	18.4
1	273	56.1	18.6
1:15	273	54.8	18.8
1:30	273	54.0	18.9
2:00	273	53	19.0
3:40	273	49	19.4
6:00	273	47.7	19.5

Rates of Adsorption.—The rates of adsorption, data for which are collected in Fig. 5, though significant, cannot be used directly for the evaluation of the activation energies accompanying adsorption. The curve for 273°K. is probably the most interesting. Even after twenty-four hours, there is still a slow adsorption. With increased temperature, this slow adsorption decreases in amount. The activity of the catalyst remains quite constant when the temperature remains below that at which the catalyst was prepared.

The rate of adsorption is practically instantaneous at liquid air temperatures; certainly it is as rapid as temperature equilibrium is produced.

TABLE VIII

EFFECT OF TEMPERATURE VARIATION UPON ADSORPTION, 298–383°

Time Hours Min.	Temp., °K.	Pressure, mm.	Volume adsorbed, cc.
...	298	48	19.6
2	308	59	18.6
3	313	68	17.7
4	321	84	16.2
5	332	102	14.4
6	353	118	13.2
7	363	124	12.8
8	370	129	12.3
9	376	131	12.3
10	378	132	12.3
11	380	133	12.2
14	383	133	12.2
15	383	132	12.2
17	383	131	12.3
20	383	129.5	12.4
25	383	129	12.5
30	383	128	12.6
45	383	126.5	12.8
1:00	383	126	12.9
2:00	383	121.5	13.2
4:00	383	118	13.6
7:00	383	115.5	13.8
10:30	383	114	14.0
13:30	383	112.5	14.1
24:00	383	111	14.2

Such an adsorption rate must indicate a widely different type of adsorption from that occurring at the higher temperatures, since an activated adsorption would be quite slow at 86°K. judging from the rates obtaining at the higher temperatures.

The character of the rate curves at all temperatures above that of liquid air indicates that, although activated adsorption with a measurable velocity is occurring, the surface is far from uniform. This is one more illustration of the wide variation in value of the surface forces present in metallic catalysts due to their finely divided nature, as often pointed out by Taylor. There are portions of the surface on which activated adsorption occurs immediately even at 195°K., whereas a second portion only adsorbs slowly and a third portion probably would not adsorb, having higher activation energies and becoming active only at higher temperatures. The increased adsorption, obtaining at 273°, in reasonable periods of observation, over those obtained at 195°K. is convincing evidence of this last conclusion.

Activation Energy in Adsorption.—It has already been pointed out by Taylor that the activation energy of the adsorption process is calculable from the rates of adsorption at two temperatures by use of the equation $d \ln v/dt = E/RT^2$. This can only be done effectively, however, in case the activated type of adsorption is separable from the rapid normal adsorption. None of the present data satisfy this condition, so that we are unable to make the calculation. Since, however, the activated adsorption is rapid in the temperature range 195–273°K., the energy of activation on the most active areas cannot be more than a few thousand calories per mole.

For the rate of adsorption to double for a ten degree temperature change at 81°K. the activation energy is 1 kg. calorie. At 273° it is 10 kg. calories and at 300° it is 45 kg. calories. From the data obtained in measuring the isotherms on the less active surfaces at 273 and 298° it is possible to calculate that the activation energy of the last portion of the gas adsorbed is around 9 kg. calories per mole. Being on the last areas covered this would necessarily be the maximum value for the activation energy. The unimolecular reaction velocity equation was found to fit the data of the rate of adsorption curves for 273 and 383° (see Fig. 5) well between the limits of fifteen minutes and three hours adsorption. If one uses the values of the constant obtained in the velocity equation, $k_1 = 0.0103$ and $k_2 = 0.0350$, one obtains a value of the activation energy of 2.3 kg. calories per mole. As expected this is less than the maximum value indicated.

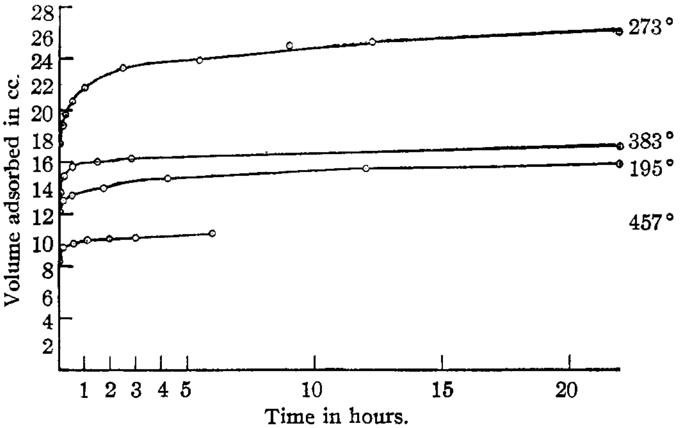

Fig. 5.—Rate of adsorption.

Heat of Adsorption.—The preceding tables furnish data from which approximate values for the heat of adsorption may be calculated by use of the Clapeyron–Clausius equation for the relation of vapor pressure and temperatures. For this calculation only data may be used which represent a single type of adsorption and from a temperature range in which equilibrium has been established between the adsorbed or condensed gas and that above the surface. Furthermore, data representing pressure equilibrium for adsorption on the same areas of the surface are necessary. This, of course, becomes more difficult the more complex the surface. In the case of palladium, for which we have already much evidence for a wide variation in the character of the surface, the results are approximate but probably indicate the proper order of magnitude. Here again the form of the equation makes it evident that the temperature at which adsorption occurs will be the predominant factor in the specific value obtained in the calculation of the heat of adsorption.

A calculation of λ for the low temperature adsorption in the range 86 to 195°K. does not seem legitimate for these isotherms. The adsorption at liquid air temperature is large and probably entirely of one type but the character of the isotherm and difficulty of desorption at 195°K. are proof that activated adsorption is present.

