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COLLOIDAL PLATINUM AND ITS BEHAVIOR AS A TYPICAL ACIDOID SOL

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For some time the author has been engaged on a series of investigations upon the structure, stability and general reactions of colloidal platinum.[1] The advancement of the work has reached a stage where it has proved desirable to present the collective evidence concerning the behavior of colloidal platinum as an acidoid sol, and to discuss the surface actions and the coagulation process, in the light of the more recent work.

Apart from its general interest as a negative hydrophobic sol, colloidal platinum presents added features of importance. Its catalytic powers are well-known and, further, the question arises as to whether each platinum particle in the presence of oxygen (or of hydrogen) does not behave as a tiny oxygen (or hydrogen) electrode. Investigations at present in hand lead to the hope that the results will ultimately throw light on catalytic actions and on electrode phenomena.

The Arcing of Platinum Poles.—All platinum sols used by the author were prepared by the Bredig method, using chemically pure platinum poles and conductivity water of specific conductivity less than 0.6×10^{-6}. The arcing was carried out in a closed vessel into which any required gas could be introduced. The negative pole showed the characteristic disintegration crater, and hence the platinum leaves this pole, probably with a negative charge. Some of the atomized platinum condenses on the positive pole, which accordingly becomes elongated. The rest is dispersed into the solution, but only a fraction of this remains suspended as the colloid. Although the solution is kept continually circulating and at a temperature close to 0°, the tips of the poles become red hot and the action there is violent. Conditions are, therefore, suitable for the reaction of the atomized platinum with the water or with the oxygen due to the electrolytic decomposition of the water. In any case, Rocasolano[2] has found

[1] See *Australian J. Exp. Biol. Med. Science*, 4, 99 (1927); *J. Chem. Soc.*, 2600 (1927); 551, 2108 (1928); 618, 623 (1929); *Kolloid-Z.*, 49, 407 (1929).

[2] Rocasolano, "Colloid Chemistry (Alexander)," Vol. I, 1926, p. 678.

that only hydrogen gas is actually given off, and therefore the equivalent amount of oxygen has been taken up by the platinum. As finely divided platinum is relatively easily oxidized,[3] one may conclude that under the conditions cited the oxygen has been taken up to form definite oxidation products, such as oxides and oxy-acids.

The dissolved oxygen does not play a controlling part in the formation of these oxidation products, for if the preparation be carried out in the presence of nitrogen and the complete absence of oxygen[4] (or of air), a comparable sol is obtained. It is acidoid, it contains the same free strong platinic acid, but it is somewhat less stable (more readily coagulated on boiling) than the corresponding sol prepared in the presence of oxygen. Such sols will be referred to as platinum–nitrogen and platinum–oxygen sols, respectively. It will be convenient to point out here that the results obtained show that whilst the surface of the particles of the platinum–nitrogen sol contains some unoxidized platinum, the surface of the platinum–oxygen (or platinum–air) sol is wholly oxidized. If a stream of oxygen is passed into the former sol, sometime after preparation, its behavior is now comparable *in every detail*, with that of the platinum–oxygen sol. From these results one can assign the part played by the dissolved oxygen in the preparation of the latter sols.

The Free Electrolyte Produced by Arcing.—On dispersing from 100 to 150 mg. of platinum in a liter of water, the specific conductivity is of the order 6 to 8 $\times$ 10^{-6}, and this may be increased to 30 $\times$ 10^{-6} (or more) by boiling. From the weight of platinum present, and from the approximate radius of the particles (30 $\times$ 10^{-7} cm.), one may calculate that the molality of the dispersed platinum is of the order 10^{-10} M, and the specific conductivity due to the particles of the order 5 $\times$ 10^{-12}. This is, of course, immeasurably small. Now the total negative charge on the platinum is equal to the positive charge on the contra ions ("gegenionen"), and these as will be shown are hydrogen ions. In order that the conductivity of these ions should approach the average error shown in conductivity measurements (0.3 $\times$ 10^{-6}, corresponding to 0.000001 equivalent of hydrogen ion), it can be shown that each platinum particle must give rise to at least 10,000 "free" hydrogen ions. (By "free ions" are understood those which contribute the whole of their conductivity to the solution.) The evidence available leads us to believe that in no case does the number of *free* contra ions ever approach this value, and hence the conductivity of both the platinum particles and their hydrogen contra ions may be neglected. This conclusion is confirmed by the following experiment. When an acid such as hydrochloric or nitric is added to a pure platinum

[3] Wöhler, *Z. anorg. Chem.*, **29**, 1 (1901); **40**, 423 (1904).

