3. In very dilute acid solutions in the presence of sodium acetate the sensitiveness of the tests for cobalt and iron is increased but not for copper.

ITHACA, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MICHIGAN AGRICULTURAL COLLEGE EXPERIMENT STATION, No. 30]

# ADSORPTION BY ACTIVATED SUGAR CHARCOAL

## II.[1] ADSORBABILITY OF HYDROGEN AND HYDROXYL IONS

BY ELROY J. MILLER

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Adsorbent charcoals are generally attributed with the power of adsorbing hydrogen and hydroxyl ions equally. In this paper data are presented which show that this assumption is based on erroneous experimental evidence. The data presented also indicate that the hydroxyl ion is last instead of first in the order of decreasing adsorbability of anions by pure charcoal.

Michaelis and Rona[2] after a study of the adsorbability of the anions of a series of ammonium salts by blood charcoal reported that the hydroxyl ion was adsorbed to a greater extent than any other of the series which included $SO_4 < Cl < Br < I < CNS < OH$.

Rona and Michaelis[3] attempted to arrive at the relative adsorbability of hydrogen and hydroxyl ions by determination of the increase in adsorption of hydrochloric, nitric and sulfuric acids and of potassium and sodium hydroxides due to the presence of increasing amounts of neutral salts. They found that while the hydroxides alone were not adsorbed to quite the same extent as the acids alone, the addition of neutral salts to each, nevertheless, caused approximately the same increase in adsorption. On the basis of these findings they concluded that, within the limits of their experiments, the adsorbability of hydrogen and hydroxyl ions by charcoal is the same. These conclusions have been widely accepted and utilized in the explanation of the adsorbent action of charcoal and of adsorption phenomena in general.[4]

From previous work with pure activated sugar charcoal the writer surmised that the results reported by Rona and Michaelis with blood charcoal might conceivably be due to factors other than pure adsorption by the char-

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[1] Published by permission of the Director of the Experiment Station.

[2] Michaelis and Rona, *Biochem. Z.*, **94**, 240 (1919).

[3] Rona and Michaelis, *ibid.*, **97**, 85 (1919).

[4] (a) Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., **1921**, p. 233. (b) Freundlich, "Kapillarchemie," third ed., Akademische Verlagsgesellschaft m. b. H., Leipzig, **1923**, p. 287. (c) Svedberg, "Colloid Chemistry," Chemical Catalog Co., **1924**, p. 177. (d) Gyemant, *Kolloid Z.*, **28**, 103 (1921). (e) Schilow and Lepin, *Z. physik. Chem.*, **94**, 25 (1920). (f) Tanner, *J. Ind. Eng. Chem.*, **14**, 442 (1922). (g) Chaney, Ray and St. John, *Ind. Eng. Chem.*, **15**, 1253 (1923).

coal. Their experiments were, therefore, repeated, using the pure, ash- and nitrogen-free charcoals prepared in the manner described in a previous paper.[5]

## Adsorption of Acid in Sodium Chloride Solutions

One hundred cc. of 0.01 *N* hydrochloric acid alone and in 0.5 *N*, *N* and 2 *N* sodium chloride solutions was shaken with 1.000 g. of freshly ignited charcoal. After 24 hours the equilibrium concentrations were determined by titration with 0.02 *N* carbon dioxide-free sodium hydroxide, using as indicator the sodium salt of Phenol Red.

The standard hydrochloric acid used in this investigation was prepared from constant-boiling hydrochloric acid. The sodium and potassium hydroxides were carbonate-free and the sodium and potassium chlorides were prepared from C. P. brands by repeated recrystallization from conductivity water. All of the volumetric flasks, burets and pipets were recalibrated.

The results which are averages of two or more separate sets of experiments appear in Table I.

TABLE I

ADSORPTION OF HYDROCHLORIC ACID FROM SOLUTIONS OF MIXTURES OF 0.01 *N* HYDROCHLORIC ACID AND SODIUM CHLORIDE

| | | | | |
|---|---|---|---|---|
| Soln. in NaCl, *N* | .... | 0.5 | 1.0 | 2.0 |
| Equilib. concn. after absorpn., HCl, *N* | 0.0074 | .0071 | .0069 | 0.0066 |
| HCl adsorbed per g. of charcoal, millimoles | .26 | .29 | .31 | .34 |

From the data in Table I it was evident that the addition of sodium chloride increased the adsorption of hydrochloric acid. Since these results were not contrary to expectations and it was evident that similar results would be obtained with other inorganic acids further work was not done on them.

