CCCXLV.—*The Constitution of Colloidal Platinum.*

By STUART W. PENNYCUICK.

THE source of the charge on colloidal metal particles, as prepared by the Bredig sparking method, has been a debatable question for many years. The older ideas, that the electrical method was one purely of dispersion and that the charge was frictional, have been shown to be insufficient and incorrect. At present two opposing views stand out. Both agree that the charge is ionic, and also that the method of preparation consists essentially in a mechanical dispersion to a vapour of perhaps atomic dimensions, with a subsequent condensation to form the colloid particles. They differ, however, as to the source of charge. One holds that the charge is due to the combination of the condensed particles with certain foreign ions present in the medium. The other claims that the mechanical dispersion is always accompanied by the oxidation of the metal, and that in the subsequent condensation the fine particles of metallic oxide combine or react with the water to form a complex kation (in the case of copper or silver), or a complex anion (in the case of gold) (see Wo. Pauli, *Trans. Faraday Soc.*, 1921, **16**, 14; Fuchs and Pauli, *Koll.-Chem. Beih.*, 1925, **21**, 195; Paine, *ibid.*, 1912, **4**, 24; Rebière, *Compt. rend.*, 1912, **154**, 1540; Beans and Eastlack, *J. Amer. Chem. Soc.*, 1915, **37**, 2667).

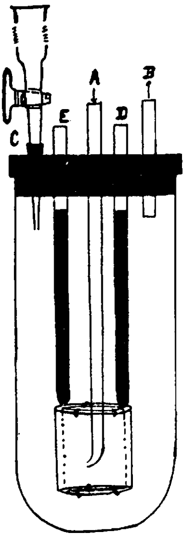
The former explanation is the one more generally accepted, but it is shown in this paper that in the case of colloidal platinum, at least, although it may be difficult to fix the structure of the complex platinum anion, nevertheless the latter explanation appears to be the correct one. It will be shown that colloidal platinum solutions can be prepared of such strengths that their high conductivities cannot possibly be due to the impurities present, and further that all such solutions are definitely acid.

The Preparation of the Platinum Sols.—It is well known that platinum sols can be prepared in the total absence of added stabilisers, and accordingly those used throughout this work were prepared by sparking pure platinum electrodes in conductivity water and in the absence of carbon dioxide. The conductivity-water still was after the design of Bourdillon (J., 1913, **103**, 791), and the water used had a specific conductivity of 0·2—0·4 gemmho at 18°. The sparking apparatus was the same as that described by Pennycuick (*Australian J. Exp. Biology*, 1927, **4**, 99). Briefly, it consisted of a short-necked 500 c.c. borosilicate flask, through the cork of which two platinum electrodes passed to a small ebonite frame above. One electrode was firmly fixed whilst the other had a small range of vertical freedom. This freedom was used to close the spark gap, and a spiral spring on the movable electrode threw the gap open to any prearranged extent. The cork also carried an inlet and an outlet tube, so that during the preparation carbon dioxide-free air could be slowly bubbled through the sol. These tubes also served for the introduction of the conductivity water and for the removal of the prepared sol. All the connexions through the cork were air-tight, and the method of preparation therefore precluded the accidental introduction of any impurities.

It was essential to make certain that the only foreign matter present was that which was initially in the conductivity water, and this was kept strictly in mind. The air used was in every case freed from carbon dioxide. The conductivity water under air pressure was siphoned into the sparking vessel until a sample from the latter showed a specific conductivity of less than 0·4 gemmho. About 450 c.c. of platinum sol were prepared at each operation, and during the sparking the sample was kept very close to 0° by the use of a freezing mixture. A direct current of about 5—6 amps. was used at 220 volts, and the time of sparking (excluding stoppages) was approximately 18—20 minutes per 450 c.c. of water.

The Conductivity Cell.—The conductivity cell was very similar in design to that used by Beans and Eastlack (*loc. cit.*). It was of borosilicate glass and had a total capacity of 120 c.c. The cell constant was 0·0107. The cell mouth was fairly wide (38 mm. diameter) and ground, and was closed with an ebonite stopper surrounded with an air-tight rubber band. The stopper carried 5 tubes (see Fig. 1)—the two electrode tubes D and E, an inlet and an outlet tube for air-stirring, A and B, and a spare tube for the introduction of any solution. All tubes were firmly fixed, and when in use the cell was air-tight. (I am indebted to Mr. J. S. Walker, B.Sc., for this cell, which proved very satisfactory.) All conductivities were measured in an electrically controlled thermostat at 25°.

