[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A Study of the Catalytic Properties of Bright Platinum and Iridium Deposits in the Activation of Hydrogen[1]

BY LOUIS P. HAMMETT AND ARTHUR E. LORCH

While there are many reasons for believing that quality of surface is at least as important as quantity of surface in determining the activity of a contact catalyst,[2] it has been in practice extremely difficult to separate these variables, and indeed to standardize conditions so that catalysts of reproducible properties may be obtained. The prospect of so doing was, however, considerably advanced by the discovery[3] that smooth bright surfaces of the platinum metals, surfaces therefore of an area as definite as may be hoped for on a solid metal, may be obtained which are very effective for the catalytic activation of hydrogen. The present study is concerned with the determination and investigation of those factors which affect the catalytic properties of electro-deposited platinum and iridium and especially the decrease in activity which occurs when such catalysts are exposed to the activated substance hydrogen.[3]

Measurement of Activity.—Catalytic activity was determined by measuring the specific rate of the electrochemical reaction

$$H_2 \rightleftharpoons 2H^+ + 2e$$

by determination of the polarization of an electrode carrying the catalyst. By means of the apparatus shown in Fig. 1 current–potential curves were obtained, the potential E being measured by a Leeds and Northrup Type K potentiometer, and the current by determination of the potential drop across a known resistance in the circuit. The slope of these curves at the point of zero current, in amperes per volt, and for a gross area of 1 sq. cm. at 25° is reported as the catalytic activity. Since there is no discontinuity of slope at the equilibrium potential, it is immaterial whether the slope be determined by experiments in which hydrogen is oxidized (ΔE and I positive), as is the case with most of the results here reported, or by experiments in which hydrogen ion is reduced.

Our interest being principally in the comparison under identical conditions of electrodes of different preparation, we designed the apparatus to hold as many as ten electrodes closely and equivalently grouped around the salt bridge outlet, and used only the gentle stirring furnished by the hydrogen stream at a rate of two or three bubbles a second. The gain

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[1] This article is based upon part of the dissertation submitted by Arthur E. Lorch to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1932.

[2] See for instance the discussion in Taylor's "Treatise on Physical Chemistry," 2d ed., D. Van Nostrand Co., New York, Vol. II, pp. 1088–1089.

[3] (a) Beans and Hammett, THIS JOURNAL, **47**, 1215 (1925); (b) Hammett, *ibid.*, **46**, 7 (1924).

in comparability of results more than compensates for the loss in precision of the measurement of absolute activity which is implied by the omission of a capillary extension of the salt bridge and by the greater effect of concentration polarization. Values of activity greater than 0.01 ampere per volt/sq. cm. are reproducible to 5 or 10%, and might be increased by very efficient stirring as much as several thousand per cent. To such figures only slight significance can be attached. Below about 0.005 the values are reproducible to about 1% and are altered only a few per cent. by increase in stirring rate.

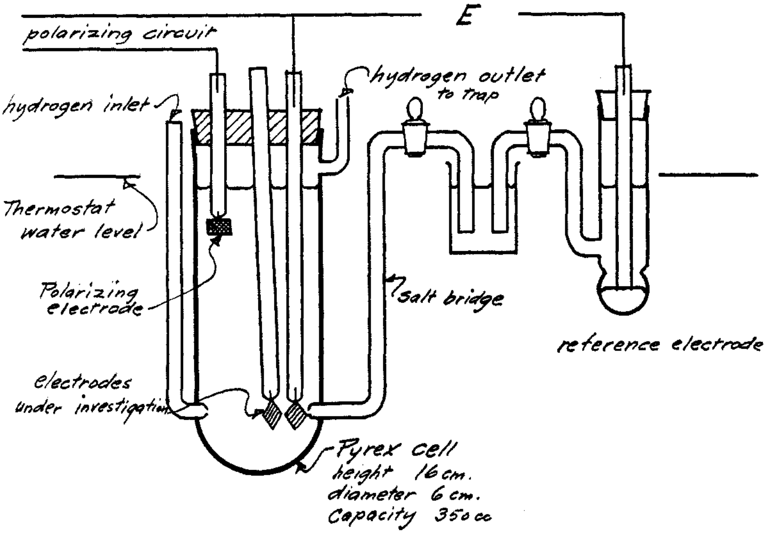

Fig. 1.

