# STUDIES ON ACTIVE CARBON

## Part III. The pH-Values of Aqueous Suspensions of Activated Charcoal

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In Part I of this series, the methods of evaluation of commercial specimens of activated charcoal were examined. In continuation of that work, it appears worthwhile to investigate the various aspects of polar adsorption by the same specimens.

It is well known that the addition of activated charcoal changes the reaction of pure water by making it either acid or alkaline. Blowski and Bon (*Ind. Eng. Chem.*, 1926, **18**, 32) obtained varying pH-values for suspensions of commercial charcoals in water and considered that this was due to impurities present in the carbon and that the pH-determinations served as a criterion of the purity of charcoal. King (*J. Chem. Soc.*, **1935**, 859) found that the pH-value of pure water was considerably altered by pure, ash-free sugar charcoal activated in air at various temperatures. He prepared specimens of pure charcoal which were capable of giving either acid or alkaline reaction with water. He observed, moreover, that the pH of carbon-suspensions increased almost linearly with the temperature of activation, ranging from 4 to 9 for temperatures between 200° and 900° C. When activated at above 900°, the pH-value of the suspensions fell rapidly. Activation at the same temperature but for different periods of time yielded specimens with slightly different pH-values, showing thereby the influence of surface-area. It was further observed that the effect of activation temperature was reversible, for a specimen of charcoal which was activated at a given temperature and thus possessed a specific pH-value in water could be re-activated at another temperature to acquire a new pH, characteristic of charcoals activated at the second temperature. It is evident, therefore, that the effect of carbon on the pH of water is due to some fundamental change in the surface of charcoal and not to the presence of impurities, as had been supposed previously.

The pH-values of aqueous suspensions of carbon are of the utmost importance, particularly in the case of decolorising charcoals employed in aqueous media, because acidity and alkalinity affect the product obtained after decolorisation. For instance, an adsorbent which gives a strongly acid reaction in aqueous suspension will be unsuitable for treating sugar solutions, because an acid medium sets about the inversion of sucrose with consequent losses.

A study of the pH-values of commercial specimens of active charcoal in pure water was therefore made with reference to the following aspects: (1) the effect of repeated digestion of the charcoal with large quantities of conductivity-water, (2) the effect of varying the concentration of carbon in the suspension used for pH-measurements, and (3) the effect of altering the initial pH of the water employed.

Four commercial specimens were employed for this work. The ash-contents, adsorptive powers and heats of wetting of the specimens (*vide* Part I) are given below in Table I.

TABLE I

| Specimen | Source and Preparation | Ash % | Sorptive capacities | | | Heat of wetting cal./g. |
|---|---|---|---|---|---|---|
| | | | Iodine mg./g. | Methylene blue mg./g. | Benzene $(p/p_s = \frac{1}{4})$ mg./g. | |
| Blood charcoal .. | Merck's medicinal product .. | 1·86 | 1560 | 586 | 510 | 43·0 |
| Carboraffin .. | Vegetable carbon produced by activation with zinc chloride. | 2·89 | 889 | 334 | 444 | 29·9 |
| Norit .. | Vegetable carbon, probably gas-activated. | 3·99 | 716 | 167 | 187 | 23·7 |
| Darco .. | Product of carbonisation of lignite and activation with calcium phosphate. | 37·50 | 401 | 103 | 111 | 18·0 |

## Experimental

The experimental work consisted of the preparation of specimens for pH-determination, the preparation of pure water and the determination of pH-values in a glass-electrode cell.

*Preparation of specimens.*—When the original specimens were used for the determination of pH, these were merely dried in an oven at 110°. When, however, the pH of washed specimens were to be determined, the specimens were prepared as follows: About 1 g. of the specimen was placed in a Pyrex beaker, and 10 to 40 litres of specially distilled water, free from carbon dioxide and ammonia, were added in successive portions of about 200 c.c. After each addition the suspension was boiled for about five minutes and the water sucked off by means of a Jena-immersion filter. After the entire lot of water had been exhausted in this manner, the specimen was dried in an oven at 110°.