FIG. 1.



The Specific Conductivity of the Platinum Sols.—Particular care was taken to keep the platinum sols pure. After preparation they were siphoned under air pressure, into thoroughly cleaned borosilicate flasks, always in the absence of carbon dioxide. They were kept for several days in order to allow the layer particles to precipitate, and the overlying sol was then siphoned into stock flasks and kept at the required temperature until wanted, the necessary quantity then being siphoned into the conductivity cell. The many samples examined are believed to be quite free from contaminations, including atmospheric carbon dioxide.

The first interesting point noticed was that the sols which had been prepared and stored at 0°, when put in the bath and allowed to come to 25°, showed a steady increase in conductivity over several days. Examples of such changes (at 25° and at 30°) are set out in Table I A.

TABLE I A.

Time interval (hrs.)	0	½	2	4	8	16	24	36	∞
κ (gemmhos) (at 25°)	5·65	6·10	6·58	7·05	7·97	9·23	9·91	10·42	14·3
κ (gemmhos) (at 30°)	5·68	6·96	8·20	9·02	10·00	11·17	11·69	12·01	14·6

An attempt was made to determine whether these changes followed any known velocity law, and, if possible, to obtain the temperature coefficient of the action; but although all solutions showed the same general changes, different samples of the same solution gave curves which did not correspond. (This is yet another example of the difficulty of reproducing exactly the same conditions in two samples of a colloidal solution.) All that could be concluded was that the change was always very rapid initially and then progressively slowed down.

The figures in Table I A, and in fact all similar figures, indicated that the specific conductivities of the platinum sols were approaching some limiting equilibrium value. Accordingly the solutions were boiled for 3 minutes and the conductivities redetermined, and it was thus found that equilibria were practically reached at 14·3 and 14·6 gemmhos in the above cases. It was observed that these values with the boiled solutions were not set up at once, but that the conductivities again changed with time. With these sols, however, the conductivities decreased, but the change was far less than before. Further investigation of the boiled and stable sols then revealed that, after any temperature changes, there was a lag in the equilibrium as indicated by conductivity measurements; a hot sample cooled to 25° always showed a steady fall in conductivity, whilst a cold sample warmed to 25° showed a corresponding rise, such changes being measurable over several days. These conclusions have an important bearing on the later work in this paper. The abnormally large lag shown by the unboiled solutions which had been made and kept at 0° (see Table I A) seems to indicate that these solutions have never reached their equilibrium; and this is supported by the fact that the unboiled platinum sols kept and *measured* at 0°, did not reach a maximum conductivity value even after 2 months.

Beans and Eastlack (*loc. cit.*), starting with conductivity water of 0·8 gemmho, prepared platinum sols of $\kappa = 3{\cdot}5$—$4{\cdot}3$ gemmhos. Further, they showed that the specific conductivity due to the charged platinum particles, calculated from their number, their charge, and their mobility, was of the order 0·0001 gemmho, and therefore negligible. They concluded that the "mechanical dispersion of the metal was followed by the formation of a colloidal complex between the dispersed metal and certain ions present in the medium." The present work goes considerably further, for, by starting with conductivity water of a maximum conductivity of 0·4 gemmho, and taking special precautions to exclude contaminations, platinum sols were readily prepared with specific conductivities which rose to 14·6 gemmhos. Further, as there was no reason to believe that this was a limiting value, stronger sols were prepared by prolonged sparking which gave specific conductivities (after boiling) as high as 16·8 gemmhos. Higher values could probably have been obtained but prolonged sparking caused abnormal platinum wastage. Higher values were actually obtained by the prolonged boiling of a platinum sol, and also of course by evaporation; *e.g.*, an unboiled sample of $\kappa = 6{\cdot}21$ was boiled in a Pyrex flask in contact with carbon dioxide-free air; after 5 minutes' boiling it rose to 12·76 and after 25 minutes to 21·46 (all readings being taken at 25°). Conductivity water, when treated in the same flask in the same way, showed a change of κ from 0·4 to 0·89 gemmho. Similar platinum sols, when boiled in a large platinum dish for 2 minutes and for 15 minutes, showed $\kappa = 15{\cdot}35$ and 41·2, respectively; evaporation probably accounted for the latter high value. The highest conductivity obtained for a platinum sol by boiling in a platinum dish was 66·1 gemmhos. It was found that these high values very slowly decreased when the sol was kept at 25° for several days, but the fact that such values are actually obtained is very interesting. It is quite impossible, in view of the experimental precautions, to imagine that these conductivities can be due to the impurities present. The alternative, and the only reasonable explanation, seems to be that an electrolyte is formed during the sparking process.