Materials.—Hydrogen was prepared by electrolysis of 30% sulfuric acid which was tested and found free from arsenic. The cathode consisted of a large copper sheet and the anode of a lead rod, the material for the latter having been specially freed from arsenic by fusion with lead chloride. The use of sulfuric acid as electrolyte eliminates the nuisance of fine spray, as when alkali is used, and in addition makes possible the continuous service of the generator for many months without appreciable solution of the electrodes. With the low currents used (0.05 to 0.5 ampere per sq. dm.) little if any reduction of sulfate ion occurs. In the purification we have especially guarded against traces of hydrogen sulfide, of sulfur dioxide, of arsine, and of lead hydride[4] as well as against oxygen. In the hydrogen line were placed long columns of cotton and soda lime, heated copper gauze, calcium chloride or "hydralo," and a coil immersed in liquid air. Rubber deteriorates in a hydrogen atmosphere, and emits foul-smelling products which we found to poison the catalysts. The stopper in our cell was a cork well soaked in paraffin wax, capped over with wax and painted with shellac when in place. Only one rubber connection was used in the hydrogen line, and in this a fresh piece of tubing was used in each experiment, and was protected from the hydrogen.

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[4] Paneth and Nörring, *Ber.*, **53**, 1693 (1920).

Water was twice distilled through a tin condenser and was stored in non-sol bottles. Hydrochloric acid was distilled in Pyrex glass.

Chloroplatinic acid was prepared by dissolving the metal in aqua regia followed by two precipitations with ammonium chloride, the precipitate being ignited each time and redissolved in aqua regia. The final solution was freed from nitrates by ten to fifteen evaporations to dryness with hydrochloric acid on a steam-bath.

Chloroplatinous acid was prepared by heating chloroplatinic acid at about 300° for one hour, and dissolving the residue in hydrochloric acid to give a solution about one molar in hydrochloric acid and with 1 to 5% of chloroplatinous acid.

"Iridium tetrachloride" from two different sources was used with equivalent results. The most likely composition for the substance usually sold as iridium tetrachloride seems to be about $IrCl_{3.8}\cdot 1.6HCl\cdot 4.5H_2O$.[5] At least it is essentially quadrivalent iridium. Tests on a small sample by the methods of Noyes[6] showed that the proportion of other noble metals present was certainly less than 3%.

Chloroiridous acid was prepared by the method of Délépine,[5] the tetrachloride being boiled with dilute alcohol in acid solution until metallic iridium began to form. The solution was then evaporated to dryness, and the residue dissolved in hydrochloric acid to give a solution about one molar in hydrochloric acid and with 1 to 3% of H_3IrCl_6.

Preparation of Electrodes.—A gold foil 0.65 cm. square free from etching and scratches was used as the base for the electro-deposit. It was found necessary to cut all electrodes for comparison from the same piece of foil in order to ensure approximately equal areas as a base for the plating operation. The square piece of foil was welded at a corner to a fine platinum wire and this was sealed into soft glass tubing in such a way as to leave a negligible amount of platinum exposed. During the sealing the gold foil was held in a pair of tweezers to keep it from melting. Prior to plating the electrodes were thoroughly cleaned (a few minutes in warm chromic acid) to ensure even deposition. This is especially important when using low current densities.

The production of bright deposits from chloroplatinic acid is difficult and uncertain, and it seems likely that the favorable results previously found[3a] with purified chloroplatinic acid depended upon the presence of chloroplatinous acid produced by over-heating in the evaporation of the chloroplatinic acid. In the absence of chloroplatinous acid we now find that high current densities lead to grayish or spongy deposits and low current densities lead to no deposit.

A plating bath of chloroplatinous acid, on the other hand, gives brilliant deposits over a wide range of current densities. Since we have found that the presence of small amounts of oxidized material during the plating greatly affects the activity of both platinum and iridium catalysts, and since it decreases the current efficiency, we have used a U-shaped plating cell in which anode and cathode compartments were separated by a plug of filter paper. When working with low current densities we have excluded oxygen by bubbling nitrogen through the cathode compartments and by providing the gas outlet with a trap.

