intensities. The best value for the parameter v is approximately $^4/_{10}$. The data on these planes are given in Table III.

Model of the Unit Cell.—A model was made by constructing molecules to scale from wooden balls as shown in Fig. 4. These were then placed at the positions of the four lattice points. The junctions along the a direction are across hydrogen atoms. The large number of orders of (0 0 1) planes reflecting indicates a concentration of the atoms in the (0 0 1) planes. The model shows this, and also explains the very complete cleavage parallel to this plane. The other cleavage (1 0 1) is likely from the model.

Summary

m-Iodobenzoic acid belongs to the monoclinic prismatic class instead of monoclinic sphenoidal. Its axial ratio is $a : b : c = 1.3252 : 1 : 5.5824$; $\beta = 91° 29.5'$. The unit cell contains four molecules and has the following dimensions: $a_0 = 6.206$ Å.; $b_0 = 4.683$ Å.; $c_0 = 26.14$ Å. The space-group is C_{2h}^5. The molecules are located within the cell at the positions (0 0 0), $(^1/_2\ v\ ^1/_2)$, $(u\ ^1/_2\ w)$, $(u + {}^1/_2, v + {}^1/_2, w + {}^1/_2)$, where u and w are approximately equal to 0, and v equals very nearly $^4/_{10}$. Model molecules, built up of wooden balls, embodying the "puckered" benzene ring fit into the cell defined above very well. The model accounts for the cleavage of the crystal.

An addition to Laue photograph technique through the use of filters has been described.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE MEASUREMENT OF THE HYDROGEN-ION CONCENTRATION IN UNBUFFERED SOLUTIONS. I. THE ADSORBENT PROPERTIES OF PLATINIZED PLATINUM

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It is a well-known fact that the measurement of the hydrogen-ion concentration in a solution with an extremely small buffer capacity is a very hard problem. If a platinized electrode is used, it takes a long time before the potential is constant and it is hardly possible to find reproducible results; moreover, it is doubtful whether the final reading of the electromotive force corresponds to the P_H of the original solution. It was our intention to make a careful study of the hydrolysis of solutions of pure zinc salts and we used a platinized platinum spiral for the measurement of the P_H.[1] However, we met with many difficulties; the e.m.f. measured always corresponded to a higher hydrogen-ion concentration than was

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[1] For electrode cell, *cf.* I. M. Kolthoff and W. Bosch, *Rec. trav. chim.*, **46**, 430 (1927).

expected from the results of other methods. Moreover, in many cases we were able to show in a colorimetric way that the solution taken from the electrode cell after the treatment with hydrogen had a more acid reaction than the original liquid. Recently a similar phenomenon has been described by H. G. Denham and N. A. Morris,[2] who found that solutions of zinc sulfate and cadmium sulfate after treatment in the hydrogen electrode became more acid. They attribute this to a reduction of the bivalent metal ions to the monovalent state, $Zn^{++} + H \rightleftarrows Zn^{+} + H^{+}$. This interpretation seems very improbable. In our experiments we observed that the solution from the electrode cell after treatment with hydrogen had no reducing properties whatsoever, which shows evidently that the original metal ions had not been reduced. There was more reason to ascribe the facts observed to the adsorbent properties of the platinized platinum, the more so since A. Frumkin and A. Donde[3] in a preliminary paper showed that platinum black can adsorb alkali from a neutral salt solution in a hydrogen atmosphere. It was shown by these authors that this hydrolytic adsorption is dependent upon the kind of gas with which the platinum black was saturated. In working with 0.2 N sodium sulfate solution they found that in a hydrogen atmosphere the platinum black adsorbed alkali to a considerable extent and the solution became strongly acid. After washing the platinum with conductivity water in a hydrogen current until the reaction did not change further, they treated the same platinum black with the salt solution, or water, respectively, in an oxygen atmosphere instead of hydrogen. Under these conditions alkali was liberated and its amount was approximately equivalent to the amount of acid originally found in the hydrogen atmosphere; though, as a rule, somewhat less alkali was given off than corresponded to acid which had been formed. The most probable explanation of the phenomena is that in a hydrogen atmosphere a double layer is formed around the platinum particles, the metal being negative and the layer of hydrogen ions at the liquid side forming the positive part. Cations from the solution may displace part of the hydrogen ions in the double layer, which results in an adsorption of the cation, whereas an equivalent amount of hydrogen ions goes into the solution. If the hydrogen is removed the electrode is discharged, and the ions in the double layer are transformed into molecular hydrogen which escapes and the adsorbed cations into the corresponding metal. If oxygen is passed through, the metal is oxidized to its oxide, which gives the hydroxide with water. Now it may be expected that an oxygen electrode will show just the reverse behavior of a hydrogen electrode. However, Frumkin and Donde were not able to show that a sodium sulfate solution in contact with platinum black becomes alkaline on passing

