

THE ADSORPTION OF HYDROGEN IONS BY
CHARCOAL

(Abstract from original paper.)

I. J. JENKS, STATE TEACHERS COLLEGE, DEKALB

INTRODUCTION

It is a well established principle of colloid chemistry that the ions of an electrolyte are adsorbed by certain precipitates and the similarity of this adsorption of gases by charcoal has been pointed out.

W. Mansfield Clark in "The Determination of the Hydrogen Ion" (Page 34) mentions the work of Bovie as showing the adsorption of both hydrogen and hydroxyl ions by charcoal, when present during an electrometric titration. Bovie (J. Med. Research 295-317-1915) found that the presence of .5g of Kahlbaum's animal charcoal in a 0.01-N solution of alkali strongly depressed the hydroxyl ions concentration and prevented also the appearance of hydrogen when the solution is titrated with .01-N HCl, the usual symmetrical curve being markedly flattened out on both sides, with the vertical rise which marks the end point entirely obliterated.

Bovie points out the similarity of the effect to that obtained in a true "buffer" solution, but attributes the buffer effect to adsorption of both hydrogen and hydroxyl ions by the charcoal.

Two objections to this interpretation of Bovie's experimental curve may be noted. In the first place it is not common to find both hydrogen and hydroxyl ions equally adsorbed; usually adsorption of hydrogen ions is much more marked. In the second place, Bovie did not take into account the possibility of salts contained within the charcoal, in spite of the fact that animal or bone charcoal almost certainly contains calcium phosphates which are among the most effective buffers. (See A. H. Clark, Masters Thesis, U. of C. 1920, Pages 19-23, 58-65.)

This research was therefore undertaken to investigate this factor and to determine whether pure charcoal shows

a similar buffer action. The results show that the apparent buffer effect produced by animal charcoal is probably caused by chemical action of the alkali or acid added upon the adsorbed gases and salts contained as impurities in the charcoal, rather than by any true adsorption by the charcoal itself. Obviously most animal charcoal contains small quantities of impurities such as phosphates, carbonates, tartrates and oxalates together with some salts of calcium, sodium, or potassium and also adsorbed gases such as carbon dioxide and hydrogen sulfide.

To test their effects, titrations were made with the various grades of commercial charcoal obtainable, and with charcoal made from pure cane sugar and containing no mineral salts. The results obtained in these titrations are plotted as curves on which the conclusions are based.

The titrations were made with a simple titration apparatus devised in the laboratory and similar to one described in Central Scientific Co. Bulletin No. 86. This method of titrations is especially suited for the purpose, because it indicates the actual hydrogen ion concentration at all times and also gives the neutralization point. Furthermore, the charcoal suspensions are so black that indicator changes could not be clearly marked.

EXPERIMENTS

The first experiment was made with a sample of commercial animal charcoal bought on the market, the titration being made with N/20 sodium hydroxide and N/20 HCl. Curve I, Plate I, represents the normal curve for this alkali and acid.

A second titration was then made by first running in 25cc. of the alkali, then adding one gram of the charcoal. No change was observed in the voltage or Ph. reading upon the addition of the charcoal, but as the titration was carried out the curve (curve II) follows the normal until near the neutral point; then instead of showing an abrupt drop it is straightened out, indicating the elimination of the hydrogen ions of the acid by adsorption or by the action of some substance which interacts with the

acid. Even the addition of a large excess of the acid brings the Ph. value down to slightly below the neutral point.

The experiment was then repeated, using oxalic acid instead of the hydrochloric, with practically the same results.

These curves are quite different from that of Bovie, as his curve is affected on both sides of the neutral point. That is, his curve is lowered much below the normal curve before reaching the neutral point, while the curve for this charcoal is only affected on the acid side of the line.

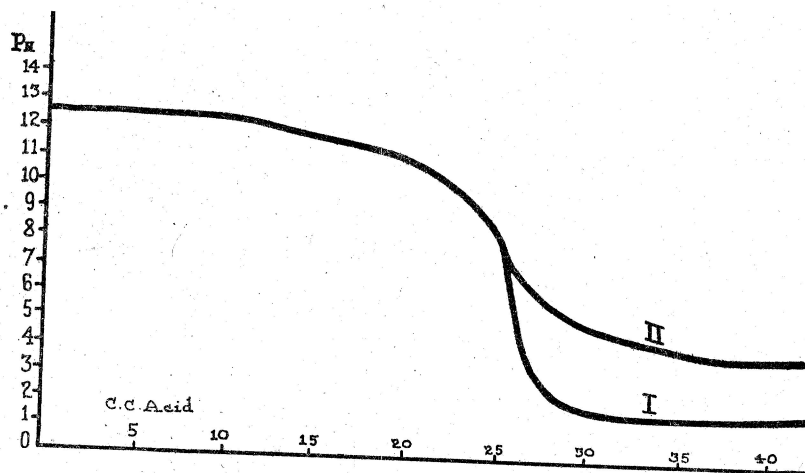


Plate I.

