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Electrochemistry of Platinum Sols.

III. Positive platinum sols

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The existence of positive platinum sols, along with the negative hydrogen- and negative oxygen-platinum sols, was predicted by A. N. Frumkin[1] in connection with the results of studies on the properties of platinized platinum electrodes, which showed that the platinum surface successively passes through three different states on transition from cathodic to anodic polarisation. The method of obtaining the negative hydrogen-platinum sol and some of its properties have been described in parts I and II of this series of papers [2,3].

Oosterman[4] recently published an investigation on the streaming potential in platinum capillaries. His results confirm the existence of a positive electrokinetic potential on the surface of platinum, the sign depending upon whether the capillary is treated with hydrogen or oxygen.

The task of obtaining a positive platinum sol, which is an intermediate stage between the negative H_2-Pt-sol and the negative O_2-Pt-sol, involves great difficulties, since even on most careful oxidation of the H_2-Pt-sol, the surface of the particles is very easily covered with oxides and becomes negative again.

We succeeded, however, not only in preparing such positive sols, but even in measuring their cataphoretic velocity; a prelimi-

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[1] A. Frumkin, Trans. Farad. Soc., **31**, 69 (1935).

[2] N. Bach a. N. Balaschowa, Acta Physicochimica URSS, **3**, 79 (1935).

[3] N. Bach a. A. Rakov, Acta Physicochimica URSS, **7**, 85 (1937).

[4] J. Oosterman, Diss. Utrecht (1937).

nary communication describing these experiments was published in 1936[5].

The present article contains a more detailed description of all the experimental results relating to the preparation of positive platinum sols, determination of their cataphoretic velocity, investigation of their stability and also to the study of the course of oxidation of H_2-Pt-sols. Moreover, it gives the results of measurements of the cataphoretic velocity of negative H_2-Pt-sols at various concentrations of acid and alkali.

A considerable number of experiments were undertaken for the purpose of studying the oxidation conditions of the H_2-Pt-sol, in order to make it possible to stop the oxidation at a definite state of the positive surface. These attempts were not successful, for reasons which will be given below, and we were not able to prepare positive sols of a desired degree of oxidation, which would remain unchanged in the course of a long interval of time.

As has already been indicated in part I, we employed the adsorption capacity of the sol particles with respect to acids as a criterion of the state of their surface in view of the fact that the H_2-Pt-sol does not adsorb acids and that adsorption occurs as a result of oxidation, passing through a maximum and then decreasing again. Every point on the adsorption curve corresponds to a definite state of the surface. Thus the methods, with the aid of which all the investigations were carried out, consisted essentially in obtaining adsorption curves and determining the cataphoretic velocity.

Experimental

The sol was prepared by the method described in part I. For the determination of the cataphoretic velocity, we employed the apparatus represented in Fig. 1, which was analogous to the one used for the measurement of the cataphoretic velocity of activated charcoal[5]. The liquid which fills the lower part *B* of this apparatus, and the sol in the upper part *A* can be saturated with gas. The electrodes inserted in the reservoir *A* and sealed into the lower part of the U-tube *C* allow of controlling the electrical conductivity of the sol and of the liquid.

The apparatus I serving for the preparation of the sol is connected, by means of tubes with ground joints, to apparatus II devised for cata-

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[5] N. Bach a. N. Balaschowa, Nature, **137**, 617 (1936).

phoresis; the system of three-way stop-cocks allows of transferring the sol from apparatus I into part *A* of apparatus II, and then of conveying it through the capillary *D* into the U-tube *C* without allowing it to come into contact with the outer atmosphere. The sol, descending through the capillary, forces out of tube *C* the liquid through which the gas has been previously bubbled.