[2] H. G. Denham and N. A. Morris, *Trans. Faraday Soc.*, **26**, 510 (1928).

[3] A. Frumkin and A. Donde, *Ber.*, **60**, 1816 (1927).

through oxygen; as a matter of fact, they always found a slightly acid reaction. It should be remembered, however, that platinum black or a platinized platinum electrode in oxygen does not behave like an ideal hydroxyl-ion electrode, because part of the platinum may be oxidized to some oxide. In this light it is worth while to mention the recent important investigations of S. W. Pennycuick,[4] who was able to prove that in the preparation of a platinum sol according to the spark method of Bredig a little of a strong acid is formed, hexahydroxyplatinic acid, $H_2Pt(OH)_6$, which is responsible for the stability of the sol. In the discussion of our results we will come back to this point.

In our preliminary experiments we tried to reproduce Frumkin and Donde's results by working with platinum black. The latter was prepared by reduction of pure chloroplatinic acid with ammonium formate; the metal was washed for several weeks with conductivity water until the conductivity of the water after the washing had not changed. The black metal powder was very heavy, and it was almost impossible to stir it up from the bottom of the cell when a strong current of hydrogen gas was passed through. Moreover, fine particles showed a tendency to coagulate in the hydrogen current; probably due to the small surface of the metal we failed in reproducing Frumkin and Donde's results, although two different preparations of platinum black have been used. Therefore we changed the experimental conditions and took a long, thin foil of platinum, 3.5 cm. long and 2.5 cm. wide, wound in a cylindrical shape. It was mounted in a pyrex glass cell. The arrangement is shown in Fig. 1.

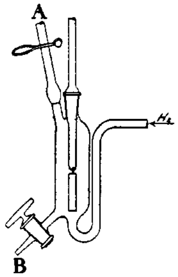

Fig. 1.

After passing the hydrogen through for a certain time, the liquid could be withdrawn from the cell in a hydrogen atmosphere by opening the glass stopcock B and closing the glass tube A. By careful electrolysis in a chloroplatinic acid-bath (without lead, of course) the platinum cylinder was coated with a black layer of platinum, then washed out with conductivity water in air and finally in hydrogen until the reaction of the water remained unchanged. The first experiments with such an electrode gave results in qualitative agreement with those of Frumkin and Donde. However, in continued investigations, a hydrolytic adsorption was no longer observed. Therefore we platinized again and washed out with sodium bicarbonate in order to remove acid which might be adsorbed by the electrode. Thereupon the washing with water was started in the way described above but no hydrolytic adsorption was found. A third electrolysis in the chloroplatinic acid-bath was made and the electrode washed out with water in a hydrogen current until the reaction did not change further. This electrode gave continuously reproducible results, even quantitatively, and showed the adsorption phenomena quite distinctly. We do not know how to explain the first irregular behavior; we may mention here that Frumkin[5] often observed the same kind of irregularities. The hydrogen and oxygen used in these experiments were taken from a tank and purified by washing through several wash-bottles (permanganate, alkaline pyrogallol, sulfuric acid, four flasks with water, two empty wash-bottles, finally through the salt solution and then through the electrode cell). At first the hydrogen washed through permanganate was passed over an electrically heated copper wire; later it appeared that alkaline pyrogallol could be used as well. In the case of oxygen purification, the alkaline pyrogallol was omitted.

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[4] S. W. Pennycuick, *J. Chem. Soc.*, 600 (1927); 551, 2108 (1928).

[5] Private communication from Professor Frumkin.

The neutral salts used were c. p. products and were recrystallized a few times from water and tested for the absence of traces of acid or alkaline impurities.