If adsorption is the cause of the effect, there is here no evidence of the adsorption of the hydroxyl ions. On the other hand the results could have been due to the presence of alkaline buffer salts in the charcoal.

These titrations were then reversed, starting with the acid, taking the voltage of Ph. reading, then adding the charcoal and completing the titration with the alkali. On adding the charcoal to the acid a sudden rise in the Ph. reading was noted, the concentration of the hydrogen ions being reduced nearly to the neutral point.

That alkaline reactions are responsible is indicated by the fact that neutralization was complete at about 10 cc. while in the normal curve 25cc. were required. If

adsorption were involved, the active concentration of ions might have been reduced, but the same amount of alkali should have been required to neutralize the acid.

There is here again no evidence of the adsorption of hydroxyl ions. (Curve IV, Plate III, shows this curve.)

Upon examination of this charcoal it was found to be very impure, containing considerable ash, and when treated with hot HCl it gave off carbon dioxide, hydrogen sulfide, and probably other gases. The presence of sulfides and carbonates as well as phosphates in the ash would allow an interaction with the hydrogen ions to cause the effect noted.

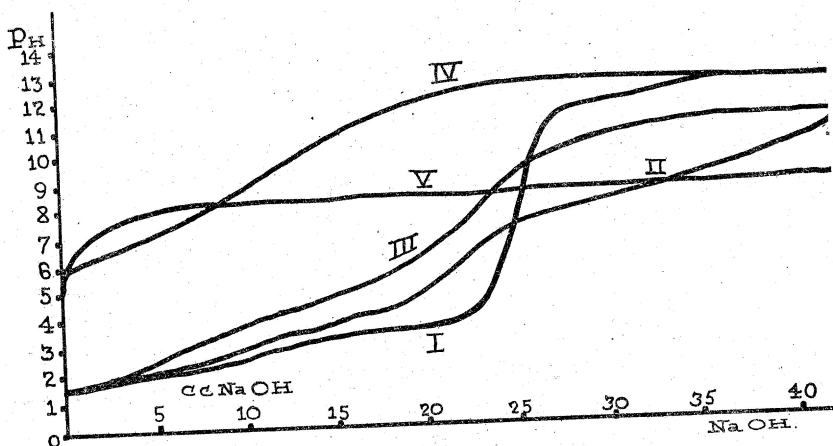


Plate III.

A sample was then boiled with strong hydrochloric acid washed with boiling distilled water and then heated to drive off the adsorbed gases, and a titration was made using one gram of this treated charcoal. The curve is much straighter, the charcoal rise from acid to alkali with no abrupt rise at the neutral point. (Curve IV). This is similar to Bovie's, and seems to show the consumption of both hydrogen and hydroxyl ions. The sample, however, was still very impure, as on burning there was considerable ash present.

The boiling with acid neutralized the alkaline salts present but evidently did not remove all the impurities, and neutral buffer salts may still have been present.

A sample of "Norit" purified charcoal was then tried in the same way. This gave a very similar curve to the commercial grade that had been treated with acid, except that the curve was slightly lower. This sample was also found to contain considerable ash and was quite impure. (Curve II).

A sample of "Norit" purified charcoal was then tried found to give about the same results as the previous commercial charcoal; however, when tried with oxalic acid instead of rising gradually after neutralization, as with the HCl, upon adding the alkali the first 5 cc. gave a sudden rise, then the curve is held to almost a horizontal line which could only be raised slightly by an excess of alkali. A large quantity of alkaline material was shown to be present since so little alkali was necessary for neutralization. (Curve V).

On the other hand, the failure of the hydroxyl ions to show up may be due to the presence of neutral buffer salts. This curve is also shown on Plate III, Curve V.

Samples of "Super-Filchar", both Pharmaceutical and Sugar grades, were tried with results similar to those of the other purified charcoals with the exception of their being slightly acid in their reactions.