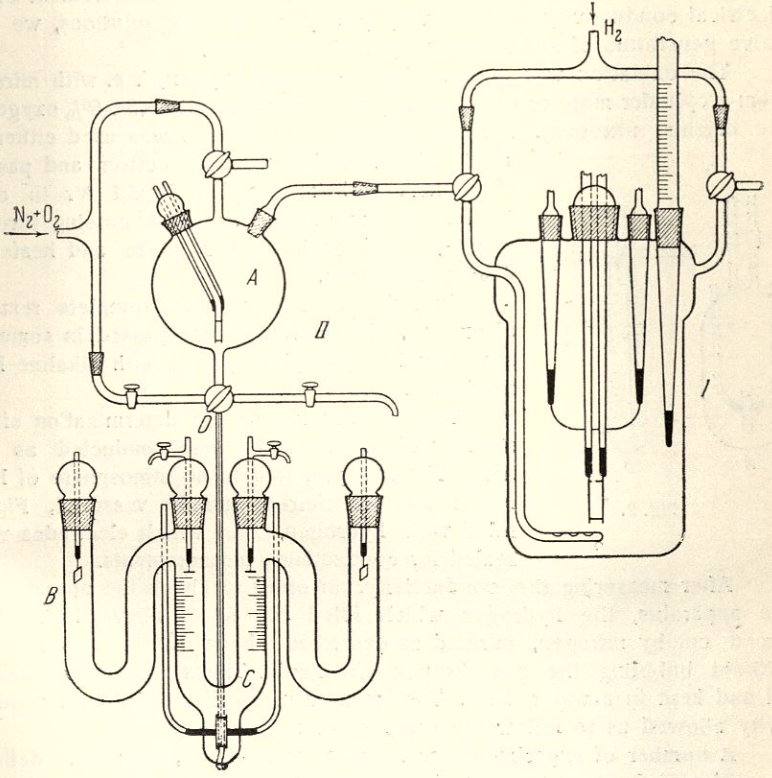

Fig. 1 .

500 cm³ of the sol were prepared in apparatus I and then transferred in portions of 25—50 cm³ to apparatus II. This made it possible to carry out a series of experiments with the same batch of sol. The sol was subjected to oxidation in part *A*. Part *B* of apparatus II was kept in a water bath with electric heater and thermoregulator. All the cataphoretic measurements were carried out at 25° ± 0,05°.

The measurement of the electrical conductivity of the sol at various moments during the passage of the gas allowed of plotting a curve characterising the surface. For the sake of simplicity, we ordinarily plotted, not the adsorption curve, but directly the curve giving the change in electrical conductivity, on which the minimum of electrical conductivity correspond to the maximum of adsorption. For the measurement of the electrical conductivity in these very poorly conducting solutions, we used valve generators of audio frequency with amplifiers.

The oxidation was performed with diluted oxygen, i. e. with nitrogen from a cylinder more or less carefully freed from oxygen (0,3-0,6% oxygen in the original nitrogen). For this purpose the nitrogen was used either directly after filtration through cotton and passing through a coil immersed in liquid air in order to remove impurities, or after passing through a tube, filled with copper gauze and heated to 400° in a furnace.

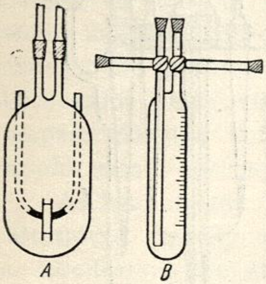

Fig. 2.

In order to obtain more complete removal of oxygen, the nitrogen was passed in some cases through a purifying system with alkaline hydrosulphite.

The experiments on the determination of the stability of positive sols were conducted as follows. The sol prepared in an atmosphere of hydrogen was transferred into the vessel *A*, Fig. 2, filled with hydrogen, into which electrodes were sealed for conductance measurements.

After measuring the conductivity, in order to check the operation of the apparatus, the hydrogen which filled the space above the sol was forced out by nitrogen, purified as described above over a copper gauze, without bubbling the gas through the liquid. The apparatus was sealed off and kept in a water bath. The measurement of the electrical conductivity allowed us to follow the progress of oxidation.

A number of experiments were also carried out, in which definite quantities of O_2 were introduced by adding various volumes of water saturated with oxygen.

The whole apparatus was made of Jena glass. Great difficulty is encountered in sealing platinum wires for all the types of electrodes into Jena glass in such a way as to obtain perfect tightness at the sealed spots. A check of the reliability of the latter is the constancy of the conductivity of the water in which they are immersed.

Preparation of positive Pt-sols

Our first problem was to show the reality of the existence of positive sols, no matter how long they could be kept after the sign of their charge and the approximate value of their cataphoretic velocity had been determined. The conditions for stopping the oxidation at a definite stage being in this case different from those under which we attempted to obtain stable positive sols, it is expedient to give a separate description of all the facts relating to the preparation of positive sols.