In all the experiments conductivity water ($K_{25} = 1 \times 10^{-6}$) was used as a solvent. The qualitative experiments with solutions of sodium chloride, potassium chloride, potassium sulfate and calcium chloride showed that they became more or less acid to methyl orange when hydrogen was passed through the electrode vessel. The solutions were then withdrawn from the cell in a hydrogen atmosphere; the vessel was filled up with water or with the original salt solution, whereupon oxygen was passed through. An alkaline reaction to thymol blue and in most cases to thymolphthalein was noticed.

Before making the next experiment, the cell and electrode were washed out with water in oxygen until the reaction did not change any more. It is peculiar that after prolonged washing in oxygen the water in the electrode cell always became very slightly acid (P_H 5.4 to 5.6 to methyl red sodium salt), whereas the conductivity water after washing with the same gas in a pyrex flask in the absence of platinum had a P_H of about 6.8 (brom thymol blue sodium salt). Probably a trace of the hexahydroxyplatinic acid is formed in oxygen. The washing in hydrogen was followed by further washing in oxygen. In order to be sure that sulfates and salts of divalent metals (zinc) were not reduced by the hydrogen electrode, 5 cc. of the solution was transferred from the cell in a hydrogen atmosphere into 0.1 cc. of 0.001 N permanganate. By comparison with a blank in water we found that *no reduction of sulfates or zinc* ions had taken place. In the quantitative experiments it appeared that equilibrium in hydrogen was attained within ten minutes. The same holds for the oxygen treatment. If the latter gas is passed through for a longer time, another phenomenon may take place which we will discuss later.

As a rule 25 cc. of the salt solution to be examined was placed in the electrode cell; hydrogen was then bubbled through from ten to fifteen minutes, whereupon the solution was withdrawn into a pyrex flask and titrated with 0.01 N sodium hydroxide, using 0.1 cc. of 0.03% methyl red sodium salt as an indicator. A blank titration was performed under the same conditions with 25 cc. of the original salt solution, washed by hydrogen. After removing the solution from the cell, the latter was filled with water in the hydrogen atmosphere, withdrawn after ten minutes and titrated. This procedure was repeated until the reaction of the wash water did not change any more. Then we continued the washing in oxygen; the water became alkaline and was titrated with 0.01 N hydrochloric acid, using methyl red sodium salt as an indicator. The procedure was repeated until the reaction of the water did not change further, whereupon the electrode finally was washed out in hydrogen again. In Table I are given only the titration figures of the first solution withdrawn from the electrode and the sum of the figures for the different wash waters.

Table I

0.1 N Potassium Chloride

In hydrogen	0.01 N NaOH, cc.	In oxygen	0.01 N HCl, cc.
Solution taken from cell......	0.30	First wash water............	0.32
Wash water (4 washings).....	.04	Wash water................	.01
	0.34		0.33

A duplicate experiment gave in hydrogen 0.33 cc. of 0.01 N sodium hydroxide; in oxygen, 0.30 cc. of 0.01 N hydrochloric acid. There is almost a complete recovery of the base adsorbed in the hydrogen atmosphere when oxygen is passed through.

Table II

Results of Experiments

In hydrogen		In oxygen	
Material	0.01 *N* NaOH, cc.	Material	0.01 *N* HCl, cc.
0.05 *M* Potassium Sulfate			
0.35 + 0.05 (4 washings).....	0.40	0.28 + 0.04................	0.32
Duplicate..................	.41	Duplicate..................	.28
0.01 *N* Sodium Chloride			
0.30 + 0.06 (4 washings).....	0.36	0.30 + 0.05................	0.35
Duplicate..................	.38	Duplicate (0.32 + 0.04).....	.36
0.05 *M* Calcium Chloride			
0.24 + 0.04 (4 washings).....	0.28	0.17 + 0.03................	0.20
Duplicate..................	.30	Duplicate..................	.22

Zinc Sulfate.—More elaborate experiments were made with solutions of zinc sulfate. The salt was purified by six recrystallizations from water and dried in a desiccator over deliquescent sodium bromide at a temperature below 25°. In this way a salt with seven molecules of crystal water was obtained. After the third recrystallization, solutions of the same concentration showed the same *P*H.