The current efficiency of the deposition of platinum was determined as follows. A piece of gold foil was carefully cleaned, heated to redness, weighed, then very loosely welded to a platinum wire which was sealed into a glass tube. The gold foil was cleaned again and half immersed in the plating bath so that no metal could be deposited near the platinum wire. The plating current was accurately measured at short time intervals by means of a potentiometer and known resistance. The finished deposit was

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[5] Délépine, *Ann. chim.*, [9] **7**, 277 (1917). See also Kraus and Gerbach, *Z. anorg. allgem. Chem.*, **147**, 265 (1925).

[6] Noyes, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Co., New York, 1927.

washed thoroughly and the gold foil was pulled away from the platinum wire. A blank experiment showed that with the proper technique this could be done without any measurable loss in the weight of the gold foil. After careful washing the gold foil and platinum deposit were heated to red heat and then weighed again. Weights, balance and current measuring devices (resistance and potentiometer circuit) were very carefully checked to ensure the reliability of the results. These are given in Table I.

TABLE I

Wt. of Pt deposit, mg.	Time of plating	Average current, ma.	Plating efficiency of current on basis $Pt^{++} \rightarrow Pt$, per cent.
20.93	6 hrs. 0 min.	0.900	106.7
16.43	7 0	.590	109.5
24.90	12 6	.537	105.5

The experimental errors connected with these determinations are estimated as less than one per cent. We can explain these results either by assuming that a tremendous amount of adsorption takes place on the platinum or by assuming the existence of monovalent platinum in the solution. It seems most likely that the latter is the correct assumption. The existence of monovalent platinum has been suggested by several investigators,[7] but is not generally accepted.

Chloroiridic acid solutions give bright deposits over a wide range of current densities, but the current efficiency is low, and we have not been able to obtain reproducible catalytic activities.

Chloroiridous acid solutions give bright deposits at current densities from 0.05 to 50 milliamperes per square centimeter when the solution is stirred. We have not measured directly the current efficiency but the assumption that the thickness of a layer of iridium required to just conceal the color of the gold base is the same as that of a platinum deposit of the same covering power leads to values between 90 and 100%. The conclusion that the efficiency is high and constant is supported by the reproducibility of the catalytic properties of the deposits.

Reproducibility of Catalytic Activity and Life.—In Fig. 2 we have the results of a test of the reproducibility of the preparation of bright iridium catalysts from chloroiridous acid solutions. The six catalysts in question were prepared in the order of their numbers at a current density of 0.418 milliampere per square centimeter over a period of twenty-five minutes. After washing they were introduced into 0.1 molar hydrochloric acid in the cell of Fig. 1, which was placed in a thermostat at 25°, the hydrogen current was started, and the activity was determined from time to time. In the figure the logarithm of the activity is plotted against time. It will be noted that with the exception of number 1, the catalysts are very nearly identical in their activity-life curves. The deviating behavior of number 1, a type of behavior which we have consistently found with the first electrode or two prepared from a fresh solution, is probably to be ascribed to the presence in the solution of quadrivalent iridium, which we have found to give catalysts of slower decay.

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[7] Lea, *Z. anorg. Chem.*, **8**, 121 (1895); Sonstadt, *Proc. Chem. Soc.*, **14**, 25 (1898); Wöhler and Streicher, *Ber.*, **46**, 1591 (1913); Wöhler and Balz, *Z. anorg. allgem. Chem.*, **149**, 353 (1925).

In Fig. 3 are given the results of a similar test with platinum, the catalysts being bright platinum plated in the order of their numbers from chloroplatinous acid solution for thirty minutes at a current density of 0.80 milliampere per square centimeter. The reproducibility of properties, while not so good as with iridium, is still excellent for a contact catalyst.