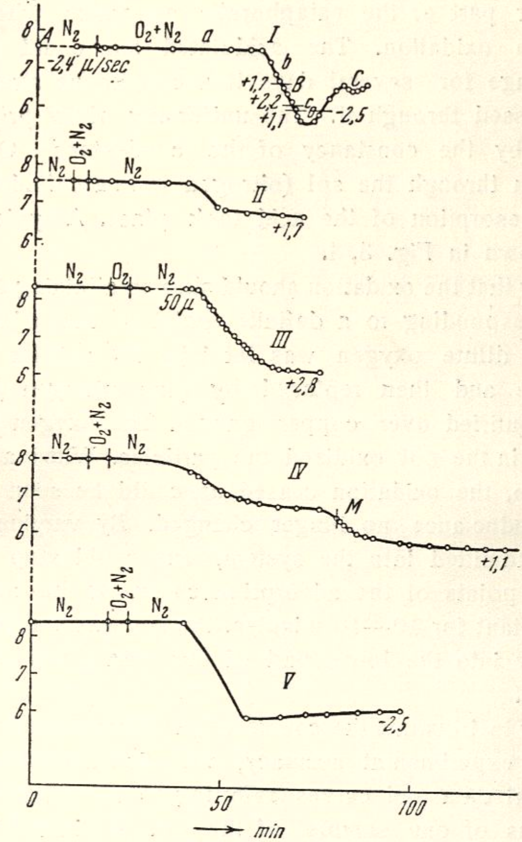

Fig. 3.

In the majority of cases the oxidation of H_2-Pt-sols occurred in presence of hydrochloric acid; a number of experiments were also carried out in sulphuric acid, and several experiments were conducted with pure sols without addition of any acid.

After the establishment of constant conductivity a definite quantity of $N/100$ HCl (usually $\backsim$ 1 cm.^{3}) was added to 500 cm.^{3} of the sol contained in the apparatus which served for its preparation. Portions of this acidulated sol were successively conveyed to the upper part of the cataphoretic apparatus where they were subjected to oxidation. The acidulated sol could be preserved without change for several days if a continuous stream of hydrogen was passed through it. The uniformity of its properties could be judged by the constancy of the conductance. On passing diluted oxygen through the sol (nitrogen from a cylinder) adsorption, and then desorption of the acid took place. A typical adsorption curve is shown in Fig. 3, I.

In order that the oxidation should stop on attaining the state of the surface corresponding to a definite point of the adsorption curve, a stream of dilute oxygen was let into the sol for a short interval of time and then replaced by pure nitrogen (nitrogen from a cylinder purified over copper gauze). The oxygen that remained undisplaced in the sol oxidized the particles. When all the oxygen was used up, the oxidation ceased as could be seen from the fact that the conductance no longer changed. By varying the quantity of oxygen admitted into the system, one could stop the oxidation at various points of the adsorption curve. If the conductivity remained constant for 10—15 minutes, the sol was transferred through the capillary into the lower part of the apparatus and subjected to cataphoresis.

In order to illustrate the course of the measurements and give an idea of the experimental accuracy, we give a detailed account of the numerical data and curves referring to the oxidation of individual portions of one sample of the sol. As in all investigations in the sphere of colloid chemistry, only the general character of the curve is reproducible, and not the exact quantitative data. The course of the variation in the conductivity of a portion of sol during its complete oxidation is given in Table 1.

The results of Table 1 are represented graphically by curve 1, Fig. 3. The abscissae correspond to the time of passage of gas from the beginning of the experiment in minutes, whilst the ordi-

Table 1

Specific conductivity of water $= 0{,}20 \cdot 10^{-6}\,\Omega^{-1}\,\text{cm.}^{-1}$.
Specific conductivity of H_2-Pt-sol $= 0{,}60 \cdot 10^{-6}\,\Omega^{-1}\,\text{cm.}^{-1}$.
Specific conductivity of H_2-Pt-sol $+ 1\,\text{cm.}^3\ N/100\,HCl = 7{,}51 \cdot 10^{-6}\,\Omega^{-1}\,\text{cm.}^{-1}$.