Solutions of zinc sulfate of different strengths showed after treatment in the hydrogen electrode a much stronger acid reaction than the original ones. The usual washing in hydrogen was continued in oxygen. In the latter the reaction became only slightly alkaline, the *P*H being about 7 to 7.5. Even after fifteen washings the reaction was still slightly alkaline and the wash water contained a trace of dissolved zinc, as was shown by a slight opalescence on the addition of ferrocyanide. In the oxygen atmosphere the adsorbed zinc is transformed into the slightly soluble zinc oxide; it would require a long time before the latter could be washed out quantitatively. Therefore, in order to remove the adsorbed zinc, the cell was filled with 0.1 *N* hydrochloric acid and oxygen passed through from thirty to forty minutes. The acid solution contained a considerable amount of zinc; in further washing with water, no zinc was given off.

In the quantitative experiments we treated the zinc sulfate solution first in hydrogen and then withdrew the solution and titrated the free acid with methyl red sodium salt as an indicator, using the original salt solution as a liquid for comparison. It was interesting to know whether an equivalent amount of zinc had disappeared from the solution. Therefore, in those cases in which we worked with 0.01 *M* zinc sulfate solution, the zinc content was determined by the oxin (*o*-hydroxyquinoline) method before and after the adsorption. When stronger zinc sulfate solutions were used, the difference before and after adsorption was so small that the analytical error would make the result rather uncertain. Therefore, after the zinc sulfate–hydrogen treatment, the electrode and cell were washed in hydrogen with water until the reaction remained unchanged; then we added 0.1 *N* hydrochloric acid, passed oxygen through and determined the amount of zinc in solution—which is equal to the amount adsorbed in a direct way by the oxin method.

TABLE III

RESULTS OF EXPERIMENTS

0.01 *M* zinc sulfate	0.01 *N* NaOH, cc.	Adsorbed, %	0.05 *M* zinc sulfate
In hydrogen	1.15	2.3	In hydrogen: 3.03 + 0.45 (6 washings) = 3.48 cc. of 0.01 *N* NaOH or 0.0348 milliequiv. of H^+ liberated.
Adsorbed zinc	1.18	2.36	Adsorbed zinc, 0.0340 milliequiv. of Zn^{++} adsorbed

Repeated experiments gave the following results

0.0350 milliequiv. of H^+ liberated and 0.039 milliequiv. of Zn^{++} adsorbed
0.034 milliequiv. of H^+ liberated and 0.037 milliequiv. of Zn^{++} adsorbed

From these experiments we learn that the results are well reproducible, that the amount of acid formed is equivalent to the amount of zinc adsorbed by the electrode and, finally, that the adsorption of zinc ions is much larger than that of cations in alkali or earth alkali salts (compare previous tables).

Ammonium Chloride.—The behavior of ammonium chloride solution was quite different from that of the other salts. It is to be expected that the platinized electrode in a hydrogen atmosphere will adsorb ammonia. In working with 1 *N*, 0.1 *N* and 0.005 *N* ammonium chloride solutions, respectively, we found that in hydrogen the reaction became very slightly more acid (colorimetric measurements of *P*H), the difference in acidity from the original solutions being so small that it could not be titrated (for 25 cc. of solution it was less than 0.05 cc. of 0.01 *N* NaOH). If the electrode was treated thereafter in an oxygen atmosphere with water after washing out, a tiny trace of alkali (ammonia) was given off.

By treating the ammonium chloride solutions in an oxygen atmosphere in the electrode cell the results were still more peculiar. The solutions became distinctly acid, more acid being formed the longer the oxygen was passed over the electrode. By passing the oxygen current coming from the electrode cell over 10 cc. of 0.004 *N* hydrochloric acid, we could prove in a qualitative and quantitative way that no ammonia was removed due to hydrolysis. Neither was it possible to detect in the solution after the oxygen treatment any oxidation products such as nitrate or nitrite. The only plausible explanation of the peculiar behavior was that the platinum black in the oxygen atmosphere is slowly oxidized to the hexa-aquoplatinic acid, which is very slightly soluble and remains for the main part on the electrode. This acid reacts with the ammonium ions in the solution by forming an insoluble ammonium salt

$$H_2Pt(OH)_6 + 2NH_4^+ \longrightarrow (NH_4)_2Pt(OH)_6 + 2H^+$$

The solution becomes acid and ammonium ions are removed from it. If this explanation gives a correct picture of what is happening, we may expect that after washing out with water in an oxygen atmosphere the water will become alkaline if the washing is continued in hydrogen, because the platinic acid will be reduced