[4] The oxygen due to the electrolytic decomposition of the water cannot, of course, be excluded.

sol and to a strictly comparable sample of the intermicellar fluid, the conductivity–concentration curves exactly coincide, even when carried right past the coagulation point. Hence the removal of the platinum with its hydrogen ion partners causes no alteration in the conductivity. The whole of the measurable conductivity of a platinum sol may, therefore, be attributed to the free electrolyte produced during the arcing process. The intermicellar fluid (referred to above) can be isolated so as to retain this electrolyte by freezing and then thawing the sol. This treatment completely coagulates the platinum and leaves the clear intermicellar fluid.

Although the amount of dissolved electrolyte is too small for exact quantitative identification, titration with bases shows that it is a strong acid. From a knowledge of the oxidation products of platinum, the author concludes that this free strong acid is hexahydroxyplatinic acid ($H_2Pt(OH)_6$), or one of its dehydration products, e. g., $H_2PtO(OH)_4$. The amount present is always small, and an average sol of specific conductivity 15×10^{-6} contains 0.00004 equivalent. It will be shown later that many acids, including the common inorganic acids, coagulate at a constant hydrogen-ion concentration, namely 0.0002 N. It therefore appears that this would also serve as an approximate limiting maximum for the concentration of the hexahydroxy acid, in the preparation of stable sols.

If platinum sols are filtered in order to remove the larger particles or the products of coagulation, the free acidity may become completely destroyed by the filter paper. The work of Kolthoff,[5] Rona and Michaelis,[6] and Mokruschin and Kryloff[7] on the action of filter paper on acids, shows either that the acid is "adsorbed," or that there is an interchange of cations. To retain an acidoid sol in the absolutely pure state, filtering must be avoided, and any flocculated products removed by centrifuging or simply allowing the sol to stand for some time.

Hexahydroxyplatinic Acid as the Stabilizing Ionogen at the Colloid Surface.—In the theory of colloid structure as developed by Duclaux,[8] Gouy,[9] Debye and Hückel,[10] McBain,[11] Bjerrum,[12] Pauli and Engel,[13] Pauli and Schmidt,[14] and others, the colloid particles are regarded as huge multivalent ions which owe their charges to the ionization of surface ion-

[5] Kolthoff, *Pharm. Weekblad.*, **57**, 1571 (1920).

[6] Rona and Michaelis, *Biochem. Z.*, **103**, 19 (1920).

[7] Mokruschin and Kryloff, *Kolloid-Z.*, **37**, 145 (1925); **43**, 387 (1927).

[8] Duclaux, *J. chim. phys.*, **5**, 29 (1907).

[9] Gouy, *J. phys.*, [4] **9**, 457 (1910).

[10] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[11] McBain, *J. Phys. Chem.*, **28**, 706 (1924).

[12] Bjerrum, *Z. physik. Chem.*, **110**, 656 (1924).

[13] Pauli and Engel, *ibid.*, **126**, 247 (1927).

[14] Pauli and Schmidt, *ibid.*, **129**, 199 (1927).

ogens. In many cases the surface ionogen has been identified.[15] With colloidal platinum, the following considerations leave no doubt that the active ionogen is the strong platinic acid, which has already been identified as $H_2Pt(OH)_6$[16] or one of its near relations.

(a) First there is the general evidence that colloidal platinum prepared in conductivity water forms a stable sol. The surface ionogen necessary for stability must therefore have been formed during the arcing process. This immediately suggests that the ionogen is identical with the free acid present in the sol, and that probably an equilibrium exists between the amount combined and the amount free.

(b) On aging or on boiling, the conductivity steadily increases. The statement[17] that "many metallic sols, e. g., colloidal platinum, coagulate quickly upon warming," is not correct. Pure platinum sols when prepared as above, can be boiled for hours. The increase in conductivity is due to the liberation (or formation) of more free electrolyte. On freezing out the platinum from the boiled sols, it can be shown, by titration with bases, that the whole of the electrolyte present (including that newly formed) is the strong platinic acid. As there is a possibility that boiling may favor the production of further acid by oxidation, the boiling has also been carried out in the absence of oxygen and in the presence of nitrogen. Similar increases in conductivity were always obtained; hence it may be concluded that the colloid particles contain some platinic acid, which is gradually liberated on boiling or on aging.

(c) On the addition of neutral salts it can be shown that the increase in acidity up to (and past) the coagulation point, is due to the ionic exchange of hydrogen contra ions for cations of the added salt. This result, together with the foregoing, offers conclusive evidence that the contra ions are hydrogen ions, the surface ionogen is an acid and the sol is an acidoid.

(d) In the presence of added acid, experiments show that the decrease in the cataphoretic velocity (or in the ζ-potential) is a linear function of the square root of the acid concentration. In terms of the Debye–Hückel theory as applied to colloids,[10] this result directly indicates that the added acid simply depresses the ionization of the surface acid until the critical potential is reached and coagulation ensues. This, in conjunction with the fact that acids coagulate at a fixed P_H, affords further direct evidence that the platinum sol is acidoid.