Now it is well known that colloidal platinum particles carry a negative charge; and as a working hypothesis, the author suggests, in conformity with the theory of Pauli (see Pauli and Perlak, *loc. cit.*), that during the disintegration process some of the platinum is oxidised, and that during the subsequent condensation some platinum particles and some oxidised platinum particles coalesce; the oxidised platinum, however, in contact with water acts as an electrolyte (probably H_4PtO_4), with the result that the growing platinum particles form a complex anion, or ionic micelle of structure $[Pt_x(PtO_4)_y]^n$, which is in equilibrium with an equivalent amount of hydrogen ions. The high conductivities obtainable indicate that at least a small proportion of the hydrogen ions are "free," *i.e.*, that some of the complex is wholly ionised; whilst the lag in the equilibrium which is always shown when the sol suffers a temperature change, indicates that some of the hydrogen ions are held at the surface or in a surface double layer, and that rearrangements are slow and probably complex. These slow rearrangements are probably related to the slow equilibria changes in colloid systems observed by Du Noüy (" Surface Equilibria of Organic and Biological Colloids," 1926, p. 155).

It now remains to be shown that the complex anions and the corresponding hydrogen ions are actually present. With regard to the former, all that can be said at present is that it has been abundantly proved that the platinum particles in the absence of foreign electrolytes are negatively charged, but the exact constitution of the micelle is so far unknown. With regard to the hydrogen ions, however, definite evidence will now be produced which clearly indicates the existence in the pure platinum sol of " free " hydrogen ions and also of slowly removable hydrogen ions, the latter being probably on the micelle surface or in the double layer.

The Titration of Platinum Sols.—Having obtained platinum sols of remarkably high specific conductivities, and believing that the charged platinum anions contributed only a negligible fraction thereof, it was considered that any real existence of hydrogen ions would be revealed by the titration of the sol with a base. For this purpose, the cell already described was utilised; 60 c.c. of the platinum sol were carefully introduced into the cell, and put into the bath at 25° until equilibrium was attained, or until the conductivity showed a negligibly small change over a period of 1 hour. A 3 c.c. burette, containing the titrating base and with a soda–lime tube on the upper end, was introduced into the opening C. A piece of rubber tubing on the lower end of the burette ensured an air-tight connexion; air was bubbled through a wash-bottle in the bath, containing a corresponding sample of the sol, and then through A into the cell for the purpose of efficient stirring and mixing. The exit tube B was connected to a water trap. Titrations were carried out initially with sodium or potassium hydroxide. These bases were prepared with conductivity water, diluted to exactly $0{\cdot}001N$, and stored in waxed bottles. They were introduced into the pipette without coming in contact with the air.

Now, if practically the whole of the conductivity of the platinum sol be due to the hydrogen ions, then from the known mobility of the hydrogen ion at 25° one may calculate at once its concentration. Writing the equivalent conductivity as equal to the sum of the ionic conductivities, we have

$$\Lambda_v = \Lambda_{\mathrm{H}^+} + \Lambda_{\mathrm{Pt\ complex}^-};$$

and neglecting the last term,

$$\Lambda_v = \Lambda_{\mathrm{H}^+} = 349{\cdot}5,$$

whence $\kappa v = 349{\cdot}5$, where κ is the specific conductivity, and v is the volume in c.c. containing 1 g.-equiv. of hydrogen ions. We have then $v = 349{\cdot}5/\kappa$, and therefore $1000/v$, or the normality in the usual units, is given by $\kappa/0{\cdot}3495 = \kappa$ in gemmhos/349,500. (The ionic mobilities in this paper are calculated from those at 18°

by the use of the corresponding temperature coefficients; see H. S. Taylor, " A Treatise on Physical Chemistry," 1924, p. 540.)