Time from the start of the experiment (min.)	Gas passed through the sol	$\varkappa \cdot 10^6$	Time from the start of the experiment (min.)	Gas passed through the sol	$\varkappa \cdot 10^6$
0	N_2	7,58	82	O_2 dilut.	5,78
28	O_2 dilut.	7,58	84	O_2	5,83
39	O_2	7,58	85	O_2	5,71
48	O_2	7,58	87	O_2	5,89
63	O_2	7,58	89	O_2	6,35
68	O_2	7,58	91	O_2	6,58
71	O_2	7,51	93	O_2	6,69
73	O_2	7,26	94	O_2	6,61
75	O_2	6,93	95	O_2	6,58
76	O_2	6,72	96	O_2	6,52
77	O_2	6,54	97	O_2	6,55
78	O_2	6,41	98	O_2	6,64
79	O_2	6,19	99	O_2	6,72
80	O_2	6,00			
81	O_2	5,83			

nates give the specific conductivity of the sol. The moment of admission of oxygen and the cataphoretic velocities corresponding to definite points of the curve are indicated in the figure.

Section *a* corresponds to the removal of the hydride film; section *c*, to the covering with an oxide film. One may expect the appearance of positive sols in section *b*, with anions in the outer sheet of the double layer.

Curves II, III and IV in Fig. 3 show the course of the oxidation of portions of the same sol with a limited amount of oxygen, the oxidation being stopped before the adsorption maximum was reached. It may be seen on curve IV how the oxidation is accelerated again after addition of extra oxygen at the point *M*. Curve V corresponds to the stopping of the oxidation after the maximum of adsorption has been reached. The cataphoretic velocities and the ζ-potential of the particles under various conditions of oxidation corresponding to different conductivities of the sol (curves II, III, IV), are given in Table 2. ζ was calculated from the classical equation $v = \frac{\zeta D}{4\pi\eta}$

Table 2

Pt-sol + HCl

$\varkappa \cdot 10^6$ initial	$\varkappa \cdot 10^6$ minim.	$\varkappa \cdot 10^6$ final	v (μ/sec. per volt/cm.)	ζ (mV)
7,58	—	6,92	−2,4	−30,5
7,58	—	6,72	+1,7	+21,6
8,24	—	6,16	+2,8	+35,6
8,24	—	5,97	+1,1	+14,6
8,34	5,83	6,03	−2,0	−25,4

It may be seen that positive sols correspond to three points in section *b* of the oxidation curve, the cataphoretic velocity increasing, reaching a maximum and decreasing again within a very narrow interval. The sols do not in all cases become negative again directly after the adsorption maximum. Data referring to positively charged sols corresponding to the rising portion of the curve are given in Table 3.

Table 3

Pt-sol + HCl

$\varkappa \cdot 10^6$ initial	$\varkappa \cdot 10^6$ minim.	$\varkappa \cdot 10^6$ final	v (μ/sec. per volt/cm.)	ζ (mV)
11,37	—	—	−3,3	−41,9
11,1	7,84	8,42	+2,8	+35,6
11,27	8,65	8,93	+3,1	+39,4

On the other hand, in some cases points in section *b* corresponded, not to positive, but to negative sols.

A reversal of the sign of charge of the platinum sol takes place, not only in HCl solutions, but also in H_2SO_4 solutions, in spite of less favorable conditions for stability, due to the presence of bivalent anions. Some data are given in Table 4.

Table 4

Pt-sol + H_2SO_4

	$\varkappa \cdot 10^6$ initial	$\varkappa \cdot 10^6$ minim.	$\varkappa \cdot 10^6$ final	v (μ/sec. per volt/cm.)	ζ (mV)
I	25,04	—	—	—2,6	—33,0
	25,04	—	23,73	4,2	+53,3
	25,04	—	23,50	1,1	+14,6
II	12,21	—	—	—2,6	—33,0
	14,47	—	11,68	2,2	+27,9
	12,63	—	10,67	2,4	+30,5
III	7,59	—	—	—2,3	—29,2
	8,01	—	7,61	1,5	+19,0

A number of experiments were also carried out on the oxidation of pure sols, without addition of acid. The results obtained are given in Table 5.

Table 5

	$\varkappa \cdot 10^6$ initial	$\varkappa \cdot 10^6$ minim.	$\varkappa \cdot 10^6$ final	v (μ/sec. per volt/cm.)	ζ (mV)
I	1,52	—	—	—3,9	—49,5
	1,62	—	1,52	—2,8	—35,6
	1,85	1,2	1,26	—2,4	—30,5
	1,30	—	—	—4	—50,8
	1,77	—	1,37	—1,8	—22,9
	1,69	—	1,17	—2,2	—27,9
	1,22	0,66	0,88	—0,7	— 8,9

As may be seen from Table 5, a decrease of negative velocity could be observed in the pure sol, but no reversal of charge took place.