For the calculation of the heat of activated adsorption only measurements above 273° may be used. A summary is given in Table IX of the values it is possible to calculate from the present data. The heat of activated adsorption in the range of moderate adsorption is around 15 kg. calories. It is surprising that in the range of pressures in which comparison can be made between 273 and 457°K. such agreement was obtained. The heat of adsorption of the carbon monoxide which is strongly adsorbed so that it was only pumped off with the mercury-vapor pump could not be determined, but must be of a higher order of magnitude than the above. Flosdorf and Kistiakowsky[34] obtained 30–50 kg. calories for the heat of adsorption of hydrogen on platinum for the same type of strong adsorption, with lower values for the moderate adsorption.

Additional experiments were made to determine the other extreme, that is, the heat of adsorption of the weakly adsorbed gas. For this purpose the carbon monoxide was desorbed to one millimeter pressure at the temperature desired and the remainder of the isotherm from that pressure to 50 mm. determined. From the values obtained one may calculate that for the very last portion of gas adsorbed, and therefore a relatively small fraction of the surface, the heat of adsorption is 7 kg. calories. It is interesting to note that for the slightly stronger adsorption occurring with 0.5 cc. less gas adsorbed, the heat of adsorption was 15 kg. calories.

The adsorption of carbon monoxide by palladium occurs at very low temperatures as a normal physical process, but above 195°K. it occurs with an activation energy and the heat of reaction of a chemical process. The actual heat of adsorption on the most active portions of the surface representing the larger amount of the gas adsorbed must be much higher than the values given in the preceding paragraphs for surfaces mainly covered with gas.

[34] Flosdorf and Kistiakowsky, *J. Phys. Chem.*, **34**, 1907 (1930).

TABLE IX

HEAT OF ADSORPTION

Temp., °K.	Pressure, mm.	Heat of adsorption, λ
	10 cc. adsorbed	
273	2×10^{-4}	14,400
383	0.4	
457	12.5	16,200
	12 cc. adsorbed	
273	5×10^{-4}	
383	1.9	15,600
457	90	18,100
	22.6 cc. adsorbed	
273	1.4×10^{-2}	
457	140	15,500
	7.9 cc. adsorbed	
273	14	
298	56	7,100
	7.7 cc. adsorbed	
273	9	
298	27	7,100
	7.2 cc. adsorbed	
273	1.5	
298	15	15,000

Summary

1. The activity of palladium in the complete reduction of nitrobenzene to aniline has been determined and the effect of solvents has been related to their desorption of the reaction product water from the surface of the catalyst. The rate of reduction is more rapid at higher temperatures but a coagulation of the catalyst occurs.
2. A 20% yield of styrene was obtained by the dehydrogenation of ethylbenzene over palladium-black at 400°. An equal yield was obtained by using air with the vapor over a supported catalyst at lower temperatures.
3. Carbon monoxide does not reduce palladium oxide and is itself a powerful inhibitor to the reduction of the oxide by hydrogen.
4. There is no carbon formation and no decomposition of carbon monoxide by palladium at temperatures below 350°.
5. An active sample of palladium reduced from the oxide was effective in the reduction of carbon monoxide to methane between 250 and 300° but was soon sintered.
6. The adsorption of carbon monoxide by palladium and the resulting isotherms were determined at the following temperatures: 86, 195, 273, 383, 405, 457 and 553°K.

7. The isotherms, and isobars prepared from them, give effective evidence for the presence of two forms of adsorption, that occurring at the higher temperature requiring an activation energy.

8. The heat of activated adsorption is calculated as 15,000 calories per mole on the less active portions of the surface.

9. The determination of the effect of the change of temperature upon the amount of adsorption is shown to be a practical method for the investigation of the various forms of adsorption.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL INSTITUTE OF THE UNIVERSITY OF COPENHAGEN]

ON THE DISSOLUTION OF METALS IN ACIDS

BY J. N. BRÖNSTED AND N. L. ROSS KANE

RECEIVED JUNE 18, 1931 PUBLISHED OCTOBER 5, 1931

1. Introduction

The power of attacking and dissolving metals with evolution of hydrogen has from early times in the history of chemistry been considered as one of the most conspicuous and important characteristics of acids. On this account a large number of investigations from various points of view have in the course of time been carried out. The present paper contains an attempt to deal with the subject from the standpoint of the extended theory of acids and bases for which the reaction appears of particular significance.

By far the greater number of investigations on this reaction have dealt with impure or *heterogeneous* metals. The effect of acids upon such materials has a great practical importance. But the laws by which these reactions are governed are different from those of the simple reactions of homogeneous metals. When intending to elucidate the kinetics of the reaction between acids and metals in its elementary form, the investigator is reduced to the use of pure or *homogeneous* material only.

The theory has been advanced by de la Rive[1] that the dissolution of ordinary metals in acids is an electrolytic reaction originating in the heterogeneity of the metal. Palmaer[2] and his co-workers in extensive publications have brought convincing evidence in favor of this theory, which is known as the "theory of local elements." As in the present paper the explanation of the mechanism is based upon the condition of homogeneity, it has not been necessary to deal with details as regards the theory of local elements.

[1] De la Rive, *Ann. chim. phys.*, **43**, 425 (1830).

[2] Erichson-Auren and Palmaer, *Z. physik. Chem.*, **39**, 1 (1901); **45**, 182 (1903); **56**, 689 (1906); Palmaer, *Ingeniörsvetenskaps-Akademiens Handlinger* (Stockholm), Nr. 93 (1929); *cf.* also Guertler and Blumenthal, *Z. physik. Chem.*, **152**, 197 (1931).