## Adsorption of Alkalies in Salt Solutions

The adsorption of sodium and potassium hydroxides alone and in various concentrations of sodium chloride and potassium chloride, respectively, was next determined.

One hundred cc. of 0.0100 *N* alkali alone and in 0.1 *N*, *N* and 2 *N* salt solutions were shaken with 1 g. of freshly ignited charcoal. After 24 hours the charcoal was filtered off and the equilibrium concentrations determined by titration with 0.02 *N* hydrochloric acid, again using phenol red as indicator. In these operations the alkaline solutions take up carbon dioxide from the air and it is essential in this titration to boil off the carbon dioxide after the later additions of standard acid until the red color of the indicator is permanently discharged and a lemon-yellow color remains.

The averages of three or more sets of experiments are given in Table II. The data indicate definitely that pure charcoal does not adsorb these hydroxides either from solutions in water alone or in the presence of high concentrations of salts. As a matter of fact, it not only does not adsorb these hydroxides from the solutions but actually sets free additional base through hydrolytic adsorption of the dissolved salt. In order to obtain

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[5] THIS JOURNAL, **46**, 1150 (1924).

TABLE II

ADSORPTION OF ALKALIES FROM SOLUTIONS OF MIXTURES OF 0.01 *N* ALKALIES AND SALTS

| | NaOH in NaCl | | | | KOH in KCl | | | |
|---|---|---|---|---|---|---|---|---|
| Soln. in salt, *N* | .... | 0.5 | 1.0 | 2.0 | .... | 0.5 | 1.0 | 2.0 |
| Equilib. concn. of alkali after adsorption, *N* | 0.100 | 0.0100 | 0.0101 | 0.0103 | 0.0100 | 0.0101 | 0.0102 | 0.0103 |

definite proof that hydrolytic adsorption of the dissolved salt takes place even in the presence of concentrations of alkali as high as 0.01 *N*, the following experiment was carried out.

Instead of the usual 1g. sample of charcoal used in the above experiments a much larger one was employed in order to secure a greater effect. To 100 cc. of a solution of 0.01029 *N* potassium hydroxide in 2 *N* potassium chloride was added 13.45 g. of freshly ignited charcoal. After the mixture had been shaken for one hour the charcoal was filtered off and the concentration of the potassium hydroxide in the filtrate determined. A 50cc. portion of the filtrate required 40.04 cc. of 0.02 *N* hydrochloric acid for neutralization. The concentration of alkali in solution had increased from 0.01029 *N* to 0.01601 *N*. The charcoal was then washed several times on the Büchner funnel and finally once by suspension and boiling in approximately 150 cc. of water. The remainder of the filtrate and the washings were titrated and found to require 46.72 cc. of 0.02 *N* hydrochloric acid.

It is evident that additional potassium chloride was decomposed in the process of washing out the remaining, mechanically-held salt solution from the charcoal, but this washing is essential to remove all of the added alkali so that the excess of alkali set free by hydrolytic adsorption of the potassium chloride may be determined. The total amount of alkali in the filtrate was equivalent to 86.76 cc. of 0.02 *N* potassium hydroxide or 1.7352 millimoles, while the total amount of potassium hydroxide added in the original salt solution was equivalent to 51.48 cc. of 0.02 *N* potassium hydroxide or 1.0296 millimoles. There was then an excess of potassium hydroxide equivalent to 35.28 cc. of 0.02 *N* potassium hydroxide or 0.7056 millimole and if this excess were due to hydrolytic adsorption of the potassium chloride, there should be on the charcoal an equivalent quantity of hydrochloric acid. That this was the case was demonstrated by one of the methods described in another place.[6] The charcoal was extracted thrice with an excess of 0.02 *N* sodium hydroxide solution. In the first extraction 51.29 cc. and in each of the second and third extractions 25.63 cc. of 0.02 *N* sodium hydroxide solution were used. The charcoal was washed and boiled with conductivity water after each extraction. The combined filtrates and washings required 67.12 cc. of 0.02 *N* hydrochloric acid for neutralization. The acid on the charcoal had neutralized 35.43 cc. of 0.02 *N* sodium hydroxide solution or 0.7086 millimole which corresponds quantitatively with the 0.7056 millimole of potassium hydroxide in

