

added to sulfuric acid (plus potassium nitrate) at a stirring speed high enough to give the maximum rate, diminishes the rate to the same extent, which does not indicate a chemically-controlled rate.

For these reasons we hesitate to call the rate at higher stirring speeds a true chemical rate until it has been investigated further. It is probable that a very high stirring speed, or a sufficiently high concentration of certain salts, would reduce the rate to the value it has with no depolarizer present, where the temperature coefficient is also high⁷; in this case the mechanism might also be identical.

The increase in the rate in nitric acid on addition of small amounts of chloride and bromide (Fig. 7) may be ascribed to an increase in the diffusion coefficient of the acid. While the diffusion coefficient of nitric acid has not been determined in the presence of salts, it is lower than that of hydrochloric acid in water ("International Critical Tables").

The maximum rates in the various acids at 2000 r. p. m. are roughly proportional to the diffusion coefficients, except for perchloric acid, as shown in Table I. Because of the irregularities found, including film formation with the weaker acids, a quantitative comparison would be impossible.

Summary

The rate of dissolution of very pure iron has

been measured in solutions of several acids, with potassium nitrate, hydrogen peroxide, potassium nitrite and *p*-nitrophenol as depolarizers. Of these only the nitrate was found to be reasonably satisfactory as a depolarizer.

The rate was studied as a function of the depolarizer concentration, the acid concentration, the concentration of various added salts, the stirring speed and the temperature. The rate was also measured in ferric chloride solutions of various concentrations, at various stirring speeds and temperatures, with and without added acid.

The rate is shown to be diffusion-controlled under all conditions in ferric chloride; at low stirring speeds in hydrochloric acid with sufficient nitrate present, and approximately so in nitric acid with certain chloride concentrations. Under other conditions (higher stirring speeds, higher salt concentrations, low nitrate concentrations) it is in whole or part controlled by a slower reaction perhaps of chemical nature at the metal surface.

Under conditions where the rate is diffusion-controlled, the temperature coefficient is about 1.35 per 10°; where it is "chemically" controlled, the temperature coefficient is 2.0-2.4 per 10°. The activation energies vary accordingly.

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Studies of Purified Palladium Sols Prepared by Electric Sparking

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The series of investigations of different purified and concentrated Bredig sols of the noble metals,² carried out at this Institute over a period of years, has been continued with the study of palladium sols. As in the previous studies our concern was to observe the relations between origin of charge and stability on the one hand and inorganic chemical properties of palladium on the other by physical-chemical methods of analysis. Thus it was possible to make comparisons in the same

way with the other sols of noble metals already investigated.

The methods of preparing, purifying and concentrating were disintegration by the electric spark and an improved process of electrodecentration.²

One of the first results was that it is impossible to prepare a palladium sol by electrodispersion in *conductivity water* (spec. cond. 7×10^{-7} mho). Regardless of the dispersion time, in every case precipitates are formed instantly. This behavior contrasts with that of platinum and silver.^{2b,c} The explanation is that pallado oxide is less acid than platino oxide³; a hydroxo acid of palladium is not known, while a hydroxo acid of platinum

(1) The experiments were carried out at the Institut für medizinische Kolloidchemie der Universität Wien in 1936 and 1937.

(2) (a) Gold sols: Pauli, *Naturwissenschaften*, **20**, 551 and 573 (1932), with many references to literature; Pauli and Russer, *Kolloid. Z.*, **58**, 22 (1932); Eirich and Pauli, *ibid.*, **67**, 186 (1934); Pauli, Russer and Brunner, *ibid.*, **72**, 26 (1935); (b) platinum sols: Pauli and Schild, *ibid.*, **72**, 165 (1935); Pauli and Baczewski, *Monatsh.*, **69**, 204 (1936); (c) silver sols: Löffler and Pauli, *Kolloid. Z.*, **60**, 146 (1932); Hoff and Pauli, to be published, with list of literature.