The stability of positive Pt-sols

A decrease in the velocity of the positive sols and occasionally a reversal of the sign of charge were frequently observed during the measurement of the cataphoretic velocity of the sols described above. Several mean velocities calculated for successive intervals of time are given as examples in Table 6.

Table 6

	Time from start of the measurement of v(min.)	Mean velocity μ/sec. per volt/cm.		Time from start of the measurement of v (min.)	Mean velocity μ/sec. per volt/cm.
I	0—10	+3,1	III	0—10	+4,
	10—30	+1,7		10—15	+1,7
	30—45	0		15—20	+0,8
II	0—15	+2,5		20—25	0
	15—35	+1,1		25—35	−1,1

These data constitute a sufficiently convincing evidence for the fact that the constancy of the conductance of the sol for 10—15 minutes does not mean complete cessation of oxidation, and that the latter continues on bubbling pure nitrogen, at the expense of oxygen present in the sol. A real cessation of the oxidation for more than 20 hours was observed only once. Sol III (Table 4) was left in the cataphoretic apparatus overnight; on the following day part of the platinum had precipitated, and the remaining sol had the same cataphoretic velocity $v = +1{,}5$ μ/sec. per volt/cm. as the day before (the coagulation of part of the sol indicates an irregularity in the oxidation of the surface; we will return to this question later).

In order to ascertain whether the conductance remains constant for longer intervals of time, the duration of conductivity measurements was extended beyond 15 minutes. It turned out that in all cases, on sufficiently prolonged passage of purified nitrogen (nitrogen from a cylinder, purified over copper gauze), following the addition of a small quantity of diluted oxygen, a complete adsorption curve was obtained, i. e. in all cases there was enough oxygen to oxidize completely the surface of the sol particles.

Under the assumption that a more careful purification of nitrogen would lead to better results, we began to purify it according to Kautsky and Thiele[6], by passing very fine bubbles through an alkaline solution of hydrosulphite after purification over copper gauze. Nitrogen purified in this way produced no measurable oxidation when it was passed through a sol saturated with hydrogen, i. e. through a sol whose particles were covered with a hydride film. The conductance remained constant for 6—8 hours or more.

In order to remove the hydride film and bring about a reversal of sign of the sol charge, a small quantity of diluted oxygen was admitted to the sol (the gas was passed through the sol for short intervals of time varying from several seconds to several minutes); after this the sol was again saturated with nitrogen purified as indicated above, which was bubbled through the liquid for a long time. It turned out to be impossible to obtain complete stopping of the oxidation; in the course of time a complete more or less extended adsorption curve was obtained in all cases. This may be explained by the fact that the amount of oxygen remaining in the nitrogen was sufficient to produce a reversal of the sign of charge once the hydride film had already been removed, i. e. by the nitrogen not being sufficiently well purified. It is also possible that the saturation with nitrogen cannot remove the oxygen from the sol to such an extent that the positive sol should not become negative again, if there has been enough oxygen for the removal of the hydride film. Anyway, we did not succeed in obtaining conditions under which it would have been possible to stop the oxidation at a definite stage, and then carry out the cataphoretic masurements by using pure nitrogen for stirring the sol, for bubbling it through the supernatant liquid and for forcing the sol under pressure through the capillary.

After it had been ascertained that cataphoretic measurements could not be resorted to in experiments of long duration, we attempted to determine the stability of the platinum sols as a function of the degree of oxidation. For this purpose, separate por-

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[6] K. Kautsky u. H. Thiele, Z. anorg. Chem., **152**, 342 (1936).

tions of the sol were sealed with definite quantities of oxygen in ampoules, into which electodres were sealed for the determination of the conductivity (Fig. 2).