The Amount of Surface Acid.—It has proved extremely difficult to obtain an approximate idea of the fraction of surface covered by the acid. Quantitative examination of the platinum particles is of little use,

[15] See Pauli and Valkó, "Elektrochemie der Kolloide," Wien, 1929, p. 95.

[16] Pennycuick J. Chem. Soc., 2108 (1928).

[17] Freundlich, "Colloid and Capillary Chemistry," English Ed., 1926, p. 457.

for apart from the surface acid there appears to be a considerable amount of acid in the interior of the particle. Experiments with barium hydroxide indicate that a maximum of 25% of the surface is the hexahydroxy acid, but later work with other bases shows that this is far too high even as a guiding maximum. By calculating the amount of hydrogen ion displaced from the surface by barium ion in the presence of excess barium chloride, one obtains a maximum of 14% of surface acid. As in such cases hydrolytic cleavage is superimposed on the ionic replacement, the actual fraction is probably considerably less than this. Furthermore, the results indicate that in the pure sol an intimate relationship exists between the charge carried and the concentration of free hexahydroxy acid. A comparison of the free acid concentration and the ζ-potential, for a variety of pure sols, gave such irregular results as to suggest that the hexahydroxy acid is bound at the colloid surface only at active points, and that the latter vary with the age and the treatment of the sol. The percentage of surface acid, therefore, varies from sol to sol, and at present no reliable value can be given in any one case.

How is the Acid Held at the Surface?—There is nothing to be gained by laboring the different points of view as to whether the hexahydroxy acid is adsorbed or chemically combined at the surface. It must be pointed out, however, that explanations of surface action (adsorption) in terms of the single physical factor, surface energy, have proved notoriously infertile and incomplete. Ellis[18] and Powis[19] have demonstrated, in the case of oil emulsions, that the supposed intimate relation between adsorption, surface tension and electric charge, does not exist at all, whilst coagulation phenomena observed with oil drops, vanadium pentoxide and also with colloidal platinum, can be shown to have no connection with changes in interfacial tension. Furthermore, Laing, McBain and Harrison[20] have obtained results which appear to be quite contrary to the predictions of the Gibbs theorem.

The more useful interpretation that surface reactions take place through oriented and polar groups is to be preferred. Adsorption forces are then identified as those which produce chemical combination, any differences being only in degree. This is the point of view adopted by the writer, who considers that the anion of the hexahydroxy acid exists at the surface as part of the micelle structure, and the following evidence indicates that it is there combined with certain active molecules which are probably oxides. It has been pointed out that a platinum–nitrogen sol contains less surface oxide than a platinum–oxygen sol. The former is, moreover, less

[18] Ellis, *Z. physik. Chem.*, **80**, 597 (1912).

[19] Powis, *ibid.*, **89**, 186 (1915).

[20] "Colloid Symposium Monograph," Chemical Catalog Co., Inc., New York, **1928**, p. 631.

stable against boiling. If, however, it receives a stream of oxygen, its stability is now comparable with the platinum–oxygen sol. The stabilizing acid is therefore more strongly held, the more the surface is oxidized. Further, if hydrogen is passed into any sol, one would expect the surface oxides to be reduced, and in keeping, the sol immediately loses its acidoid properties; if oxygen is now re-introduced the acidoid properties are recovered. One therefore concludes that the hexahydroxy acid is only combined when there are surface oxides present.

The Nature of the Rest of the Surface.—As colloid reactions are fundamentally surface reactions, a knowledge of the nature of the surface is of primary importance. It has been shown that the hexahydroxyplatinic acid appears to be combined at the surface with oxides of platinum, and the evidence will now be briefly summarized which indicates that the rest of the surface is also some form of oxidized platinum.

Platinum sols can take up large amount of bivalent bases. Measurements show that these amounts are not only more than sufficient to neutralize the surface acid, but that they are approximately sufficient to cover the whole of the colloid surface with a unimolecular layer. If a stream of hydrogen is passed for a limited period into a pure sol, two results become evident, first, the acidoid properties immediately disappear, and, second, the sol cannot now take up any barium hydroxide at all. Under the action of the hydrogen the surface properties have thus become completely altered.[21] If a stream of oxygen be now passed, both the acidoid properties and the power of removing bases are restored, although both are somewhat weakened. The obvious explanation of these phenomena is that the particles of colloidal platinum, when in the presence of oxygen (or of air), are coated with some form of oxidized platinum which confers upon them their characteristic properties. The addition of hydrogen immediately reduces the surface oxides and hence destroys these properties. (The hydrogen also probably reduces some of the free hexahydroxy acid, but this action is relatively slow and is not allowed to become complete.) In keeping with the above it is found that a sol prepared and handled in the presence of nitrogen takes up less base than a normal sol, i. e., one prepared in the presence of air. If, however, a stream of oxygen is passed into the former sol its power of removing bases is considerably increased. It therefore appears that the surface of the platinum–nitrogen sol contains some unoxidized platinum, which is turned into the oxide simply by passing oxygen.