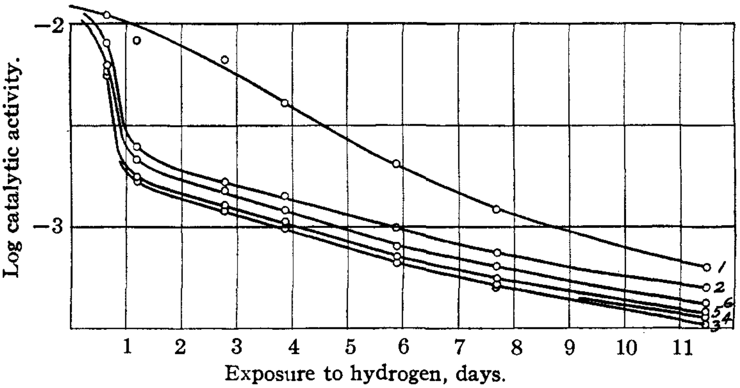

Fig. 2.

We have found that differences in temperature during the plating of as much as 10° have a negligible effect upon catalytic properties.

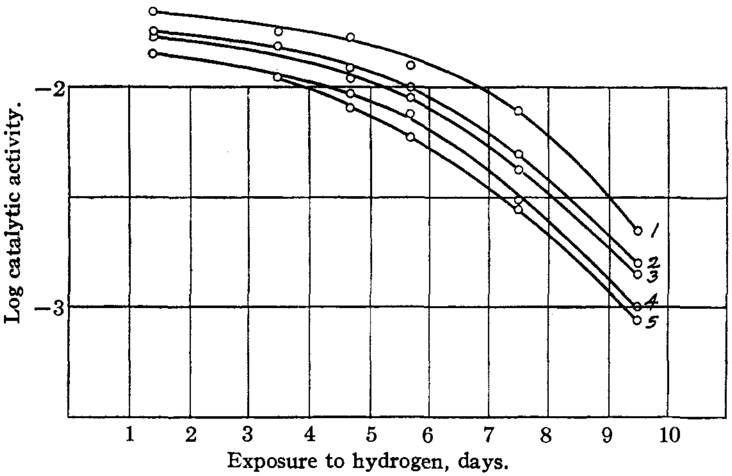

Fig. 3.

The Nature of the Decay in Catalytic Activity.—The decay in activity in a hydrogen atmosphere may be explained in terms of (1) reversion of active and unstable atoms or atomic groupings on the surface to less active states, a process inhibited by the presence of adsorbed oxygen, and accelerated by hydrogen only because of the removal of this inhibition; (2) a relation between the activation of hydrogen and the exhaustion of the catalyst; (3) a poisoning of the catalyst occurring only when the protecting layer of oxygen is removed by hydrogen.

We reject the third explanation on the basis of the following considerations. The very carefully purified hydrogen used in these experiments produces a decay qualitatively identical with that produced in earlier work by commercial tank hydrogen and by hydrogen made in the laboratory by electrolysis of sodium hydroxide solutions with nickel electrodes. The omission of the liquid-air trap in our hydrogen train produced no measurable change in the rate of decay. The known poison, hydrogen sulfide, is reversible in its effect, the activity increasing when the poison is removed; and the decrease in activity produced by saturated hydrogen sulfide solution is less than that produced on long aging in the presence only of the purest hydrogen, water, and hydrochloric acid. In further experiments a number of tubes containing hydrogen were sealed with two platinum electrodes apiece. The electrodes were variously exposed in these tubes. Some were immersed in 0.1 *N* hydrochloric acid, some in pure water, some in water which had never been in contact with glass. The tube in this latter case had been coated with paraffin and the water had been distilled through a tin condenser directly into the tube. Some electrodes were kept entirely out of the solution, being suspended above it in the hydrogen atmosphere. In all these cases the rate of decay of the catalysts was the same, within the limits of experimental error. These limits, it must be admitted, are somewhat wider than those prevailing in other sections of the work, since measurements can only be obtained on the catalysts by transferring them to a cell, a process which causes them to be reactivated to some extent by the air.

Either of the other explanations implies that the decay in activity which takes place at elevated temperatures under any conditions[8] is related to that which we observe at room temperature. This suggests that there should be a difference in the rate of this so-called sintering at elevated temperatures according to the environment, that hydrogen should have a catalytic effect upon the sintering. Such an effect is shown by the experiments described in Table II. In these, eight platinum catalysts prepared so as to be as nearly identical in properties as possible were heated in a Pyrex tube under various conditions, and were then transferred to the cell of Fig. 1. After a lapse of three days in hydrogen in the cell to allow the effects of the temporary activation by the air during the transfer to wear off, the activities were determined. Similar experiments at other temperatures confirm the conclusion that hydrogen does indeed accelerate the decay in activity over a wide range of temperatures.