We intended to judge of the stopping of oxidation at a definite degree by the constancy of the conductance, and of the stability, by the outer appearance. We expected to obtain the stability of the sol as a function of the degree of oxidation by comparing the stability with the conductance. The introduction of various amounts of oxygen was accomplished either by displacement of the whole volume of nitrogen or part of it with dilute oxygen (nitrogen from a cylinder), or by introduction of a definite quantity of water saturated with oxygen into the sol. The water was saturated with oxygen in the graduated test tube shown in Fig. 2 *B* and then transferred from it into the ampoule with the sol. The adsorption curve was determined on one sample of the sol before sealing it off, in order to be able to judge of the state of the surface by the conductance. In a number of cases, the portions of the sol sealed in small tubes were perfectly stable, and their conductance in the region of positive sols remained strictly constant. These determinations, however, were of poor reproducibility, so that only irregular points were obtained. Since it was not possible to draw regular curves through these points, with maxima and minima of stability at definite conditions of the surface, these data are of no interest and will not be given here.

Thus, we have not succeeded in obtaining sols of a positive sign which could be determined electrophoretically and whose properties would remain for a long time without change. Therefore, we are not in a position to judge of the stability of positive sols in terms of the usual concepts of colloid chemistry. We do not know whether positive sols at a definite degree of oxidation are stable, or whether they coagulate because the double layer alone fails to secure sufficient stability, since in our experiments these sols were always completely oxidized on sufficiently long keeping, so that they became negative.

The poor reproducibility of individual determinations as well as the fact that negative sols were obtained in some cases over the descending section of the conductance curve, and positive sols, over the ascending one, leads us to believe that the surface was non-uniformly oxidized. The last part of the investigation of positive sols was devoted to the study of slow oxidation and determination of adsorption curves under various conditions.

Slow oxidation of Pt-sols

Curve 1 in Fig. 3 exhibits a second minimum of conductance (maximum of adsorption) in the oxide film region *c*. This course of the curve is not accidental; on almost all adsorption curves there are additional maxima and minima in the oxygen part.

Assuming that their presence may be explained by the non-uniformity of oxidation, leading to the simultaneous presence in the sol of particles with various surface conditions, we carried out a series of experiments with different rates of oxidation in order to see whether the character of the curves would vary.

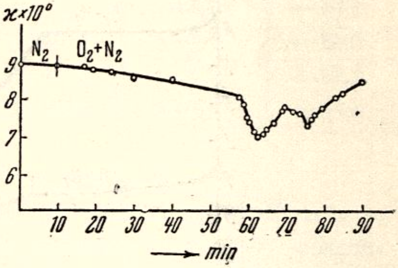

Fig. 4.

The curve in Fig. 4, gives the variation of the conductivity on oxidation by oxygen whose concentration was 0,3—0,5% (nitrogen from a cylinder). The first adsorption maximum is reached within appoximately one hour from the start of the experiment. Fig. 5 shows two curves corresponding to the oxidation of two different samples of the sol with considerably more dilute oxygen (nitrogen from a cylinder passed over copper gauze at 400°).

It may be seen that the first minimum is reached after 20—25 hours, but in spite of such strong retardation, the general character of the curves remains the same as in the case of fast oxidation. The second minimum of conductivity is ordinarily as deep as the first one, but the maximum between them does not reach the initial value. The presence of these two adsorption maxima seems to be connected with the existence in the sol of two different types of particles with hydride films requiring very different lengths of treatment with oxygen for their complete removal. The combined effect of desorption on particles of the first type and adsorption on those of the second type, leads to the observed course of the curves.

The non-uniformity of the surface of the particles, manifested during the oxidation must thus be ascribed to a non-uniform state of the surface existing from the very origin of the particles, and cannot be eliminated by varying the course of the oxidation.

The measurement of cataphoretic velocity and conductivity gives, at any given moment, a resultant value which is determined by the state of the different particles and varies with time according as the properties of the individual particles are changed. This explains the failure of our attempts to obtain stable positive sols.

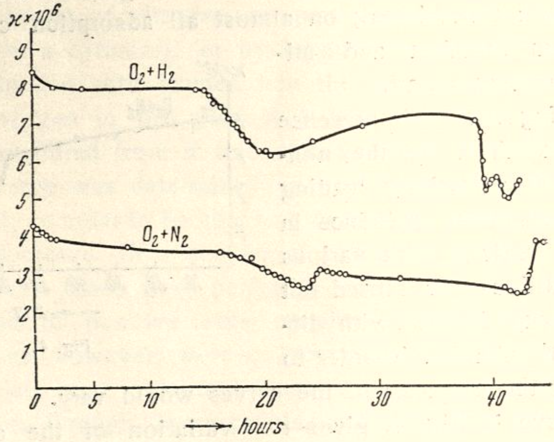

Fig. 5.