(3) P. Pascal and P. Baud, "Traité de Chimie Minérale," Tome XI, Masson et Cie, Paris, 1932, p. 793.

has been shown to be the charging group of Bredig platinum sols in conductivity water.⁴ On the other hand, palladium is more noble than silver (silver oxide is a strong base). In the case of silver the anodic oxidation (during electrodispersion) furnishes the stabilizing complex by forming ultimately silver hydroxide,^{2c} which in the case of palladium in conductivity water is not possible. This demonstrates a similarity with gold, which for analogous reasons does not form an electrodispersion sol in conductivity water.⁵

We found similar conditions by electrodispersion in sulfuric acid ($1 \times 10^{-3} N$). An adhering surface complex could not be expected because of the high solubility of palladium sulfate in water.³ Since the formation of an oxo complex (as a result of electrolysis) is not possible either, we have no sol formation. Silver and gold form very unstable colloids in dilute aqueous sulfuric acid solutions. The corresponding experiments with platinum have not yet been undertaken. Such experiments would be interesting because of the great number of complex acids known to be formed by platinum and the sulfate radical.

The behavior of palladium when dispersed in solutions of potassium chloride was unexpected. Within the concentration range 1×10^{-4} to $1 \times 10^{-2} N$ a dark brown sol is formed, but it coagulates within one day at the most. These sols, therefore, are still less stable than the corresponding silver sols. The explanation probably is that the reaction of palladium metal while being dispersed in potassium chloride solutions does not lead to a noticeable complex formation. The formation of silver sols (dispersed under the same circumstances) was favored by the simultaneous formation of oxo complexes. Thus one may consider the Bredig silver sols in potassium chloride solutions as stabilized by chloro hydroxo mixed complexes (Löffler-Pauli^{2c}), so that the extraordinary sensitiveness of the pure hydroxo silver sols to carbon dioxide was considerably decreased.

The question was raised, therefore, to what extent the behavior of palladium would prove analogous. For this purpose the electrodispersion in sodium hydroxide solutions (optimal concentration $1 \times 10^{-3} N$) was tried. We obtained dark

brown sols which were stable for months if sufficiently protected against carbon dioxide. As hydroxo sols (which they obviously are) they showed a high sensitiveness to carbon dioxide and electro dialysis, just as do the corresponding silver sols. The exchange of sodium ion for hydrogen ion forced by membrane hydrolysis processes during electro dialysis leads again to rapid discharge by complex decomposition. The reaction is the same as of silver sol (Löffler-Pauli^{2c}), namely, a neutralization of the hydrogen ions by the complex hydroxo groups (see also the silver nitrate titration of a chloro hydroxo palladium sol discussed later in this paper).

Sols dispersed in nitric acid solutions proved not to be resistant to carbon dioxide or electro dialysis in spite of the fact that the nitrate ion is a favored complex partner of palladium. They were even less resistant than the sols dispersed in sodium hydroxide. This behavior would suggest the presence of hydroxo nitrate mixed complexes. If perfectly protected from carbon dioxide, the sols are stable for a long time. This demonstrates that the coagulation is due not only to the high solubility of the palladium complex mentioned, but also to its decomposition. This decomposition is caused by hydrolytical processes aided by reaction with carbon dioxide or electrolysis.

By far the best sols were obtained by electrodispersion in hydrochloric acid solutions. In the optimal concentration ($1 \times 10^{-3} N$) the time of dispersion may be extended to three hours. Excellent sols with a content up to 0.2 g. of palladium per liter are attainable directly; they are not sensitive to carbon dioxide and laboratory air. Only sols with a smaller content (0.12 g. of palladium per liter and one to two hours time of dispersion) which may easily be concentrated to more than 1 g. of palladium per liter are suitable for electrode cantation. The conductivity of the dispersion medium decreases during dispersion (by 5–8%) and continues to decrease after completing the electrodispersion.⁶ After eighteen to twenty days the limiting value of conductivity (equilibrium) is reached. In case the primary sols were too concentrated (0.2 g. of palladium per liter), the period of decreasing conductivity is interrupted by an increase about the thirteenth day after dispersion. Shortly thereafter these sols coagulate spontaneously.

(6) Under certain favorable circumstances observations have been made of an analogous behavior of gold and platinum sols. After dispersion the complexes are filled up by consumption of free acid.

(4) S. W. Pennycook [*J. Chem. Soc.*, 2108 (1928); 623 (1929)] has postulated a hexahydroxo platini acid as charging complex. A platino hydroxo acid $H_2Pt(OH)_6$ is more probable. This acid possibly is in oxidation and detachment equilibrium with a platini complex (Pauli and Baczewski^{2b}). For further details, see Pennycook, *Kolloid Z.*, **49**, 407 (1929); *Z. physik. Chem.*, **148**, 413 (1930).