[8] Vavon, *Compt. rend.*, **158**, 409 (1914); Wright and Smith, *J. Chem. Soc.*, **119**, 1683 (1921); Smith, *ibid.*, **123**, 2088 (1923); Taylor, *Proc. Roy. Soc.*, (London) **A108**, 106 (1925); Constable, *J. Chem. Soc.*, 1578, 2995 (1927); Bowden and Connor, *Proc. Roy. Soc.*, (London) **A128**, 317 (1930).

Effect of Thickness of Deposit and of Rate of Plating.—Figure 4 shows the life curves of five iridium catalysts of different thickness. These were plated for varying times at the same current density (0.27 ma./sq. cm.) from the same solution of chloroiridous acid in the order of the numbers attached to the curves. The average thickness of the deposit calculated on the basis of 100% current efficiency is given in the figure. Figure 5

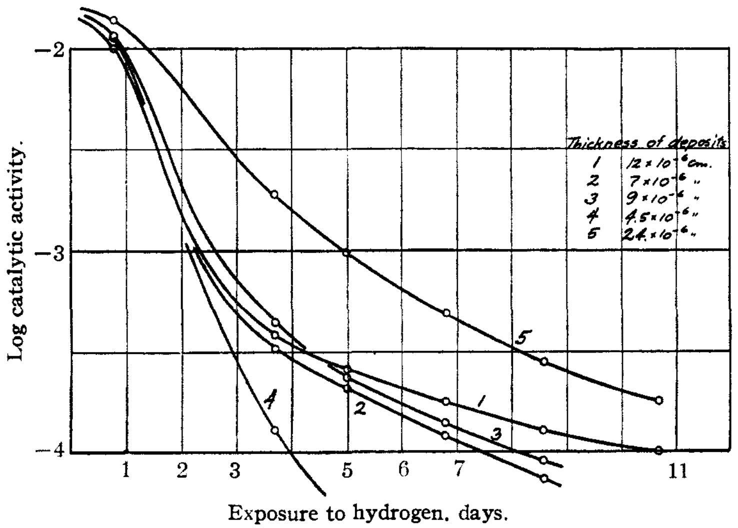

Fig. 4.

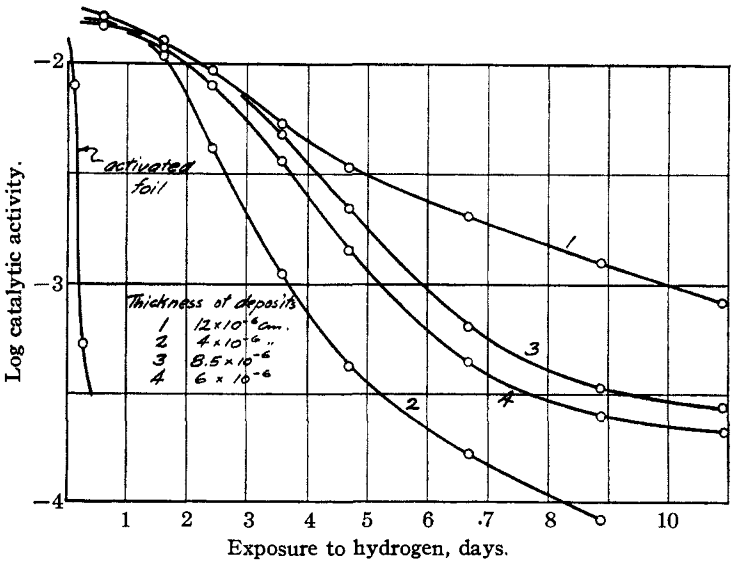

Fig. 5.