Cataphoretic velocity of H_2-Pt-sols in acid and alkaline solutions

In connection with the experiments described above, it was necessary to determine the cataphoretic velocity of H_2-Pt-sols in solutions of HCl and KOH of various concentrations. The determination was carried out by the moving boundary method. The conductivity of the supernatant liquid — acidified or alkalified conductivity water saturated with hydrogen — was adjusted to the conductivity of the sol containing the added electrolyte. The reproducibility of the results is not completely satisfactory. The results given below are average values taken over a large number of determinations. (See Tables 7 and. 8).

Table 7

Cataphoretic velocity of H_2-Pt-sols in HCl solutions

Concentration of HCl (normality)	Cataphoretic velocity (μ/sec. per volt/cm.)	ζ (mV)
0	—4,6	—58,4
$1 \cdot 10^{-5}$	—4,5	—57,1
$1 \cdot 10^{-4}$	—3,8	—48,3
$1 \cdot 10^{-3}$	—2,9	—36,8

Table 8

Cataphoretic velocity of H_2-Pt-sols in KOH solutions

Concentration of KOH (normality)	Cataphoretic velocity μ/sec. per volt/cm.	ζ (mV)
0	—4,1	—52,1
$1 \cdot 10^{-5}$	—5,4	—68,6
$1 \cdot 10^{-4}$	—4,5	—57,1
$1 \cdot 10^{-3}$	—3,5	—44,4

The corresponding curves are given in Fig. 6.

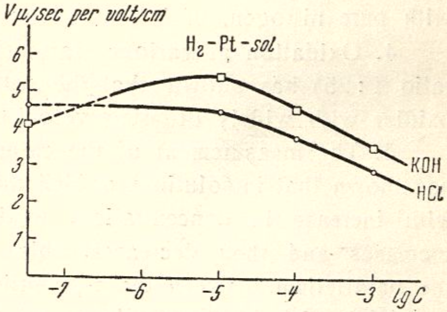

Fig. 6.

It may be seen that the cataphoretic velocity of H_2-Pt-sols in acid solutions steadily decreases with incresing electrolyte concentration. The variation of the ζ-potential is in this case parallel to that of the total interface potential ε, which decreases on increasing the concentration of the H^+-ions in solution (hydrogen electrode). In alkaline solutions, at first an increase and then a falling off of the ζ-potential is observed. This is entirely in agreement with what may be theoretically predicted: the total interface potential ε grows upon increasing the concentration of OH'-ions in the solution. Therefore, the ζ-potential also increases at first. But at the same time, owing to the general increase of the concentration of ions in solution, the double layer is compressed and the electrokinetically active part of the potential drop in the liquid decreases. The combined effect of these two factors leads to the passage of the curve through a maximum. These results show that, in the case of H_2-Pt-sols in solutions of HCl and KOH, as in the case of other simple systems (for instance active charcoal in solutions of simple electrolytes in an atmosphere of hydrogen and oxygen[7]), there is a distinct parallelism between the ζ-potential and the ε-potential.

Summary

1. The state of the surface of platinum sols in various gaseous atmospheres exactly corresponds to the state of the surface of the platinum-gas electrode.

On careful-oxidation of negative H_2-Pt-sols, positive O_2-Pt-sols are obtained, which, on further oxidation, pass into negative oxidized sols. One may judge of the state of the surface by the adsorption of acid.

2. The absolute value of the cataphoretic velocity of positive O_2-Pt-sols is of the same order as that of negative sols.

3. It was not possible to preserve the positive sols without change for long intervals of time. Oxidation did not stop at a definite state of the surface but continued even on saturating the sol with pure nitrogen, until the surface became again negative.

4. Oxidation at various rates (the extreme rates being in the ratio 1 : 25) has shown that the sol particles are not uniform and oxidize with widely differing velocities.

5. The measurement of the cataphoretic velocity of H_2-Pt-sols has shown that in solutions of HCl the ζ-potential steadily decreases with increase in concentration, whilst in KOH solutions it first increases and then decreases. This course of the curves confirms the parallelism between the ε-potential and the ζ-potential.

We wish to express here our sincere thanks to Prof. A. N. Frumkin for the advice he has given us in the course of this work.

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[7] N. Bach, Koll. Z., **64**, 153 (1933); Pilojan, Bach u. Kriworutschko, Koll. Z., **64**, 287 (1933).