(5) Beans and Eastlack, *THIS JOURNAL*, **37**, 2607 (1915) and ^{2a}.

The electrodispersion sols (before electrodecentration) contain nearly the same concentration of chlorine and hydrogen ions (about $8 \times 10^{-4} N$), ascertained by conductometrical titration. But this amount of ions is not yet sufficient to explain the total conductivity. Therefore we have to assume a further amount of electrolyte (about $3-6 \times 10^{-4} N$). We suppose it is the colloid electrolyte with the "gegenions" (contra-ions) H^+ and Pd^{++} which is present besides molecularly disperse hydrochloric acid and pallado chloride. The molecularly disperse contaminations are removed to a large extent by electrodecentration. In order to avoid an entire hydrolysis of the complexes the electrodecentration has to be stopped at the right moment. Besides, a decomposition equilibrium seems to exist between the charging groups and pallado chloride. In sols purified and concentrated by electrodecentration, a small amount of pallado chloride therefore is always present.

The sols concentrated and purified by electrodecentration show a continual increase of conductivity with time, accompanied by spontaneous layer formation and partial flocculation. Nevertheless, among our number of specimens were some sols with nearly constant conductivity after concentrating. These sols show the same amount of (free) hydrogen ions titrated either by sodium hydroxide or barium hydroxide. On the other hand, all sols the conductivity of which increases with time show a sodium hydroxide consumption greater than the concentration of free (conductance-active) hydrogen ions and a consumption of barium hydroxide still larger than that of sodium hydroxide. The greatest number of our sols obviously possess further heteropolar surface groups which may be filled up to chlorohydroxo mixed complexes, besides the charging complexes. In this respect they are similar to the chloro platinum sols (Pauli-Schild^{2b}).

With our concentrated sols which are freed to a large extent from molecular electrolytes (in so far as these are not re-formed by complex decomposition), we also found the amount of titrated hydrogen ions insufficient to explain the total conductivity. They contain on the average the same concentration of other cations (Pd^{++}). Less highly purified sols are more strongly charged (the membrane hydrolysis of surface complexes is not so far advanced), but they contain up to twenty times as many other cations as hydrogen

ions. A part (up to one-half) of this amount of cations can be ascribed to molecularly disperse pallado chloride, as may be ascertained by simultaneous determination of free chlorine ions by conductometrical titration.

This may be illustrated by some results:

	Sol VII	Sol XXII	Sol X
Content, g. Pd/liter.....	0.35	0.66	1.10
k of last upper layer, mho $\times 10^6$	7.0	2.7	5.7
k of sol, mho $\times 10^6$	2.36	1.09	2.80
Concn. of active H^+ , $N \times 10^6$...	0.92	2.1	4.6
Concn. of cations other than H^+ , $N \times 10^6$	20	1.5	9.6
Concn. of free chloride ion, $N \times 10^5$	8.9	<1	~ 3.1

Sol VII incompletely purified, sol XXII highly purified, sol X middle degree of purification; k = specific conductivity at 25°.

As one may see from this table, continued purification causes removal of molecularly disperse pallado chloride and exchange of the "gegenion" (contra-ion) Pd^{++} for H^+ . This is in agreement with the previous experience with other negative colloids. Simultaneously the absolute amount of charging ionogen groups is decreased by the accompanying complex decomposition.

Coagulation by freezing produces a decrease of conductivity in the freezing liquid (liquid produced by thawing the frozen colloid and by separation from the coagulum, without Tyndall phenomenon). The sols mentioned above as of constant conductivity are exceptions: they maintain their constant conductivity in the freezing liquid also after coagulation. In all cases where the conductivity of the freezing liquid is lower than that of the sol, the hydrogen ion concentration of the sol is decreased in the freezing liquid. The cations present other than H^+ are in some cases increased, in some decreased, by freezing. This leads to the conclusion that the bulk of hydrogen ions, being "gegenions," goes into the coagulum or vanishes by reaction with the hydroxyl groups of the charging chloro hydroxo complex which is partially destroyed, and pallado chloride is set free. But the amount of pallado chloride liberated by freezing in some cases may be ten times as much as could be produced by complex decomposition at the maximum. This abundance of pallado chloride is probably originated by non-ionogen heteropolar surface groups of the sol particles which are rich with chlorine. In other cases, on the contrary, the amount of pallado chloride is considerably decreased by