The question might be raised as to whether the oxygen held at the surface is merely physically adsorbed and not chemically combined. This is really of secondary importance, the major point being that it is the surface

[21] The sols containing hydrogen, although no longer acidoid, are quite stable in the absence of air. Such sols are at present under investigation.

oxygen which confers the normal properties on colloidal platinum. However, the indications are that definite compounds are formed. Freundlich[22] quotes general evidence that "oxygen appears to be bound by platinum in the true chemical sense," e. g., platinum containing oxygen dissolves in acid in proportion to its oxygen content; the temperature coefficient of the fixation is positive, and oxygen cannot be pumped off at ordinary temperatures. These observations were made with platinum metal, and as it is well known that substances in a finely divided state, particularly when newly formed, are more reactive than when in the coarse state, the same general conclusions doubtless hold for the colloidal metal. In fact the author has shown that colloidal platinum particles, in the presence of air, take up 20 to 30 times as much barium hydroxide as an equal area of platinum gauze or foil. As it has been shown that bases are only taken up by the surface in the presence of oxygen, we must conclude that the colloid surface is far more reactive toward oxygen than the metal surface. Again the fact that ordinary platinum sols, when placed in a reflux condenser and in a stream of nitrogen, can be boiled for hours, is further evidence that the surface oxygen is particularly strongly held.

Reactions at the Surface of Colloidal Platinum.—The simplest formula for a platinum sol would be of the nature

$$[x\mathrm{Pt} \cdot y\mathrm{PtO_2} \cdot z\mathrm{Pt(OH)_6}]^{2z-} \ldots \ldots 2z\mathrm{H}^+$$
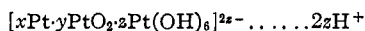
Here the Pt represents, very incompletely, the constitution of the interior of the particle, PtO_2 conveniently represents the surface oxide, and $H_2Pt(OH)_6$ the surface ionogen. From all points of view the formula is incomplete, but the representation of the surface is sufficiently accurate to serve as a basis for the discussion of surface reactions. In keeping with the Debye–Hückel theory of the colloid as a strong electrolyte,[10] the surface ionogen is shown as completely ionized. One might compare this formula, especially with regard to surface structure, with that proposed by Pauli[23] for silicic acid sols, namely

$$[x\mathrm{SiO_2} + n\mathrm{H_2O} \cdot y\mathrm{SiO_3H}]^{y-} + y\mathrm{H}^+$$
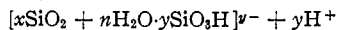
Reactions at the surface fall into three distinct classes, and these will be discussed separately.

First, there is the ionic replacement of the hydrogen contra ions by the cations of added electrolyte. Although the $H_2Pt(OH)_6$ in the above formula is represented as wholly ionized, the hydrogen ions form an ionic atmosphere around each particle, and only a small fraction can be regarded as actually "free." On the addition of any salt, e. g., barium chloride, some of the barium ions enter the ionic atmosphere, displacing the equivalent amount of "bound" hydrogen ion. This is the fundamental action leading up to coagulation and, in keeping, both the replacement and the coagula-

[22] Freundlich, Ref. 17, p. 153.

[23] See Pauli and Valkó, Ref. 15, p. 509.

tion depend upon the concentration, the valence and the specific properties of the cations concerned. This will be discussed in the section on "Coagulation;" it is sufficient to say here that in the case of colloidal platinum ionic replacement has been demonstrated with all types of salts.

Second, the surface oxide is an acidic oxide, and by combination with such added electrolytes as bases, etc., it may form either simple or complex salts. These act as fresh surface ionogens, and cause an increase in the charge, greater stability and so on. These conclusions are based on considerable experimental evidence; for example, it may be shown with sodium hydroxide that a definite amount of base is removed by the colloid, and at the same time cataphoretic velocity of the particle, and the ζ-potential, are increased by more than 100 per cent. The combination of the base at the surface has thus produced fresh surface ionogens, and these are interpreted in the nature of salts. All bases act in a similar manner. Further, it may be shown that some few electrolytes, e. g., HCN, $K_4Fe(CN)_6$ and $K_2Pt(CN)_6$ are also removed by the colloid and at the same time cause an increase in the ζ-potential of the colloid particles, and hence a production of fresh surface ionogens. This reaction is interpreted as due to the formation of complex salts between the surface oxide and the added electrolyte, e. g., $[PtO_2 \ldots CN]^- + H^+$, or $[PtO_2 \ldots (CN)_6Pt]^- + 2K^+$. In keeping with the acid nature of the surface oxide, it is always a complex anion (never cation) which is formed, and this being bound at the surface increases the negative charge of the colloid. This also serves to explain the combination of the hexahydroxy acid itself at the surface, for as has already been pointed out this acid is bound only so long as there are platinum oxidation products there.