[6] Ref. 5, p. 1156.

excess after adsorption. In other words, hydrolytic adsorption of the potassium chloride takes place even in the presence of 0.01 *N* potassium hydroxide solution, the charcoal adsorbing hydrochloric acid and setting free potassium hydroxide. It is indeed surprising that charcoal should adsorb easily detected quantities of hydrochloric acid from an alkaline solution of potassium chloride. This experimental fact, as well as the others reported in this and in previous papers, however, has been demonstrated many times with numerous entirely distinct samples of activated sugar charcoal.

## Concentration Relationships

It is evident from the data in Table II that the higher the concentration of the salt in solution the greater the increase in concentration of alkali and concomitant adsorption of acid by the charcoal. There is an equilibrium established which depends upon the concentrations of alkali and salt in solution and the amount of acid on the charcoal. This equilibrium may be shifted by varying either or both the concentration of the alkali or salt. Thus, the amount of acid on the charcoal increases when the concentration of salts is increased. On the other hand, when the salt is completely removed and the concentration of the alkali increased, part of the acid leaves the charcoal and neutralizes some of the alkali until a new equilibrium is established. If this process is repeated a number of times the acid is entirely removed from the charcoal.

## Negative Adsorption of Bases

When the data in Table II were obtained it was noticed that there seemed to be a very slight but perceptible increase in concentration of the sodium and potassium hydroxides after the treatment with charcoal. The total amount of alkali in solution, however, never exceeded that added and it was at once suspected that a negative adsorption was operating to produce this effect. In order to test this point, larger samples (18 g.) of charcoal were used with 0.01 *N* and 0.005 *N* potassium hydroxide solutions. The concentrations of the solutions before and after adsorption and the total amount in solution after treatment were determined. The results in Table III were obtained.

Table III

Negative Adsorption of Potassium Hydroxide

| Concn. of soln. | | Millimoles of KOH in solution | |
|---|---|---|---|
| Before adsorption *N* | After adsorption *N* | Before adsorption | After adsorption |
| 0.010104 | 0.010496 | 1.0104 | 1.0114 |
| .005013 | .005208 | 0.5013 | 0.5013 |
| .005013 | .005208 | .5013 | .5009 |

The data show, first, that there is an increase in concentration of the solution when in contact with the charcoal and second, that the total amount of alkali present does not increase. The only explanation for these facts is that the potassium hydroxide is negatively adsorbed, that is, the charcoal adsorbs some of the water and leaves the alkali concentrated in a smaller volume.

Negative adsorption of potassium hydroxide was also demonstrated by gravimetric determination of potassium in the solutions before and after adsorption. Negative adsorption of sodium hydroxide was also observed. For the sake of brevity the data are omitted.

## Effect of Concentration on Negative Adsorption

According to the Gibbs adsorption theorem those substances that lower the surface tension with increasing concentration are positively adsorbed at an interface, while those substances which raise the surface tension with increasing concentration are negatively adsorbed. There are no data in the literature which indicate that the strong inorganic bases that raise the surface tension of water are negatively adsorbed by charcoal. It was, therefore, of interest to study the effect of concentration on negative adsorption. This was carried out as follows.

Eighteen g. samples of charcoal[7] were placed in platinum shaped, silica crucibles with tightly fitting covers (crucibles and covers were ground with carborundum powder) and heated to a temperature of about 1200°. The charcoal, when it had cooled to room temperature, was added to 100cc. portions of the alkaline solutions in Pyrex Erlenmeyer flasks, the mixture thoroughly shaken during the course of one hour to insure complete wetting, and the charcoal then filtered off in a small Büchner funnel with the aid of slight suction. Care was taken to avoid loss of water vapor by the use of prolonged suction. The rubber tube leading from the suction flask was closed by means of a screw clamp as soon as sufficient vacuum had been obtained to insure filtration. Loss of water vapor in this way was kept within 0.15 g. The concentration of the filtrate was then determined by titration with 0.02 *N* hydrochloric acid. Phenol red was used as indicator and the precautions before mentioned with regard to boiling off the carbon dioxide were observed.