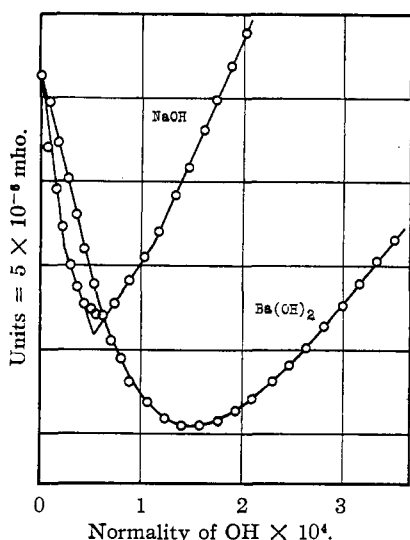


Fig. 1.—Correlative sodium hydroxide and barium hydroxide titrations of 3 cc. of sol X.

freezing. This may be due to a filling up of non-ionogen heteropolar surface groups that are low in chlorine. Thereby the cation (Pd^{++}) will be inactivated. This behavior is in agreement with the results of the barium hydroxide titration. Figure 1 shows an example of a characteristic pair of correlative sodium hydroxide and barium hydroxide titrations.

The existence of non-charging heteropolar surface groups in addition to the charging groups had been proved in the case of platinum sols (Pauli-Baczewski,^{2b} Penny-uck⁴) by comparison of sodium hydroxide and barium hydroxide titrations. A filling up of the heteropolar surface groups to ionogen complexes is more favored in the presence of barium hydroxide than of sodium hydroxide because of the more strongly inactivating and associating divalent barium ion.

The presence of palladium ions in the freezing liquid could be proved in all cases by a special palladium test.

This palladium test is analogous to the platinum test of Pauli-Schild.^{2b} The procedure is reduction of the palladium compound by formic acid under special conditions and addition of phosphorous-molybdenic acid. The blue color of the solution indicates palladium concentrations of 0.2-1 γ per cc.; green color.

The determination of the colloid equivalent—number of palladium atoms per one free charge—was possible only in cases where nearly all gegenions were hydrogen ions. The calculated values varied between 100 and 300.

The conductometrical determination of chlorine had to be carried out by silver sulfate titra-

tion instead of the usual silver nitrate titration, for some sols had the capacity of taking the nitrate radical into their complexes. This could be proved by titration with potassium nitrate, nitric acid and by the comparison of silver sulfate and silver nitrate titrations. This behavior was obvious with freezing liquids which had been reduced by hydrogen gas. If titrated by silver nitrate they showed a less consumption of the reagent after reduction than before. The explanation is that the complex present in the freezing liquid and capable of adding the nitrate radical, loses this capacity by reduction.

A further interesting result of titration analysis was also found by silver nitrate titration. The charging complexes of some sols are destroyed by reaction with silver ion, *i. e.*, after removal of chlorine, a reaction between hydrogen ion and complex hydroxyl groups takes place. The nitrate radical instead of chlorine cannot form a stable complex. In such cases the silver nitrate titration diagrams show the particular character of acid-base titration plots, since during titration the hydrogen ion is stoichiometrically consumed (Fig. 2). There seems to be only one equation possible for the corresponding reaction: $[\text{Pd}(\text{OH})_2\text{Cl}_2]\text{H}_2 + 2\text{AgNO}_3 = 2\text{AgCl} + \text{Pd}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$, because for one hydrogen ion conductivity equivalent that vanishes, one salt conductivity equivalent has been found to be set free.

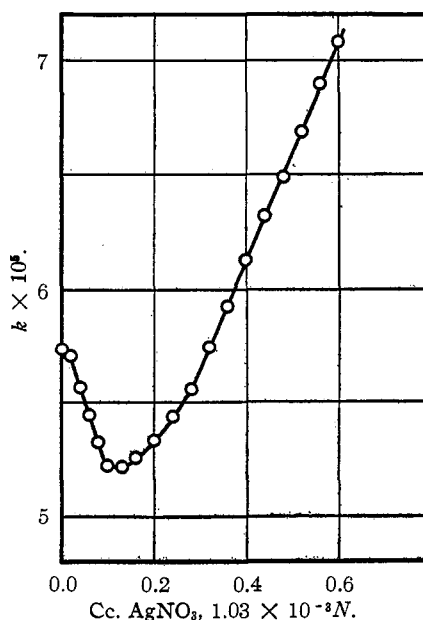


Fig. 2.—Complex decomposition during silver nitrate titration: sol IX, 3 cc.