Every platinum sol titrated showed with all bases used a minimum in the titration curve, indicating very clearly the presence of an acid or of titratable hydrogen ions—acids and salts showed no such minima. Further, with sodium and potassium hydroxides, all the platinum sols of various strengths showed a very good agreement between the hydrogen-ion concentration as calculated above from direct conductivity and that obtained from the minimum on the titration curve. Several normal cases are set out in Table I B. The differences in the minima shown by the two hydroxides are negligible.

TABLE I B.

	1.	2.	3.	4.	5.	6.	7.
κ (gemmhos)	6·57	7·00	12·76	15·03	15·35	21·46	41·2
(A) Normality of H^+ (calculated from κ) × 10^6 ...	19	20	36	43	44	61	120
(B) Normality of H^+ (by titration) × 10^6.	17	16	37	44	45	65	140

The normality marked (A) is calculated from κ (gemmhos)/349,500; that marked (B) is the normality of the solution with regard to total alkali hydroxide at the minimum on the titration curve. The figures in cols. 1 and 2 are for two unboiled samples. As such samples are not in equilibrium they were titrated fairly rapidly and the titration minima are approximate only. The figures in cols. 3, 4, and 5 are for samples which were brought to equilibrium by boiling for 2—5 minutes. Cols. 6 and 7 relate to samples boiled in Pyrex for 25 minutes, and in an open platinum dish for 15 minutes, respectively. They titrate fairly well.

From the agreement between the figures in Table I B, three conclusions may be drawn : (*a*) Colloidal platinum sols are definitely acid; (*b*) practically the whole of their conductivities can be attributed to the hydrogen ions present (the complex anion having negligible mobility); and (*c*) platinum sols behave as strong acids, for only strong acids show the correct conductivity minima when titrated with alkali hydroxides (see Eastman, *J. Amer. Chem. Soc.*, 1925, **47**, 332). A more detailed consideration, however, indicates that whilst the first of these conclusions is undoubtedly correct, the second and third cannot both be true. Table II shows the figures obtained on titrating platinum sols with each alkali, and also those obtained by titrating hydrochloric acid with potassium hydroxide. The latter figures allow a comparison to be made between the platinum sol and a strong acid, and they serve also to show that certain irregularities in the platinum sol titration curves are not inherently due to the abnormally small concentrations with which we are here dealing (*q. v.*).

TABLE II.

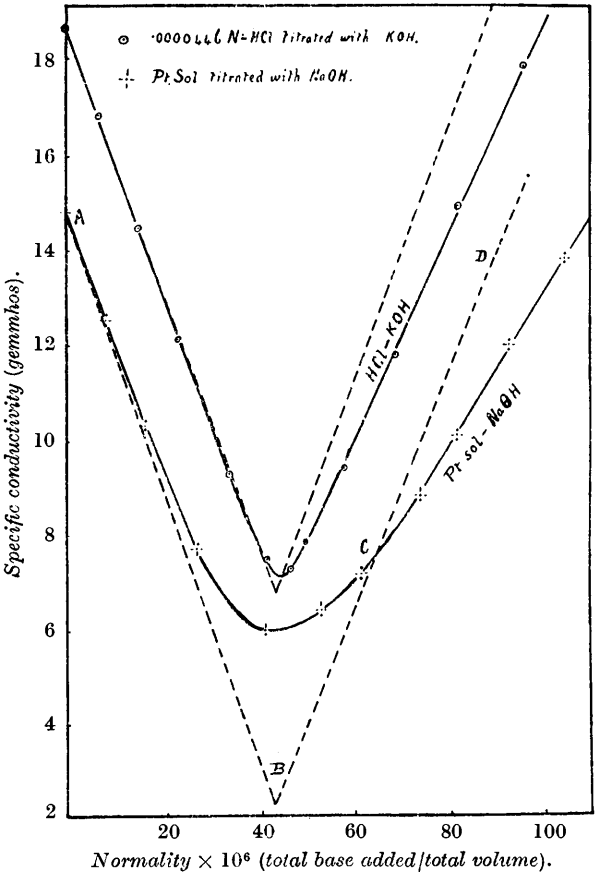
Titration of platinum sols.				Titration of 0·04446*N*-HCl.	
With KOH.		With NaOH.		With KOH.	
Normality $\times 10^7$.	κ.	Normality $\times 10^7$.	κ.	Normality $\times 10^7$.	κ.
—	15·14	—	15·03	—	18·65
123	12·05	79	12·55	62	16·90
228	9·62	164	10·38	151	14·44
307	8·10	276	7·73	236	12·12
400	7·14	415	6·04	340	9·34
476	7·18	536	6·46	420	7·54
566	7·80	625	7·24	463	7·35
669	8·67	741	8·84	504	7·88
783	10·17	826	10·14	583	9·43
895	12·05	937	12·03	828	14·92
1004	13·82	1045	13·80	963	17·86

The normality refers to that of the solution in respect to total sodium or potassium ions present, and is the quotient Total base added/Total volume of solution.