The data for solutions of potassium hydroxide of various concentrations are given in Table IV. The values are the averages of at least three separate determinations.

TABLE IV

EFFECT OF CONCENTRATION ON NEGATIVE ADSORPTION OF POTASSIUM HYDROXIDE

| Concn. of soln. |  |  |  |
|---|---|---|---|
| Before adsorption *N* | After adsorption *N* | Increase in concn. *N* | Millimoles of KOH "negatively adsorbed" per g. of charcoal |
| 0.005012 | 0.005215 | 0.000203 | 0.00113 |
| .010104 | .010486 | .000382 | .00212 |
| .02019 | .020725 | .000535 | .00297 |
| .03989 | .040823 | .000933 | .00518 |
| .09960 | .10114 | .00154 | .00855 |

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[7] It is essential that freshly ignited charcoal be used, for charcoal exposed to air quickly absorbs appreciable quantities of water vapor. In a test to determine how much of a factor this might be, 17.87 g. of charcoal took up 4.10 g. of water or more than 20% of its weight.

From the results presented in Table IV it is evident that "negative adsorption" increases with increase in concentration but not proportionally. The amount of water adsorbed decreases with increase in concentration of the alkali which would naturally be expected from a consideration of osmotic effects. It should be more difficult to adsorb the water from the more concentrated solutions.

Negative adsorption of bases is in striking contrast to the positive adsorption of acids. It agrees very well, however, with the general behavior of these ash-free charcoals toward acids and bases in attempts to remove them after treatment. When the charcoal has been added to a solution of base it is a very simple matter to free the charcoal completely from the last traces of that base. Boiling once or twice with water removes it quantitatively. With acids it is quite another matter. It is very difficult, if not entirely impossible, to free charcoal from adsorbed acid by the simple process of washing with water. With pure, ash-free charcoal it is possible to obtain quantitative information on this procedure as is illustrated by the following experiments.

Two and three-tenths g. of charcoal had adsorbed 0.294 millimole of hydrochloric acid. The charcoal was suspended in 200 cc. of conductivity water at room temperature. After the charcoal had been separated, the filtrate was found to be strictly neutral in reaction. The charcoal was again suspended in 200 cc. of water, the mixture boiled and filtered while hot. The filtrate was slightly acid. Fifteen such extractions, in which the length of time of boiling varied from five minutes to eight hours, yielded a total of 0.15 millimole of hydrochloric acid. The charcoal was then boiled once with an excess of 0.02 $N$ sodium hydroxide solution and 0.142 millimole was neutralized. Of the 0.294 millimole of hydrochloric acid originally on the charcoal, 0.293 was accounted for. As an additional check, the chloride content of the extracts was determined by titration with silver nitrate and found to be equivalent to 0.291 millimole.

The experiment illustrates clearly the difficulty of removing the last traces of adsorbed acids from charcoal by washing with water alone.

## Positive and Negative Adsorption from Salt Solution

In a previous publication the writer stated that, from preliminary experiments, it was indicated that adsorption was entirely hydrolytic in the case of some salts, while with others it was partially hydrolytic and partially molecular. Subsequent work has verified the earlier statement. Adsorption of a series of potassium salts was studied.

A mixture of 200 cc. of approximately 0.02 $N$ salt solution with 13.5–18 g. of freshly ignited charcoal was shaken. After three or four hours the charcoal was filtered off, and the amount of potassium hydroxide set free and the increase or decrease in concentration of the potassium were determined. The same precautions that have been described in connection with the work on negative adsorption were observed in filtering off the charcoal and in titrating the free base. The potassium in the solutions before and after adsorption was determined gravimetrically as potassium chloroplatinate.[8]

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[8] The writer is indebted to Mrs. Marion G. Musselman for the potassium determinations made in the course of this investigation.