$$(NH_4)_2Pt(OH)_6 + 2H_2 \longrightarrow Pt + 6H_2O + 2NH_3$$

Actually we found that the first washing with hydrogen gave an acid reaction; thereupon if the cell was filled with water again, the reaction became strongly alkaline; by means of Nessler's reagent it was very simple to detect the presence of considerable amounts of ammonia. It appears strange that the first washing in a hydrogen atmosphere gives an acid reaction. This is explained by the fact that strong acids are adsorbed by platinized platinum in an oxygen atmosphere and not in hydrogen (see later). The acid adsorbed in the oxygen treatment is rapidly displaced from the electrode by the first washing in the hydrogen atmosphere. Thereupon the reduction of the ammonium salt of the aquoplatinic acid takes place and the reaction changes to alkaline. Some of the practical results are reported in Table IV.

TABLE IV

RESULTS OF EXPERIMENTS

NH_4Cl, normality (25 cc.)		0.1	0.1	0.1	0.005	0.005
Oxygen passed for, hours		$^1/_6$	12	17	$^1/_6$	3.5
NaOH[a] for solution, cc.		0.25	1.10	1.13	0.17	0.53
NaOH[a] for washings, cc.		(4) .17	(8) 0.29	(5) 0.40	(6) 0.14	(4) 0.22
Washed in hydrogen	NaOH[a] cc., 1st	.12	.14	.09	.04	.04
	HCl,[a] cc., 2d	.12	.24	.32	.02	.03
	HCl[a] for more washings, cc.	(3) .12	(3) .12	(4) .16	(3) .01	(3) .03

[a] NaOH and HCl, 0.01 *N*.

The amount of base recovered in the hydrogen current is always much less than the amount of acid formed in oxygen. It may be that the adsorbed ammonia is not completely removed by washing out in hydrogen.

TABLE V

RESULTS OF EXPERIMENTS

Normality of $(CH_3)_3NCl$ (25 cc.)		0.1	0.1
Oxygen passed through for, hours		$^1/_6$	24
NaOH[a] for solution, cc.		0.09	0.70
NaOH[a] for first wash water, cc.		.11	.10
NaOH[a] for later washings, cc.		(3) .06	(3) .06
Washing in hydrogen	NaOH[a] for first	.22	.49
	NaOH[a] for later	(5) .06	(4) .19
Washed in oxygen again	First	No change	.09 HCl[a]
	Later (3)	No change	(3) .02 HCl[a]

[a] NaOH and HCl, 0.01 *N*.

We also made some experiments with the salt of an organic cation, trimethylammonium chloride. Qualitatively it behaved more or less in the same way as ammonium chloride, the only difference being that after treatment in oxygen and washing with the same gas, much more acid was liberated later in hydrogen than in the case of ammonium chloride.

Experiments similar to those described for ammonium chloride were made with 0.1 *N* potassium chloride. After passing oxygen through for twenty-five hours, the solution was very slightly acid and took 0.03 cc. of 0.01 *N* sodium hydroxide. The wash water (five times) took 0.06 cc. 0.01 *N* sodium hydroxide. Then the washing was continued in hydrogen. The first wash water was distinctly acid and took 0.06 cc. of 0.01 *N* sodium hydroxide; the second wash water, 0.12 cc. With four more washings the reaction did not change further. Thereupon we turned back to the washing in oxygen. The first wash water was distinctly alkaline, and took 0.05 cc. of 0.01 *N* hydrochloric acid and the second wash water, 0.02 cc.; by further washing the reaction remained unchanged.

These results, which are reproducible from a qualitative point of view, show that the behavior of the salt solution in oxygen is fairly complicated. After passing oxygen through for twenty-five hours, the reaction is distinctly acid, due to the formation of hexa-aquoplatinic acid. Moreover, it seems that a trace of free acid is hydrolytically adsorbed from the salt solution and that a trace of potassium is adsorbed by the platinic acid. The adsorbed acid is not given off in an oxygen atmosphere but is easily removed in hydrogen (see next section).