Both samples contained considerable ash, showing them to contain salts of some kind.

Acids stronger than the N/20 were then tried with the different charcoals. Here it was found that instead of a gradual rise in the curve as with the weaker acids, the curve remained horizontal until near the neutral point, then rose abruptly in a vertical line to nearly the full concentration of the hydroxyl ion, similar to that for the acid and alkali alone.

This action is similar to that of other buffer solutions, such as acetates, and phosphates which do not give a buffer effect with strong acids, and gives rise to the theory that the different reactions caused by the various

charcoals are caused by the adsorbed salts and gases rather than by the charcoal.

CANE SUGAR CHARCOAL

To prove the theory some charcoal containing no metallic salts was prepared from pure cane sugar, and a two gram sample tried with N/20 sodium hydroxide and titrated with N/20 hydrochloric acid (curve represented on plate VII). This shows no depression of the curve at either end or adsorption of ions, but does show the presence of acids, as the neutral point is reached with about five cc. less acid than when no carbon is used. However, after numerous successive washings with boiling distilled water the curve was made to nearly follow the normal curve. Although it was practically impos-

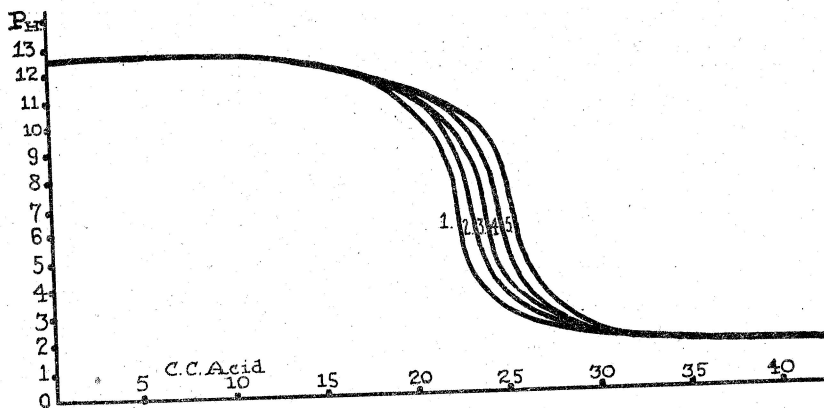


Plate VII.

sible to remove all the adsorbed organic acids from the charcoal by this method, the results of the successive washings show that the change in curve was due to impurities rather than to the charcoal.

To check the work of Bovie a sample of this sugar charcoal was also titrated with solutions of N/100 acid and alkali, and it was found that the sugar charcoal follows the normal curve of the acid and alkali. Samples of the other so-called purified charcoals gave curves very similar to that obtained by Bovie.

CONCLUSIONS

A. H. Clarke defines a "Buffer", or regulator, as any substance which tends to preserve the original hydrogen-ion concentration of its solution upon addition of acid or base, and states that the hydrogen ion concentration of a buffer solution depends upon the disassociation of the acid and base formed by hydrolysis of the salt used. This could not well be caused by pure carbon.

E. W. Washburn (*Jour. Am. Chem. Soc.* 30-31-46, 1908) states that a solution will automatically keep itself at any desired hydrogen concentration even though small quantities of acid or base be added to it, provided it contains something which will remove both hydrogen and hydroxyl ions when acid or alkali are added to the solution, and states that a solution which contains the salt of a weak acid or base together with an excess of the acid or base has the property of automatically maintaining itself at practically constant concentration. He gives a list of acids, including NaH_2PO_4 , H_2CO_3 , and bases including Na_2HPO_4 , NaHCO_3 , which will do this. These are the common "buffers".

Charcoal prepared from animal matter, wood, nut shells, or other sources will naturally contain some of these salts together with some adsorbed gases, which cannot be removed by the ordinary methods of purification, owing to the great adsorbant power of the charcoal, and are therefore present in varying quantities in most animal charcoals, which upon addition of the weaker acids or bases will hydrolyze to give the buffer effect observed.

From the fact that we are unable to obtain this buffer effect from charcoal made from sources containing no mineral salts, we are led to believe that the removal of ions obtained from the commercial grades was caused by such impurities and not by the pure carbon.

The differences between the various commercial charcoals may be readily noted from the curves.

The writer wishes to express his appreciation of the help and criticism of Dr. G. L. Wendt, in the preparation of this paper.