The results are summarized in Table V.

TABLE V

ADSORPTION FROM SOLUTIONS OF POTASSIUM SALTS

| Solution Potassium | Concn. in potassium Before adsorption $N$ | Concn. in potassium After adsorption $N$ | Increase or decrease in concn. of potassium $N$ | Millimoles of KOH found in soln. after adsorption |
|---|---|---|---|---|
| Sulfate | 0.019944 | 0.020512 | 0.000568+ | 0.3452 |
| Nitrate | .019520 | .020168 | .000648+ | .6560 |
| Chloride | .020024 | .020696 | .000672+ | .3846 |
| Oxalate | .020200 | .021072 | .000872+ | .3708 |
| Citrate | .019680 | .019768 | .000088+ | .... |
| Benzoate | .019632 | .009768 | .009864− | 1.5860 |
| Salicylate | .019608 | .008568 | .011040− | 1.5240 |

Inspection of the data in Table V reveals a number of interesting points. First of all, it is plain that the sulfate, nitrate, chloride and oxalate of potassium are not molecularly adsorbed. The concentration of potassium in these solutions is appreciably greater after adsorption, and if no further examination of the solutions were made, it would immediately be concluded that the adsorption of these salts is negative or that the increase in concentration is due to displacement of adsorbed potassium from the charcoal. In these experiments, however, the latter possibility is precluded because the charcoal is free from adsorbed impurities. Furthermore, a control experiment was carried out but not a trace of potassium could be detected in the extract of 18 g. of the charcoal. It is evident, then, that in so far as the potassium ions in these solutions are concerned, the adsorption is negative. Column five, however, shows that appreciable quantities of potassium hydroxide appeared in the solutions after adsorption and that there must have been adsorbed by the charcoal an equivalent quantity of the corresponding acid. Examination of these charcoals after adsorption showed that also to be true. There was, therefore, a decrease in concentration of the negative ion and the adsorption of that ion from solution was positive and exactly equivalent to the number of millimoles of potassium hydroxide set free. The data prove conclusively that the adsorption of these salts by activated sugar charcoal was entirely hydrolytic, since absolutely no potassium was adsorbed along with the negative ion; only the acid arising from hydrolysis of the salt was adsorbed.

Adsorption from solutions of potassium benzoate and potassium salicylate is quite different from the instances just considered. It will be observed that the concentration of potassium after adsorption had decreased to approximately half its former value. It is also evident that the potassium remaining in solution was largely in the form of potassium hydroxide along with a smaller quantity in the form of the potassium salt. The charcoal had adsorbed a large portion of the negative ion as the acid, and also a considerable quantity in the form of the potassium salt. Adsorption from these solutions was both molecular and hydrolytic in nature. It was also decidedly positive adsorption.

### Bearing of Results on Orders of Adsorbability

The order of adsorbability of various ions usually has been arrived at by determination of the adsorption of a series of salts with a common cation or common anion. In these determinations the factor of hydrolytic adsorption was either entirely overlooked or ignored and the assumption tacitly made that the salt was molecularly adsorbed as such. From the results obtained with the potassium salts and activated sugar charcoal it is evident that there are a number of factors such as negative adsorption and hydrolytic adsorption which must be considered in attempting to determine the order of adsorbability of a series of ions or of a series of salts. It is obvious that a comparison of the adsorption of various salts is complicated by the fact that some salts are entirely hydrolytically adsorbed while others are both hydrolytically and molecularly adsorbed. One thing is certain, however, and that is that the bases such as potassium and sodium hydroxides do not come first in the order of decreasing adsorption of salts and bases by pure charcoal as is usually given in texts on colloid chemistry.[9] It would seem that the logical place should be at the end of the series since the adsorption from their solutions is purely negative. The same would seem to hold true for the hydroxyl ions in the order of decreasing adsorbability of anions. It should be last instead of first. On the other hand, it is obvious that the hydrogen ion does not come last in the order of decreasing adsorbability of cations for, as a general rule, acids are adsorbed to a greater extent than their salts and in the adsorption from salt solutions the hydrogen ion is adsorbed along with the anion in preference to the cation of the salt.