*Preparation of pure water.*—Water having a pH-value between 6·9 and 7·1, was prepared in an all-Pyrex still by distilling laboratory-distilled water successively through alkaline permanganate, phosphoric acid (1:1) and saturated baryta, while maintaining a steady stream of nitrogen through the still and also through the receiving vessel. The object of distilling through phosphoric acid is to remove ammonia.

A diagrammatic sketch of the still is given in Fig. 1. *A, B* and *C* are three flasks, provided with ground-in wash-bottle necks and containing, respectively, 1 5 litres of alkaline permanganate, 400 c.c. of 1:1 phosphoric acid which had been previously boiled to remove volatile impurities, and 400 c.c. of saturated baryta. The flask *A* could be replenished with fresh quantities of distilled water through the stoppered tube *s*. Nitrogen, purified by bubbling through solutions of caustic potash and phosphoric acid, was passed at a steady rate through the three solutions in the flasks *A, B* and *C,* which were maintained at gentle boiling by controlled electric heaters. The steam condensed in *D,* and the water collected in the receiver *E* at the rate of about 1 c.c. per minute. An auxiliary current of pure nitrogen was passed through the water contained in *E*. The three-way stop-cock *g,* attached to *E* served either to collect the water in the burette *F,* or to draw it off into another vessel. Measured quantities of water could be drawn from the burette directly into the cell for pH-measurements, out of contact with air. The current of nitrogen leaving the receiver *E* was conducted again through the top-portion of the burette and the final escape-tube was guarded with pellets of soda-lime.

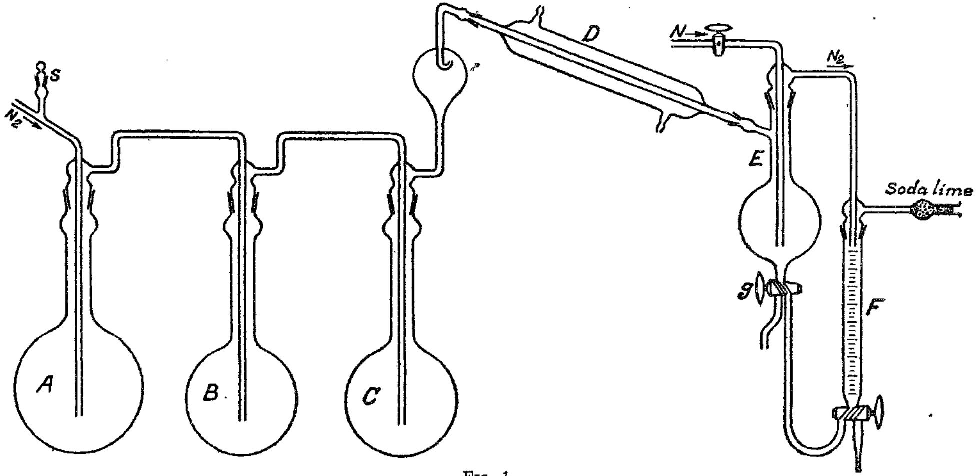


FIG. 1

The taps and other ground-glass portions of the still were very carefully prepared and required no grease for smooth operation.

*The pH-measurements.*—These were made with a glass-electrode cell similar to that devised by Morton (*J. Sci. Inst.*, 1930, 7, 187) with some modifications. The electrode-vessel, shown in Fig. 2, was constructed entirely of Pyrex-glass. The quinhydrone-electrode, which served as a reversible internal electrode inside the glass-electrode, and the calomel-electrode were small compact units supplied by Messrs. Leeds and Northrup, along with their glass-electrode cells. Each of these miniature units consisted of a glass