The corresponding curves are shown in Fig. 2. The KOH–Pt sol curve is omitted, because it is of exactly the same form as the NaOH–Pt sol curve; in fact, the differences between the two curves agree remarkably well with the calculated differences between the mobilities of the potassium and sodium ions. This is also the case with the corresponding hydrochloric acid–strong base curves. Accordingly only the two curves shown in Fig. 2 need be discussed.

The initial specific conductivity of the platinum sol was 15·03 gemmhos, which, on the assumption that the hydrogen ion is practically the sole contributor to the conductivity, represents a hydrogen-ion concentration of 43×10^{-6}. The minimum on the curve appears to lie between 42×10^{-6} and 44×10^{-6}. At this minimum, the corresponding specific conductivity of the solution is 6 gemmhos; but if the platinum sol is behaving as a strong acid, then the minimum point on the curve will indicate that the whole of the hydrogen ions have been replaced by sodium ions, and the specific conductivity of 43×10^{-6} equivs. of sodium ion is only 2·27 gemmhos. The broken-line curve, ABCD on the figure, is that calculated from the mobilities of hydrogen, sodium, and hydroxyl ions on the foregoing assumptions. Although the curves are similar in shape and situation, the divergence is pronounced. In order to see whether titrations at such low concentrations were trustworthy, hydrochloric acid of approximately the same normality (*viz.*, $44·6 \times 10^{-6}$) was titrated with various bases, and the HCl–NaOH curve also appears in Fig. 2. Other and weaker hydrochloric acid solutions were similarly titrated, and in every case the theoretical and experimental end points showed remarkably good agreement. In the curve illustrated, the end point corresponds to a concentration 45×10^{-6}, and the broken-line curve is the corresponding theoretical curve calculated from mobilities. The close approximation of the turning points in these two curves (Found : $\kappa = 7{\cdot}18$. Calc. : $\kappa = 6{\cdot}81$) shows that such titrations are quite trustworthy; and the divergence of the two curves after the turning point is doubtless due to the mutual repression of ionisation of the sodium chloride and hydroxide present.

Fig. 2.



Returning then to the platinum sol titration curve, the difference between the specific conductivities at the experimental minimum (6 gemmhos) and at the theoretical minimum (2·27 gemmhos) needs explanation. It appears either that some of the conductivity of the sol is contributed by other than the hydrogen ions, or that the colloidal platinum does not function as a strong acid. If either of these suggestions be true, then the agreement between the concentrations set out in Table I B would appear to be largely fortuitous This may actually be the case, for although a wide range of platinum sols was taken, the titrating bases were chemically similar. Accordingly, the titrations were repeated with calcium and barium hydroxides, both prepared with the usual precautions and diluted with conductivity water to 0·001N. The two curves differed only slightly, and the difference could be directly ascribed to the difference in the mobilities of the barium and the calcium ions. Accordingly, Table III and Fig. 3 contain the details for only one of these bases. As a titration curve for a weak acid is also necessary for comparison, Table III and Fig. 3 contain the details of the titration of acetic acid of comparable conductivity (0·000141N) with sodium and calcium hydroxides.

FIG. 3.

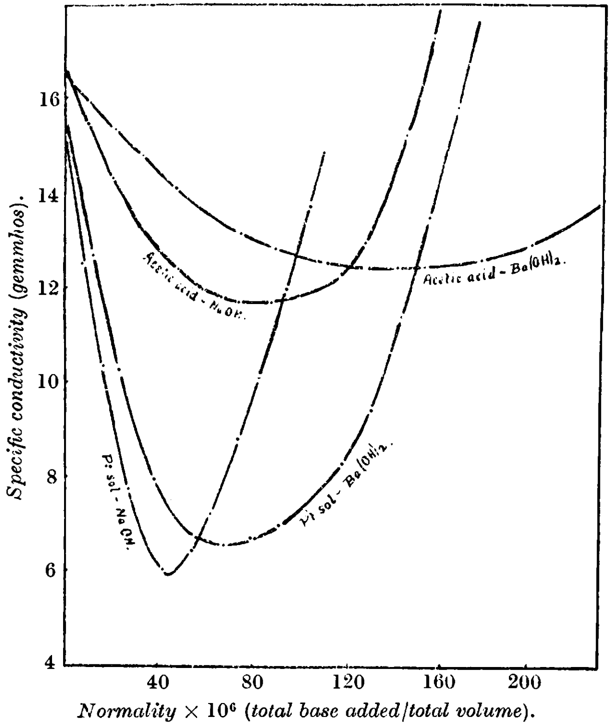


TABLE III.