### Effect of the Hydroxyl Radical on Adsorption

It is an interesting and significant fact that pure charcoal not only does not adsorb the strong inorganic hydroxides but the introduction of the hydroxyl group or radical into an organic acid results in an hydroxy acid which is less adsorbed than the unsubstituted acid.[10] The significance of these facts becomes evident at once when they are considered in the light of their effects on interfacial tensions.

### Applicability of the Gibbs Adsorption Theorem to Charcoal-Solution Systems

Since there is no method known whereby the interfacial tension of a solid-liquid system can be measured, there is no way of determining

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[9] Freundlich, Ref. 4 b, p. 274. Ref. 4 c.

[10] Bartell and Miller, This Journal, **45,** 1106 (1923).

whether the relationships of the interface between charcoal and aqueous solution fit in with the adsorption theorem of Gibbs except by uncertain analogy with liquid-gas or liquid-vapor systems. The theorem seems to apply to charcoal-solution systems, but there are a number of discrepancies. Chief among these are the apparent positive adsorption of the strong inorganic bases[11] which invariably raise the surface tension of water and also the apparent positive adsorption of many salts whose solutions have surface tensions which vary but little from that of pure water.

A review of the adsorption of these substances by pure activated sugar charcoal reveals the fact that these anomalies do not appear and that the data make the analogy between adsorption at charcoal-solution interface and adsorption at liquid-liquid and liquid-gas interfaces more complete. In the first instance pure charcoal does not adsorb the strong inorganic bases which is satisfactory as far as it goes but, theoretically, these substances that raise the surface tension with increasing concentration should be negatively adsorbed. Evidence has been presented which indicates that this, too, is true for charcoal-solution systems. The charcoal adsorbs the water and leaves the solution more concentrated with respect to the alkali. In the second instance, the results obtained in a study of the hydrolytic adsorption of salts[5] show that the selectivity of adsorption for those substances which lower the surface tension, manifests itself in the adsorption of that product of hydrolysis of the salt which lowers the surface tension and rejection of that product which raises the surface tension. That is, the acid resulting from hydrolysis is adsorbed while the base is set free and remains in solution.

When the effect of the hydroxyl group is considered in the light of its relation to surface tension, it is seen that the behavior of charcoal-solution systems is again similar to that of the other systems. For example, the introduction of one and two hydroxyl groups into succinic acid to form malic and tartaric acids, respectively, is accompanied by an increased raising of the surface tension of their solutions over that of succinic acid solutions.[12] This effect is at once reflected in the adsorption of these substances from aqueous solution by charcoal. Malic acid is less adsorbed than succinic acid, and tartaric acid is in turn less adsorbed than malic. The introduction of the amino group causes a still greater decrease in adsorption. This again is in complete harmony with the findings of Harkins, Davies and Clark[13] that the amino group is more polar than the hydroxyl group. These facts make it seem entirely probable that the charcoal plays the same role in a charcoal-solution interfacial system that the organic liquid plays in organic liquid-aqueous solution systems and that the

[11] Ref. 4b, p. 83.

[12] King and Wampler, This Journal, **44**, 1894 (1922).

[13] Harkins, Davies and Clark, *ibid.*, **39**, 541 (1917).

Langmuir-Harkins theory of the effect of polar groups applies to the adsorption from solution by charcoal. The theory of Michaelis and Rona[14] that the adsorption of organic substances by charcoal is a manifestation of the attraction of the carbon of the charcoal for the carbon atoms of the carbon compound fits in with the Langmuir-Harkins theory of the existence of electromagnetic force fields at the surfaces of solids and liquids. The attractive forces of the carbon of the charcoal for the carbon of the solute are opposed by the tendency of the polar groups to keep the solute in the body of the solution. This opposing effect is manifested in the cutting down of the adsorption. That the experimental facts coincide with this theory has been abundantly illustrated in the data for the adsorption of hydroxy and amino organic acids by activated sugar charcoal.[10] The introduction of the hydroxyl and amino groups invariably resulted in a decrease in adsorption.