Therefore, the first washings with hydrogen were distinctly acid. Moreover, the hydrogen reduces the aquoplatinic acid and its potassium salt; in the latter case potassium hydroxide is formed. However, as we shall see later, a trace of adsorbed hydroxide cannot be removed in a hydrogen atmosphere but is given off in oxygen. Therefore, in the final washing in oxygen we found a slightly alkaline reaction.

On account of the complex nature of the phenomena described, it is evident that they are of no significance from a quantitative point of view.

Adsorption of Hydrochloric Acid by Platinized Platinum.—After the electrode had been carefully washed out with water in hydrogen, oxygen and hydrogen, the adsorption of hydrochloric acid was studied in a hydrogen atmosphere.

We worked with 0.01 *N*, 0.002 *N*, 0.001 *N* and 0.0005 *N* hydrochloric acid, respectively; the results showed that there *was not even a trace of acid adsorption in a hydrogen atmosphere.* Similar experiments were performed in an oxygen current. The oxygen was passed through for ten minutes; a longer treatment had no effect on the results. The titrations were made with 0.01 *N* sodium hydroxide using a micro buret for the more dilute solutions and methyl red as indicator. The original solutions of the acid were treated for ten minutes with oxygen in the absence of platinum black and titrated in the same way. The difference between the two titration figures gave the amount of acid adsorbed by the platinized platinum in the oxygen atmosphere. In order to be certain that there was an equivalent adsorption of the hydrogen and chlorine ions, the concentration of the latter was determined before and after the adsorption in a gravimetric way. The results agreed very closely with those obtained by the volumetric determination of the hydrogen ions. Therefore, from our experiments, we may conclude that there is *an equivalent adsorption of hydrogen and chloride ions from hydrochloric acid solution by platinized platinum in an oxygen atmosphere.* The results are summarized in the following table. In all cases 35 cc. of the acid solution was used for each experiment. The first line gives the original concentration of the acid, the second the concentration after the adsorption, the third the number of micromoles adsorbed and the fourth the decrease of the concentration of the acid due to the adsorption expressed in per cent.

TABLE VI

ADSORPTION OF HYDROCHLORIC ACID BY PLATINIZED PLATINUM IN OXYGEN

Init. concn., N	Final concn., N	Micromoles of HCl adsorbed	Adsorption, %
0.00978	0.00946	10.2	3.2
	.00951	9.5	2.7
	.00950	9.7	2.8
.00490	.00468	7.7	4.4
.00092	.00081	3.9	12
.00050	.00039	3.7	22

The curve in Fig. 2 gives a graphical representation of the change of the adsorption with the final concentration in the solution. The absolute amount of adsorbed acid increases with increasing final concentration, whereas, relatively, the adsorption decreases at higher concentrations. Therefore, the adsorption isotherm has the normal appearance. A longer treatment in oxygen did not affect the results.

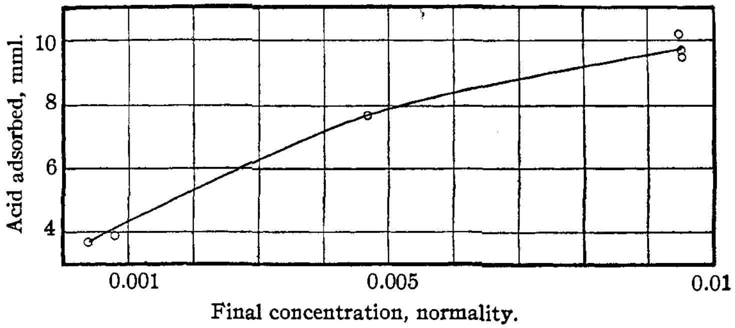


Fig. 2.—Adsorption of hydrochloric acid by platinized platinum in oxygen.