Titration of Pt sol with $Ba(OH)_2$.		Titration of $0{\cdot}000141N$-acetic acid			
		with NaOH.		with $Ba(OH)_2$.	
Normality $\times 10^6$.	κ.	Normality $\times 10^6$.	κ.	Normality $\times 10^6$.	κ.
—	15·40	—	16·56	—	16·48
11·9	12·71	9·8	15·44	11·2	15·88
23·7	10·28	20·4	14·31	21·4	15·32
38·1	7·98	33·0	13·28	32·9	14·74
55·7	6·69	47·3	12·44	46·8	14·11
68·0	6·59	58·1	12·03	75·3	13·25
79·4	6·69	65·6	11·85	89·4	12·93
90·9	6·95	77·1	11·73	115·6	12·59
118	8·30	87·7	11·74	128·6	12·49
130	9·44	99·3	11·89	141·5	12·48
143	11·43	111·8	12·23	153·4	12·50
155	13·58	127·2	13·00	176·3	12·64
167	15·80	145·4	15·19	198·3	12·97
189	20·72	157·2	17·28	229·0	13·90
				242·9	14·50
				257·7	15·29

Now strong acids, such as hydrochloric acid, when titrated at this high dilution with sodium and barium hydroxides, show the same correct turning points and strictly comparable curves. The differences again are entirely due to the differences in the mobilities of the sodium and barium ions, and accordingly the HCl–$Ba(OH)_2$ figures are not quoted. On the other hand, weak acids such as acetic, when titrated with these two alkalis, show quite different curves, and give no indication of the *true* end point. It is of interest, however, that at these high dilutions these curves show remarkably good agreement with the theoretical titration results deduced by Eastman (*loc. cit.*). With the platinum sols, whilst the curves of sodium and potassium hydroxides are comparable, and those of barium and calcium hydroxides are also comparable, Table III and Fig. 3 show that the sodium and barium hydroxide curves differ radically, the minima appearing at $44 \times 10^{-6}N$ and $68 \times 10^{-6}N$, respectively. It is therefore evident that platinum sols are not strictly comparable with strong acids. On the other hand, they seem to be far stronger acids than acetic; in fact, their behaviour indicates that they approximate more closely to strong than to weak acids. The author believes that they are really unique, and that they cannot strictly be compared either with strong or with weak acids. This belief is based, not only upon the above facts, but also upon certain peculiarities which were noticed in every platinum sol titration: all conductivity readings showed a steady drift if followed over some considerable time; the drift was very slow and if time were allowed for each to come to equilibrium, every titration would have spread itself over many days. (An attempt is now being made to follow the complete equilibrium titrations.) Some preliminary investigations showed that these drifts were so slow that if the titrations were carried out fairly rapidly their effects could be neglected. Accordingly all titrations were performed within a total time limit of 80 minutes.

Discussion.

The explanation of the various phenomena outlined above appears to be as follows. The pure platinum sol contains a certain amount of relatively free or " diffused " hydrogen ions which contribute the greater part of the conductivity; further, each platinum anion has a surface layer (or double layer) of non-diffused hydrogen ions. Any temperature change causes a disturbance in the equilibrium between the diffused and the surface hydrogen ions, and all such rearrangements are not instantaneous but measurably slow. This explains the temperature lag invariably obtained with pure platinum sols (see p. 2602). Boiling not only disturbs the equilibrium, but as the conductivity never reverts to its previous value, it would appear that boiling breaks up the complex anion, or at least sets free from it further hydrogen ions, which were probably held in the interior.