Third, we have the possibility of hydrolytic cleavage. One of the striking features of colloidal platinum is its great affinity for bases. As this is due to the acid nature of the surface, it follows that on the addition of a salt the ordinary partition effects would hold and the surface would claim its share of the base. Salts of weak acids, such as potassium acetate, contain a certain amount of free base by hydrolysis, and the results show that the platinum surface takes its share of this. Recent work, which will be published in detail elsewhere, shows that even with neutral salts the platinum surface takes a small but important fraction of base from the salt, leaving free acid behind.

The whole of the work carried out with colloidal platinum has not revealed the necessity for any further classification of surface reactions. All the so-called "adsorption" phenomena come under one of the above three headings. It is advisable to make this quite clear. It is generally accepted that adsorption compounds are Werner compounds, or at all events that they are essentially chemical at basis. Moreover, in the case of electrolytes (and electrolytes only are considered in this paper) the

adsorption is polar. If the anion be oriented in toward the surface, the most probable and the most useful interpretation is the formation of a complex anion as described in the second case above. Now, the surface is essentially acidic, and whilst the formation of complex anions with the surface acid oxide (e. g., $[PtO_2 \ldots CN]^- + K^+$) is exceedingly probable, combination of the acidic oxide with cations (e. g., $[PtO_2 \ldots K]^+ + CN^-$) is exceedingly improbable. In keeping with this conclusion there is no experimental evidence that the distinctly acidoid sol, colloidal platinum, ever combines with a cation. Whenever cations are removed from solution and found at the surface, the action can always be traced either to ionic replacement or, to a lesser extent, to hydrolytic cleavage.

The reversal of sign experienced by colloidal platinum when ferric chloride or aluminum chloride is added, is generally interpreted as due to the adsorption of the cation at the surface. This explanation is not in keeping with the conclusions above, and in a paper which will appear shortly it will be shown that experiments with colloidal platinum demonstrate that the cation is not the reversing agent. Reversal is due to the reaction at the surface of the initial products of hydrolysis, probably the basic chloride, and the surface compound formed is of the nature

$$\left[PtO_2 \begin{matrix} \diagup OH \\ \diagdown OH \end{matrix} Fe \right]^{++} + 2Cl^-.$$ When excess of this is formed, the sol

changes sign and becomes positive.

Coagulation

(a) **Coagulation by Acids.**—With acids such as hydrochloric, nitric, sulfuric and acetic, the evidence shows that there are no surface reactions beyond the attenuation of the hydrogen ionic atmosphere, due to the increase in the hydrogen-ion concentration of the solution. This is based largely upon three facts, (a) none of the added acid is taken up by the colloid, (b) the decrease in the ζ-potential is proportional to the square root of the acid concentration, and (c) acids coagulate at a fixed P_H.[24] With acids which react at the surface, e. g., hydrocyanic, the production of fresh ionogens exercises a stabilizing action which is opposed to the depression of the ionization due to the increase in the hydrogen-ion concentration of the solution. Such acids show a maximum in the ζ-concentration curve, and coagulate at a higher acidity depending on the extent of the surface action.

(b) **Coagulation by Bases.**—With univalent bases, e. g., sodium hydroxide, the outstanding features are the rapid increase in the ζ-potential to a maximum, and the high coagulation concentration. These are obviously related and are due to the base reacting with the surface oxide to form fresh ionogens. The whole of the contra ions are univalent sodium

²⁴ See *J. Chem. Soc.*, 551 (1928).

ions, and the increased charge on the particles necessitates an abnormal increase in the sodium-ion concentration to produce coagulation (compare coagulation concentrations, NaOH $= 0.02\ N$, NaCl $= 0.003\ N$).