Adsorption of Sodium Hydroxide by Platinized Platinum.—As we have seen before, platinized platinum adsorbs the base from a neutral salt solution, in a hydrogen atmosphere. Therefore, we may expect a much larger effect if dilute solutions of sodium hydroxide are in contact with platinized platinum in a hydrogen atmosphere. This is actually the case, though the amount adsorbed reaches a maximum at a fairly low alkali concentration; if the latter is increased, the amount adsorbed drops again. Thirty-five cc. of the solution was introduced into the cell and then hydrogen passed through for ten minutes (a longer treatment in this gas did not change the results). The solution was withdrawn in the hydrogen atmosphere and 25 cc. was titrated. The cell was washed with water in hydrogen until the reaction remained unchanged. Thereafter the washing was continued in oxygen; the wash water always was distinctly alkaline and in most cases the alkalinity was determined quantitatively. This phenomenon shows that it is impossible to remove all of the adsorbed base from the electrode in a hydrogen current. After the washing in oxygen, it was repeated again in hydrogen. In several cases we started with 20 cc. of the sodium hydroxide solution instead of with 35 cc. and analyzed later a 10-cc. portion. In the latter case only half of the electrode was covered by the solution. The titrations were made at boiling temperature with phenol red as an indicator. The original solutions have been analyzed under similar conditions. From the difference between the titration figures the amount of base adsorbed could be computed. All the results were reproducible and are summarized in Table VII.

TABLE VII

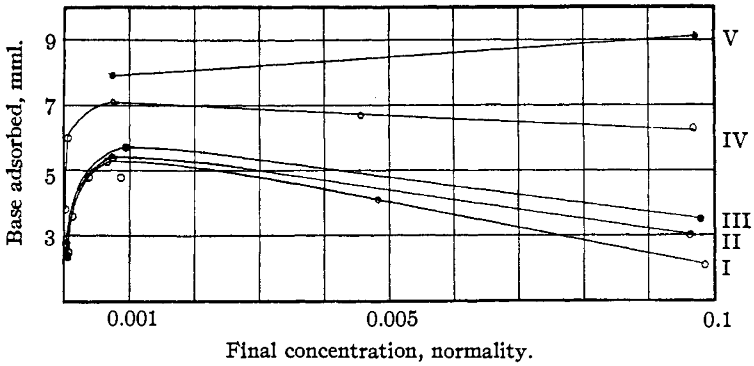
ADSORPTION OF SODIUM HYDROXIDE BY PLATINIZED PLATINUM IN HYDROGEN

Init. concn., *N*	Vol. of base taken, cc.	Final concn., *N*	Adsorbed, micromoles
0.00992	35	0.00986	2.1
.00978	20	.00963	3.0
.0049	35	.00482	4.1
.0010	35	.00086	4.8
.0010	20	.00072	5.4
.0008	35	.00066	5.3
.0005	35	.00037	4.8
.0002	35	.00011	3.6
		.00012	3.4
.00012	35	.00005	2.5
.00017	20	.00002	2.7

In Fig. 3 the results are combined in a graph; the ordinate gives the number of micromoles adsorbed and the abscissa the final concentration in the solution. It is quite evident that there is a maximum in the adsorption at a final concentration of approximately 0.0007 *N* sodium hydroxide. It should be remembered that a very small analytical error in the titration of the stronger solutions causes a large deviation in the amount adsorbed. Still, we believe that the general shape of the curve is right, because the values have been reproduced several times.

The shape of the curve looks similar to that representing the change of the electrokinetic potential of a platinum sol at different alkalinities. It seems to us, however, that there is no connection between the adsorption of the sodium hydroxide by platinized platinum in hydrogen and the electrokinetic potential, and it is hard at the present time to explain the maximum.

It was thought that the adsorption of the sodium ions might be increased if a sodium salt such as sodium chloride was added to the sodium hydroxide solution. This, indeed, was the case; the force required to remove the sodium ions from the solution in the presence of an excess of sodium salt is smaller than when they are absent. Under these conditions we have, moreover, the advantage that the adsorption of the hydroxide at different concentrations takes place at about the same sodium-ion concentration in the solution.



I, NaOH (35 cc.); II, NaOH (20 cc.); III, NaOH in 0.1 *N* NaCl; IV, NaOH in 1.0 *N* NaCl; V, NaOH in 3.0 *N* NaCl.

Fig. 3.—Adsorption of sodium hydroxide by platinized platinum in hydrogen.

The analytical procedure was the same as that described for the solutions of sodium hydroxide alone. In all cases we started with 35 cc. of solution. The results are summarized in Table VIII and graphically in Fig. 3; Curve III represents the adsorption from 0.1 *N* sodium chloride Curve IV from 1 *N* sodium chloride and Curve V from 3 *N* sodium chloride.

At larger concentrations of sodium chloride there is a decided increase in the adsorption of sodium hydroxide. Moreover, the maximum in the adsorption, which had been found at about 0.0007 *N* hydroxide in the absence of salt, disappears when enough sodium chloride is present.