The chlorohydroxo palladium sols (even if not concentrated and purified) are coagulated by boiling. The conductivity is then slightly increased, the charging groups are probably detached entirely, and the titrable hydrogen ion is transferred completely into the "boiling liquid."

Summary

1. Preparations of palladium sols by sparking under the solvents: conductivity water, and 10^{-3} normal solutions of sulfuric acid, sodium hydrox-

ide, nitric acid, potassium chloride, hydrochloric acid, are related and discussed briefly.

2. The charging group of the sols prepared in the case of the chlorides very probably is a chlorohydroxo mixed complex of varying constitution. This complex maintains a decomposition equilibrium with molecularly disperse pallado chloride. Besides there are heteropolar groups on the particle surface that are non-ionogen and therefore not charging. These groups may react in a variety of ways.

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The Quantum Yield of Monochloroacetic Acid Hydrolysis

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A direct comparison of the uranyl oxalate and monochloroacetic acid photolyses at 2537 Å. shows, on the basis of the published quantum yields for these reactions, a startling discrepancy. Since both reactions have been widely used as chemical actinometers and results interpreted on the basis of the existing quantum yields, it seemed necessary to find the source of this discrepancy. In a recent note¹ the authors reported a redetermination of both yields. A solution 0.01 *m* in uranyl sulfate and 0.05 *m* in oxalic acid gave an average quantum yield at 2537 Å. of 0.60, in agreement with the value reported by W. G. Leighton and Forbes² for this wave length. For a solution 0.5 *m* in monochloroacetic acid at room temperature and 2537 Å. the quantum yield was found to lie between 0.3 and 0.4, as compared with the value of 1.07 given by Rudberg.³ We, accordingly, have reinvestigated this reaction, and now find the quantum yield to be strongly dependent on temperature.

Experimental

Monochloroacetic acid was purified by a series of distillations in an all-glass apparatus, starting samples from several sources being employed. Freshly prepared solutions, before exposure to light, showed no chloride ion. Quantum yields were based on the amount of chloride ion produced, which was determined by potentiometric titration against standard (0.0075 *m*) silver nitrate. The cell consisted of a calomel electrode connected to an Ag-AgCl

electrode by a saturated potassium nitrate bridge (Cl⁻ free). The method was checked by titration of standard chloride solutions. Radiation at 2537 Å. was supplied by a mercury arc in conjunction with a quartz monochromator. The rectangular reaction cell was entirely of fused silica and contained 8.23 cc. of solution in which the average light path was 25 mm. Absolute energies were determined by thermopile, calibrated against U. S. B. S. radiation standards. In the course of the investigation, two independent monochromators, four light sources, including lamps giving both reversed and non-reversed lines at 2537 Å., as well as lamps giving both continuous and intermittent radiation (with respect to time), two thermopiles, one surface and one linear, and four U. S. B. S. standard lamps were used, all with uniform results.

Energy measurements were carried out by the method of horizontal integration⁴ taking thermopile readings at 2-mm. intervals across the back of the cell. The length of the monochromator slit was adjusted so that the divergent beam, after passing through the cell filled with water or solution, fell entirely within the vertical limits of the thermopile surface. Variations in arc intensity during a run and between different series of integration measurements were followed by placing the thermopile in a fixed and reproducible position at the front of the cell. The methods of applying corrections and of computation were those employed by the authors in previous work.^{2,5}

For runs at elevated temperatures the cell, with the exception of the front window, was enclosed in an insulated heating jacket and energy measurements were made as before except that variations in intensity were not followed during the course of the run. Rates of decomposition by the dark reaction were determined for several different temperatures, and from a plot of $\log k$ vs. $1/T$ the correction for the amount of decomposition due to the dark reaction during a photolysis was determined.

(1) W. G. Leighton, R. N. Smith and P. A. Leighton, *THIS JOURNAL*, **60**, 2566 (1938).

(2) W. G. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930).

(3) Rudberg, *Z. Physik*, **24**, 247 (1924).

(4) Leighton and Leighton, *J. Phys. Chem.*, **36**, 1900 (1932).

(5) P. A. Leighton and G. S. Forbes, *THIS JOURNAL*, **51**, 3549 (1929).