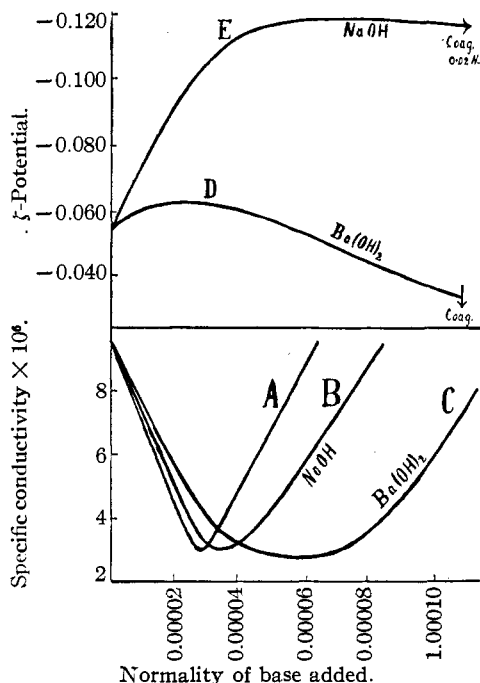Bivalent bases, e. g., barium hydroxide, show some characteristic differences   The amount of base removed is four to five times greater than in the case of univalent bases, the increase in the ζ-potential is very much less, whilst the coagulating concentration is very low. These differences are brought out in Fig. 1. It may be assumed that the barium hydroxide reacts at the surface in the same way as the sodium hydroxide, namely, to form surface salts of the nature [PtO$_2$...O|Ba, but the very small increase in the ζ-potential, and likewise the low coagulation concentration of the barium ion, show that the surface ionization is relatively small. The well-known fact that the concentration of the coagulating ion decreases very rapidly with valence is beyond doubt intimately connected with the interionic attractive forces between the colloid ion and the coagulating contra ions. When the valence of the latter is high, the ionic atmosphere is more confined or attenuated, the colloid charge is low and the sol is less stable. Accordingly small increases in the concentration of the free higher-valenced cations are sufficient to depress the ζ-potential to the critical value.

Fig. 1.—Curve A is the titration curve of the intermicellar fluid with NaOH and with Ba(OH)$_2$. Curve B is the titration curve of the platinum sol with NaOH.   Curve C is the titration curve of the platinum sol with Ba(OH)$_2$.   Curves D and E are the ζ-concentration curves for Ba(OH)$_2$ and NaOH, respectively (ζ-potential = cataphoretic velocity $\times$ 187.1).

(c)   Coagulation by Salts.—On the addition of a salt, the first step, and the one which ultimately leads to coagulation, is the ionic replacement of the hydrogen contra ions by the cation of the added salt. This has been well illustrated in the case of barium chloride, as the following experiment shows.   From a comparison of the curves obtained by following the conductivity changes on the addition of barium chloride to a platinum sol, and also to the intermicellar fluid, one may calculate the amount of hydro-

gen ion set free by exchange at any concentration of salt. With a sample of the same sol one may also follow the decrease in the ζ-potential for progressive additions of the same salt. By choosing convenient scales and plotting these changes on the one figure, it is found that the curves coincide (Fig. 2). Hence the changes due to ionic replacement agree step by step with those in the ζ-potential. It would thus appear that in such cases, the replacement of the hydrogen ion is the primary cause of the decrease in the ζ-potential and therefore in the stability of the colloid.
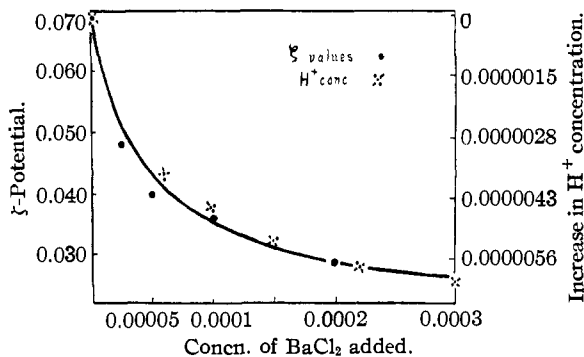

Fig. 2.

For many years it has been the practice to explain the coagulation of negative sols in terms of the "adsorption of the oppositely charged ion." It would now appear that for every oppositely charged ion "adsorbed," a surface contra ion is set free.[25] Hence the explanation in terms of the "adsorption of the oppositely charged ion"—an explanation which has been subject to rather loose usage—may be considered as having served its purpose. It should now be discarded and replaced by the more definite idea of ionic replacement.

Besides the usual replacement, some salts show appreciable formation of surface compounds or exhibit hydrolytic cleavage. The foregoing generalization may be extended to meet these cases. For example, with potassium cyanide, not only does the cyanide ion combine at the surface to form fresh ionogens but the potassium hydroxide of hydrolysis does likewise. Moreover, the extent of the combination increases with the concentration of potassium cyanide. Experiment shows that at low concentration this stabilizing action predominates and the charge increases, but at high concentration these are outweighed by the depression

[25] See also Linder and Picton, *J. Chem. Soc.*, **61**, 114 (1892); Whitney and Ober, *Z. physik. Chem.*, **39**, 630 (1902); Pauli and Matula, *Kolloid-Z.*, **21**, 49 (1917); Michaelis and Rona, *Biochem. Z.*, **97**, 57 (1919); Pauli and Schmidt, *Z. physik. Chem.*, **126**, 247 (1927); Rabinowitsch and Dorfmann, *ibid.*, **131**, 313 (1928); Ganguli, *Phil. Mag.*, [VII] **7**, 317 (1929).

of ionization due to the increase in concentration of the free potassium ions and this ultimately leads to coagulation.