TABLE II

		Catalytic activity (a)	Catalytic activity (b)
Group I	No treatment	0.0080	0.0072
Group IV	Placed in dry tube. Air displaced by N_2 and this by H_2. Catalysts heated in H_2 for 1/2 hour at 350 °C. H_2 then displaced by N_2 and tube opened	.0000045	.0000015
Group V	Placed in dry tube. Air displaced by N_2 (free from O_2) and tube heated for 1/2 hour at 350°	.000084	.00015
Group VI	Heated in oxygen for half an hour at 350°	.000041	.0018

TABLE III

Order of plating	1	2	3	4	5	6	7	8	9	10
Time of plating, min.	30	30	30	15	10	8.5	76	135	175	9.75
Current density ma. per sq. cm.	0.405	0.405	0.405	0.875	1.52	3.38	0.167	0.115	0.0892	8.25
Time for concealment of gold base, min.	7	7	6	3.5	2.5	2	15	30	40	2.25
Estimated thickness:[a]										
Assuming constant 100% current eff., cm.	2.1×10^{-5}	2.1	2.1	2.2	2.7	5.1	2.2	2.7	2.7	14.0
From time to conceal base, cm.	2.1×10^{-5}	2.1	2.4	2.1	2.0	2.1	2.4	2.2	2.1	2.1
Exposure, days	Catalytic activity									
0.6	0.0105	0.0125	0.0113	0.0135	0.0109	0.0102	0.0115	0.0132	0.0146	0.0133
1.5	.0090	.0098	.0087	.0092	.0087	.0066	.0089	.0087	.0097	.0088
3.6	.0028	.00150	.00145	.00089	.0016	.00085	.00112	.0030	.00130	.00146
4.7	.00100	.00044	.00049	.00027	.00049	.00025	.00032	.0017	.00068	.00050
6.5	.00023	.00020	.00021	.000119	.000128	.000101	.000145	.00081	.00036	.00017
8.6	.000117	.000103	.000115	.000064	.000054	.000052	.000085	.00037	.00018	.000073

[a] Due to a miscalculation the figures for thickness given in the thesis upon which this article is based were in error by a constant factor of 0.7.

contains the results of similar experiments with platinum catalysts obtained from a solution of chloroplatinous acid at a current density of 0.141 ma./sq. cm. Similar results have been obtained in other experiments, and we conclude that for electrodeposited platinum and iridium catalysts of equal gross area the catalytic life is greater the thicker the deposit.

The decay curve for an ordinary platinum foil activated by anodic oxygen evolution for five minutes is included in Fig. 5, and shows a very rapid decay rate. This is further confirmation because such an activation should produce only a very thin active layer.

In Table III are given the results of an experiment designed to test the effect of rate of deposition upon the properties of iridium catalysts. The catalysts were all prepared from the same 3% chloroiridous acid solution in the order of the numbers, and it was attempted to make them all of the same thickness by varying the rate of deposition in inverse proportion to the time of plating. The first three were plated at the same rate and the agreement of properties between 2 and 3 shows that the bath had reached a steady condition. The thickness calculated on the basis of constant 100% current efficiency is given and, as a check, the value calculated from the time required to just conceal the color of the gold base. The agreement is excellent except in the case of the two electrodes plated at the highest current densities, and we have discarded the results on these. The accepted results are plotted in Fig. 6, from which it is clear that the best iridium catalysts are those plated at the lowest rate.

Figure 6 also contains the life curve of a catalyst prepared from an iridium tetrachloride solution, and estimated from the time required to conceal the gold base to be somewhat less in thickness than the other catalysts included in the figure. Because of the low current efficiency prevailing in such solutions, this required a current of 0.26 ma./sq. cm. for five and one quarter hours. The characteristically long life may be due to a specific effect of the oxidized iridium as a source of the deposit or possibly to the very slow rate of deposition.

With platinum the difference in properties arising from variation in rate of deposition is certainly smaller than with iridium, and it is difficult to be certain whether any such effect exists, especially in view of the poorer reproducibility of platinum catalysts.

Both the effect of thickness of deposit and the effect of rate of deposition are not obvious conclusions from usual theories of contact catalysis. All of the catalysts for which we have here given results appeared perfectly smooth and lustrous to the naked eye or under magnification of 750 diameters. Nevertheless the quantity of metal required to conceal the color of the gold base corresponds to a thickness of from 1 to 2.5×10^{-6} cm. or about 40 to 100 atomic layers. This suggests that crystal growth starts from centers scattered over the surface of the gold and proceeds laterally as well as upward until adjacent crystals touch. The surface of the deposit might then be expected to have a saw-tooth cross section with a tooth height of some 80 to 200 atom diameters. Since, however, an increase in thickness beyond that required to obscure the base results in increased catalytic life, it must be supposed that fissures or pores much deeper than the average depth of the saw-teeth exist, and have a very marked effect upon catalytic properties.