Adsorption of Sodium Hydroxide by Platinized Platinum in Oxygen.—If a sodium hydroxide solution is in contact with platinized platinum in an oxygen atmosphere, an apparent adsorption of the base takes place.

Table VIII

Adsorption of Sodium Hydroxide in the Presence of Sodium Chloride by Platinized Platinum in a Hydrogen Atmosphere

Concn. of NaCl, *N*	Init. concn. of base, *N*	Final concn. of base, *N*	Micromoles adsorbed
0.1	0.0099	0.0098	3.5
.1	.00097	.00080	5.7
.1	.00011	.0000	2.4
1	.0099	.0097	6.3
1	.00475	.00456	6.7
1	.00095	.00075	7.1
1	,00022	.00005	6.0
1	.00013	.00001	3.8
3	.00998	.00972	9.1
3	.00097	.00074	7.9

However, this is not a true adsorption, the amount of base which disappears from the solution increases the longer the oxygen is passed through. Some figures are shown in Table IX.

Table IX

Apparent Adsorption of Sodium Hydroxide by Platinized Platinum in Oxygen

Concn. of base, *N*................	0.01	0.001	0.001	0.001	0.0001
Passage of oxygen, hours...........	$^1/_6$	$^1/_6$	3.5	24	$^1/_6$
Mml. of base removed from soln.....	2.8	1.8	3.2	4.4	0.36

This abnormal behavior can be explained by a reaction between the platinum black and the oxygen. The strong hexa-aquoplatinic acid is formed, which neutralizes part of the sodium hydroxide in the solution. The longer the oxygen is passed through, the more of the platinic acid is formed and the more base is neutralized. That this interpretation is right could be proved in the following way: 0.001 *N* sodium hydroxide was treated for twenty-four hours with oxygen in the presence of the platinized platinum. The solution was withdrawn and the vessel washed out twice with water in an oxygen atmosphere. The last wash water was practically neutral. Then water was added again and hydrogen passed through, whereupon the reaction did not change; at least the wash water required less than 0.02 cc. of 0.01 *N* hydrochloric acid with methyl red as an indicator. After two washings in hydrogen we turned back to oxygen. The first wash water was distinctly alkaline and took 0.11 cc. of 0.01 *N* hydrochloric acid; the second portion, 0.03 cc. Continued alternate washings in oxygen and hydrogen did not change the reaction of the water. The phenomena described are well reproducible from a qualitative point of view. The sodium salt of the hexahydroxyplatinic acid which was formed in the oxygen atmosphere and adsorbed by the platinized platinum is reduced to metallic platinum and sodium hydroxide in a hydrogen gas current but, as we have seen, the platinized platinum adsorbs a trace of base in a hydrogen atmosphere very strongly. In order to liberate the base formed, oxygen has to be passed through again. It is hard to say whether the formation of the hexahydroxyplatinic acid is the only factor responsible for the disappearance of the hydroxide from the solution. It is still possible that part of the hydroxide is removed by some kind of an adsorption process.

Summary

1. The irregularities observed in the measurement of P_H of unbuffered solutions with the hydrogen electrode, using platinized platinum as an electrode, are probably due to adsorption phenomena.
2. Frumkin and Donde's experiments with neutral salts in contact with platinum black were repeated with a platinized electrode. It was confirmed that platinized platinum in a hydrogen atmosphere adsorbs the cation from a neutral salt solution and an equivalent amount of free acid is found in the solution.
3. Hydrochloric acid is not adsorbed by platinized platinum in a hydrogen atmosphere, whereas a small but distinct adsorption takes place in oxygen.
4. Sodium hydroxide is strongly adsorbed by platinized platinum in a hydrogen atmosphere; a maximum occurs at a final concentration of about 0.0007 *N*. Sodium chloride increases the adsorption, whereas in the presence of large amounts of this salt the maximum disappears.
5. Sodium hydroxide is apparently adsorbed by platinized platinum in an oxygen atmosphere. This, however, is not true adsorption, but probably a neutralization of sodium hydroxide by the hexahydroxyplatinic acid which is formed by the action of oxygen on the platinized platinum.
6. On the same basis the abnormal behavior of ammonium chloride solutions in contact with platinized platinum in an oxygen atmosphere has been explained.

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