The effect upon coagulation of changing the P_H of an acidoid sol may now be generalized. If the sol be made more acid the colloid charge is depressed, and salt coagulation occurs at a lower concentration, whilst if the sol be made basic, fresh ionogens are formed and more salt is required to bring the ζ-potential to the critical coagulation value.

Action of Hydrocyanic Acid on Platinum Sols.—Hydrocyanic acid has an extremely important poisoning action on colloidal platinum, and although the investigations in this direction are incomplete, the results so far obtained may be presented here.

Experiments have been carried out to determine the effect on the cataphoretic velocity of increasing additions of hydrocyanic acid. For the purpose the Landsteiner–Pauli apparatus was used, with the intermicellar fluid as the overlying liquid. From the cataphoretic velocity, the ζ-potential is calculated by the usual formula.[26] The results are set out in Table I and shown by Curve A in Fig. 3. In contradistinction to the normal depression shown by hydrochloric and nitric acids, we find with hydrocyanic acid that there is an initial increase in the velocity of the particles,

TABLE I

CHANGE IN THE ζ-POTENTIAL ON THE ADDITION OF HYDROCYANIC ACID ($\zeta = 6\pi\eta u/DH$).

TEMPERATURE, 18°

Concn. of HCN	$u \times 10^5$	ζ
....	−33.5	−0.063
0.000101	−40.0	− .075
.00024	−40.4	− .076
.00050	−33.8	− .063

and a maximum at a concentration of approximately 0.0002 N. From the course of the curve it may be concluded that at low concentrations of hydrocyanic acid, the production of fresh surface ionogens and the consequent increase in charge predominate, whilst at higher concentrations the effect due to the depression of the surface ionization is the greater. We thus not only have a direct indication of the removal of hydrocyanic acid by the colloid surface, but we also have the interesting fact that the "poisoned" particle carries a bigger charge than normal. Now in the catalysis of hydrogen peroxide it is well known[27] that sodium hydroxide greatly increases the catalytic velocity, whilst the author has shown (see Fig. 1) that the same base causes an abnormal increase in the colloid charge. Other results agree in pointing to a relationship between the velocity of decomposition and charge carried. The nature of the interrelation is unknown, but the fact that hydrocyanic acid increases the charge

[26] Debye and Hückel, *Physik. Z.*, **25**, 49 (1924).

[27] See discussion and references, Freundlich, Ref. 17, p. 489.

and at the same time poisons the catalyst, appears to the author to afford direct confirmation of the view that the poisoning is due to the combination of the hydrocyanic acid with catalytically active centers at the colloid surface.

Previous work with colloidal platinum has failed to give any information as to the amount of hydrocyanic acid combined with the surface. As the conductivity method has been used successfully by the author to measure small amounts of surface change, e. g., ionic replacement, this sensitive method was applied to follow the changes in the platinum sol on the addition of hydrocyanic acid. For the purpose, samples of the very pure platinum sol and of the intermicellar fluid of exactly the same conductivity were placed in conductivity cells having suitable cell constants. Increasing amounts of hydrocyanic acid were added and the conductivity changes followed. The results are shown in Table II and by Curve B in Fig. 3. Bearing in mind that similar pairs of curves for hydro-

Fig. 3.—Curve A shows the change in cataphoretic velocity with concentration (ζ-potential = cataphoretic velocity × 187.1). Curve B shows the change in conductivity with concentration both for the platinum sol and for the intermicellar fluid.

chloric and nitric acids showed exact correspondence, it was expected that the platinum sol curve, owing to the removal of hydrocyanic acid would
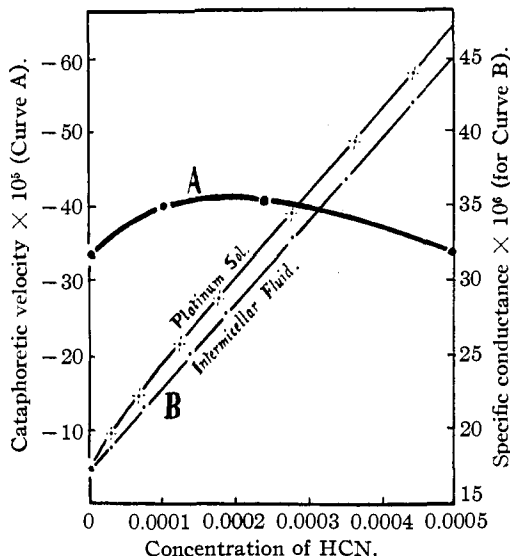
TABLE II

CHANGE IN THE SPECIFIC CONDUCTIVITY ON THE ADDITION OF HYDROCYANIC ACID. TEMPERATURE, 18°

Platinum sol		Intermicellar fluid	
Concn. of HCN	k	Concn. of HCN	k
....	17.36	....	17.18
0.000028	19.72	0.000028	18.92
.000069	22.42	.000073	21.52
.000125	25.83	.000137	25.13
.000177	28.98	.000188	27.94
.000277	34.62	.000278	32.93
.000366	39.49	.000353	36.88
.000448	43.89	.000449	42.01

lie below that of the intermicellar fluid. The opposite was found to be the case, for the platinum sol curve always lay above that of the comparable solution. Hence at all concentrations the decrease in conductivity due to the removal of hydrocyanic acid is completely overshadowed by some action which increases the conductivity. Two explanations of the latter action suggest themselves.