## Bearing of Results on the Explanation of the Adsorption of Several Solutes

Lachs and Michaelis[15] found that potassium hydroxide decreased very much the adsorption of potassium chloride by blood charcoal. Bancroft's explanation[16] of this is that the strongly adsorbed hydroxyl ion cuts down the adsorption of the chloride ion. In the light of the data presented in this paper Bancroft's explanation is untenable, for the hydroxyl ion is not strongly adsorbed. The more probable explanation is that the presence of the high concentration of potassium hydroxide prevented the hydrolysis of the potassium chloride. Under those conditions the chloride content did not decrease, since potassium chloride, as such, is not adsorbed and only the hydrochloric acid arising through hydrolysis is adsorbed.

On the other hand, Lachs and Michaelis found that the presence of small amounts of sulfuric acid in the potassium chloride solution increased markedly the adsorption of the chloride ion. This, Bancroft points out, is in accord with the results of Osaka that potassium chloride is adsorbed more than potassium sulfate or sodium sulfate. This explanation, likewise, is not the correct one, since it is incorrect to say that potassium chloride is adsorbed more than potassium sulfate, for it is only the acids resulting from the hydrolysis of these salts that are adsorbed. Here again the true explanation of the effect of the sulfuric acid on the adsorption from the potassium chloride solution is that the adsorption of the chloride ion is increased by the presence of the higher concentration of hydrogen ions which are adsorbed along with the chloride ions as hydrogen chloride. When adsorption is from potassium chloride solution alone, the hydrogen ions must come from the water, and the potassium hydroxide that is set free soon prevents further hydrolysis of the salt. The addition of sulfuric acid

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[14] Michaelis and Rona, Ref. 3, p. 57.

[15] Lachs and Michaelis, *Z. Elektrochem.*, **17**, 1 (1911).

[16] Ref. 4 a, p. 114.

furnishes hydrogen ions without hydrolysis and simultaneous formation of potassium hydroxide and more hydrochloric acid is therefore adsorbed.

## Summary

1. The data presented in this paper indicate that the view that hydrogen and hydroxyl ions are equally adsorbable by charcoal is based on erroneous experimental evidence.

2. It has been demonstrated that pure, activated sugar charcoal adsorbs more hydrochloric acid from mixtures of sodium chloride and hydrochloric acid than from hydrochloric acid alone.

3. It has been demonstrated that the addition of sodium chloride to sodium hydroxide and of potassium chloride to potassium hydroxide does not cause these hydroxides to be adsorbed. On the contrary, the addition of these salts results in an increase in concentration of alkali due to hydrolytic adsorption, whereby hydrochloric acid is adsorbed and an equivalent amount of base is set free.

4. Evidence has been presented which proves that the strong inorganic bases are "negatively adsorbed" by pure charcoal.

5. Adsorption from solutions of some salts is exclusively hydrolytic in nature, while from others it is partially hydrolytic and partially molecular.

6. It has been pointed out that the adsorption of electrolytes by activated sugar charcoal is in accord with the adsorption theorem of Gibbs, whereas the results obtained with blood charcoal under the same conditions are anomalous.

7. An explanation is offered for the effect of acids and bases on adsorption from salt solutions.

EAST LANSING, MICHIGAN

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[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

# OPTICAL ROTATION AND ATOMIC DIMENSION. IV[1]

BY D. H. BRAUNS

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The third article of this series[1] showed that the differences Cl-F, Br-Cl- and I-Br in specific rotations of monohalogen-triacetyl-*l*-arabinose are also approximately proportional to the differences in atomic diameters recorded by Bragg. The specific rotations for chloro- and bromo-tri-

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[1] This article is a continuation of "Fluoro-acetyl Derivatives of Sugars. III. Optical Rotation and Atomic Dimension" [THIS JOURNAL, **46**, 1484 (1924)]. The investigation of the fluoro-acetyl derivatives of sugars has not been concluded, as other fluoro-acetyl derivatives as, for example, of maltose, have been prepared. Fischer's bromination method yielded, however, a crystalline dibromo maltose derivative, instead of a monobromo derivative as reported by Fischer. Their preparation and general properties will be reported in a forthcoming paper in THIS JOURNAL.