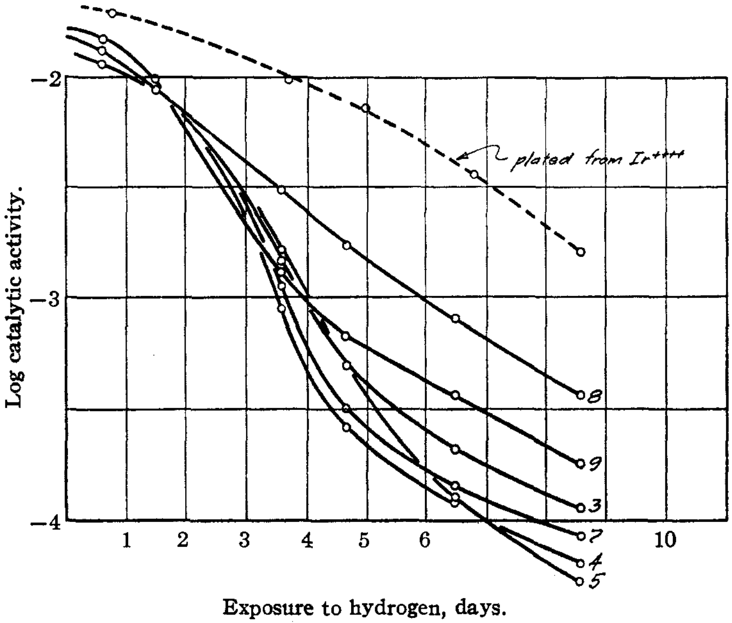

Fig. 6.

All of the curves show an initial rapid decay whose rate is very nearly the same in all cases. This initial decay is therefore independent of the thickness of the deposit and is to be attributed to the loss in activity of that part of the catalyst in which all these catalysts are identical, the ordinary or external surface. It is only after this, which furnishes most of the initial activity, has decayed that the properties of that part of the catalyst which depend upon thickness become significant. Furthermore, the differences in slope of the later parts of the curves in Figs. 4 and 5 indicate that thicker deposits lead to inner surfaces (of the fissures or pores) whose specific rate of decay is smaller, whereas the parallelism (on the semi-logarithmic plot) of the later part of the curves in Fig. 6 suggests that differences in rate of deposition result in differences in activity of the inner surface but not in the fractional loss of activity in unit time.

In other words, the external surface, which is the most exposed to hydrogen, decays most rapidly, and of the inner surfaces, those present in the thicker deposits, and therefore least accessible to the hydrogen, decay at the lowest rate. This experimental conclusion may also be derived as a corollary from Tanner's recent theory of contact catalysis,[9] according to which activation depends upon the existence of local excesses in temperature at the active points. It follows that contact with and consequent activation of the reactant should tend to produce decay of the catalyst and that those areas which are most exposed to hydrogen and on which the reversible reaction

$$\begin{aligned} 2H^+ + 2e &\rightleftharpoons H_2 \\ \text{or}\quad 2H &\rightleftharpoons H_2 \end{aligned}$$

proceeds at the greatest rate should be those on which loss of activity is most rapid.

Summary

Methods have been perfected for the preparation by electrodeposition of platinum and iridium catalysts of reproducible properties for the activation of hydrogen.

The loss in activity which such catalysts undergo in the presence of hydrogen at room temperature has been shown to be dependent upon the hydrogen itself and not upon poisons, and to be closely related to the so-called sintering which takes place at higher temperatures.

The dependence of decay upon thickness of deposit and upon rate of deposition has been investigated, and the conclusion reached that these apparently smooth solid deposits have an inner surface of great importance for their catalytic behavior.

Indications have been found that it is the actual activation of hydrogen which is responsible for the decay, and the relation of this conclusion to Tanner's theory of contact catalysis has been pointed out.

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[9] Tanner, THIS JOURNAL, 54, 2171 (1932).