First, although hydrocyanic acid is a weak electrolyte, its combination at the surface may, and probably does, result in the formation of complex ionogens which are strong and highly ionized.[28] The increase in conductivity could then be attributed to the ionization of these fresh surface ionogens. Now it has been shown that pure platinum sols, with a cataphoretic velocity of 33.8 × 10^{-5} cm. sec. volt cm., do not contribute any measurable fraction of the conductivity; it may safely be concluded that when the velocity is increased to 41 × 10^{-5} units, the conductivity due to the particles (and their contra ions) would still be of a negligible order of magnitude.

The second explanation, which is probably correct, is that when the hydrocyanic acid combines with the surface, some (or even the whole) of the surface hexahydroxyplatinic acid is displaced. Such replacement is not unusual[29] and is due to a difference in affinity of the surface for the substances concerned. The removal of the weakly ionized hydrocyanic acid from solution, and its replacement by the strong acid $H_2Pt(OH)_6$, serves to explain the increase in conductivity found. If we assume that the whole of the increase, namely, 2 gemmhos[30] at high concentration, is due solely to this effect, then calculation shows that for one liter of sol, 0.000007 equivalent of $H_2Pt(OH)_6$ is replaced. This approaches the total amount of the hexahydroxy acid held at the surface as given by the barium chloride figures, namely, 0.000011 equivalent. Making allowance for hydrolytic cleavage in the latter case, it would appear that at higher concentrations the hydrocyanic acid replaces the greater part (and maybe all) of the bound platinic acid. Such effects in the presence of other surface active substances, particularly sodium hydroxide, must not be overlooked.

Until further experimental evidence is at hand, it is not considered advisable to present any conclusions which may be drawn connecting these surface actions with the catalytic phenomena.

[28] Compare the results obtained with hydrogen sulfide by Rabinowitsch and Kargin, *Z. physik. Chem.*, **143**, 21 (1929).

[29] See, for example, Warburg, *Z. Physiol.*, **76**, 331 (1911).

[30] A gemmho is a reciprocal megohm.

Summary

The general behavior of colloidal platinum as a typical acidoid sol is discussed from the point of view of more recent work.

Experiments are quoted which show that the whole of the colloid surface appears to be coated with a layer of oxidized platinum. On passing hydrogen the oxide layer is reduced and the acidoid properties disappear. On repassing oxygen or air the acidoid properties are recovered.

The $H_2Pt(OH)_6$ combines with part of the surface oxide to form Werner compounds, which act as the stabilizing surface ionogens.

The rest of the oxidized surface remains uncombined, but exhibits the properties of an acid oxide.

All the reactions of colloidal platinum are intimately connected with the acidic nature of the surface. They may be divided into three classes: ionic replacement, complex or salt formation and hydrolytic cleavage.

The general action of acids, bases and salts is interpreted in terms of these three reactions.

It is shown that hydrocyanic acid increases the charge carried by the colloid particle, and at the same time appears to displace the surface hexahydroxyplatinic acid.

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THE DENSITY OF WATER ADSORBED ON SILICA GEL[1]

BY DWIGHT T. EWING AND CHARLES H. SPURWAY

It is well known that water adsorbed on a surface of a solid has undergone a thermodynamic change in state and that it is held to the surface by a force of great magnitude which may be expressed in terms of pressure, compressibility, etc. Among the early investigators to advance this idea were Rose,[2] Jungh[3] and Parks.[4] That silica gel holds adsorbed water as if under a high pressure is also more recently confirmed by data on the heat of adsorption of water by Lamb and Coolidge,[5] and Patrick and Grimm.[6] The object of this investigation was to measure by a direct method the volume of water adsorbed on silica gel and to determine its density when present in small amounts.

[1] This paper represents the thesis submitted by Charles H. Spurway to the Graduate School of the Michigan State College, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] Rose, *Ann. Phys.*, **73**, 1 (1849).

[3] Jungh, *Ann. Phys. Chem.*, **125**, 292 (1865).

[4] Parks, *Phil. Mag.*, **4**, 220 (1902); **5**, 517 (1903).

[5] Lamb and Coolidge, THIS JOURNAL, **42**, 1146 (1920).

[6] Patrick and Grimm, *ibid.*, **43**, 2144 (1921).