On the addition of a small quantity of a base, *e.g.*, sodium hydroxide, we have a particularly favourable and simple colloid system to deal with, for the solution contains only sodium, hydrogen, and colloid complex ions, and no foreign anions at all. The added base immediately neutralises some of the free hydrogen ions, and as this disturbs the hydrogen-ion equilibrium, some of the surface ions diffuse into the solution. In other words, the platinum sol behaves as a weak acid, but with the difference that, whereas weak acid ionic equilibria are instantaneous, these are measurably slow. There is, however, a second and even more important difference. It is well known that coagulated colloids always carry down with them ions of the opposite charge (see, *e.g.*, Whitney and Ober, *J. Amer. Chem. Soc.*, 1901, **23**, 842; Gann, *Koll.-Chem. Beih.*, 1916, **8**, 127; Freundlich, *Z. physikal. Chem.*, 1910, **73**, 385).

It must be concluded, therefore, that in the case under discussion some of the sodium ions go to the surface, and that a definite sodium-ion equilibrium is reached. Platinum sols thus differ from weak acids in that their " salts " are not wholly ionised. The rate of this ionic rearrangement would probably differ for different kations, but in any case the results indicate that it is not instantaneous. If these equilibria were all infinitely slow, then the platinum sols would titrate as strong acids. The curves show that these rearrangements are actually taking place during the time limit of the experiment. All the readings before (and for a short distance after) the neutral point were drifting towards a greater conductivity, due to the greater mobility of the hydrogen ions leaving the surface compared with the sodium ions joining the surface. Towards the latter part of the titration the drift was in the opposite direction owing to the latter effect predominating, the sodium-ion concentration in the solution being now abnormally high.

The difference in the titration end points obtained with univalent and with bivalent bases is due, not only to the difference in the various equilibrium ratios (or equilibrium constants) for the different kations, but also to the different rates at which these equilibria are set up. The fact that the univalent bases give the same acid (titration) values as those obtained on the assumption that the hydrogen ion contributes practically the whole of the conductivity of the pure sol, may be due to a similarity in the univalent equilibrium ratios and equilibrium rates. On the other hand, it is not beyond question that the true acid concentration is really less than that obtained by these methods. An attempt has been made to settle this matter by a determination of the p_H of the pure sol with the quinhydrone electrode. Steady values are obtained and these are always lower than those read off from the titration curves, but it has not yet been determined whether quinhydrone acts normally in the presence of colloidal platinum. Work in this direction is proceeding. Colorimetric tests are out of the question; and the hydrogen electrode itself gives varying and untrustworthy values in these unbuffered solutions.

The slow equilibria between diffused or free ions and ions at the surface seem to be of fundamental importance in the coagulation of colloids. For instance, it is well known that if the bare minimum of electrolyte necessary to produce coagulation is added to a colloidal solution, the coagulation is invariably slow and may extend over several hours and even days. This is evidently due to the slowness of the equilibria under discussion. Further, according to Gann (*Koll.-Chem. Beih.*, 1916, **8**, 65), Steiner (*Z. physikal. Chem.*, 1910, **73**, 507), and Galecki (*Z. anorg. Chem.*, 1912, **74**, 174), the rate of these slow coagulations is best expressed by an empirical autocatalytic equation. No satisfactory explanation has so far been advanced for this, but the following qualitative suggestion may ultimately be of value. Before coagulation can occur a certain quantity of the coagulating ion has to move to the surface. This rearrangement being slow, a definite time interval will elapse over which practically no coagulation occurs. As the colloid particles vary in size, in shape, and in total charge, then, as the necessary equilibria are approached, the particles which are more favourably constituted will reach their coagulation condition first, followed more and more rapidly by the other colloid particles, the tota effect thus appearing to be autocatalytic.

Summary.

Colloidal platinum prepared in water of specific conductivity 0·4 gemmho, and rigorously kept free from contamination, can be made to yield a specific conductivity of 41·2 gemmhos at 25°.

It is suggested that oxidation accompanies the sparking process and that a colloidal complex acid is formed.

Pure platinum sols have been titrated with various bases, and the titration curves are discussed. Whilst the platinum sols titrate more like strong acids than weak acids, they cannot strictly be compared with either.

There appears to be a slow equilibrium between the diffused hydrogen ions and the hydrogen ions held at the surface of the complex platinum anion.

A similar equilibrium exists for any other added kation.

The consequences of the slow velocities of these equilibria are discussed.

THE UNIVERSITY OF ADELAIDE,
SOUTH AUSTRALIA.

[*Received, August 29th,* 1927.]