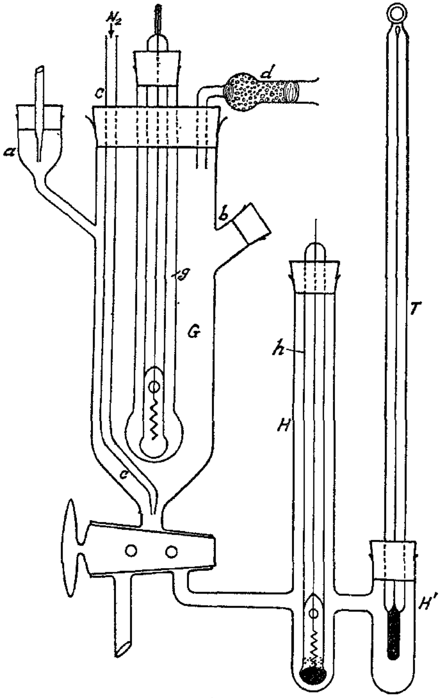


FIG. 2

tube about an inch in length and sealed at both ends. A thin strip of platinum-foil almost as long as the small tube was sealed inside the tube and connected to an external lead contained in a capillary tube fused on to the cell-tube. A small hole was provided on the side of the tube near the upper end to communicate with the solution outside the tube. The quinhydrone-electrode was made up with a standard phosphate buffer of $\mathrm{pH} = 4{\cdot}00$. The calomel-electrode, *h*, prepared in the usual way, was immersed in saturated potassium chloride solution in the vessel *H*. A thermometer *T* was inserted in the short side-tube *H'*. The test-solution was contained in the vessel *G*. The film of liquid which was formed on the stop-cock served as the electrical bridge between the two half-cells, *G* and *H*. There was no grease on the stop-cock except at its two ends. A clean film of liquid therefore formed a satisfactory bridge. When the electrode assembly was used for the first time, the stop-cock was first turned to admit a little of the potassium chloride solution into the cell *G* and then run out of it. This operation was repeated until the solution in the vessel *H* was in level with the stop-cock. This procedure precluded any tendency of the potassium chloride solution to creep past the stop-cock into the vessel *G*. The stop-cock was not communicated with the cell *H* once the level of the solution in it was adjusted in this way. The cell *G* was then washed thoroughly with specially distilled water and rinsed with the experimental solution before use. Potassium chloride, or any other impurity, thus having been removed from the cell and the stop-cock, the test-solution was in contact with its own film formed on the stop-cock during the rinsing operation. Contamination of the experimental solution was thus avoided.

The E.M.F. of the cell was measured by means of a Leeds and Northrup electrometer-valve potentiometer giving direct readings of the voltage down to one millivolt.

In the apparatus, shown in Fig. 2, water was admitted into the cell through the side-tube *a*, which carried the delivery jet of the burette of the water-still by means of a stopper. The specimen of charcoal was introduced through the side-tube *b*. Nitrogen, purified by passage through caustic potash and phosphoric acid, was bubbled through the solution in the cell *G* by means of a narrow tube *c* which reached the bottom of the cell. The escape-vent was guarded from atmospheric contamination by means of a soda-lime tube.

The determination of the pH of aqueous suspensions of charcoal was done as follows: A measured volume (30 c.c.) of water, prepared in the still, was introduced from the burette *F* (Fig. 1) into the cell *G* (Fig. 2), after rinsing the latter with several c.c. of the same water. In spite of all the precautions taken to introduce the water out of contact with air, it was found that the pH of the water was usually about 6. This was probably due to traces of carbon dioxide. On passing a steady stream of pure nitrogen through the water, its pH gradually reached a value between 6 9 and 7·1, where it remained constant for about thirty minutes. When necessary, the pH of the water could be lowered below 7 by admitting a very minute quantity of carbon dioxide through the tube *c*. When the desired initial pH (7· or lower) of the water was obtained, a weighed amount (about 50 mg. to start with) of the charcoal-specimen was added through the side-tube *b*. A uniform suspension was formed by the nitrogen bubbling through it. The pH-reading was taken one minute after addition of the carbon and again ten minutes later. Further quantities of the specimen were then added and the pH values determined in the same way, until the total concentration of the solid in the suspension reached about two per cent.

Similar sets of measurements were made with water having different initial pH-values and also with specimens which had been digested with different amounts of water.

## Results

The results of the determination of the pH of carbon-suspensions in water are given in Tables II and III. The tables show variations in the pH values, produced (1) when specimens washed to different extents were employed for the measurements; (2) when the concentration of carbon employed for the determinations was altered; and (3) when water of varying pH was used for producing the suspensions.

It must be mentioned that when the specimen of Carboraffin was agitated with water, one portion of it settled quickly, while the other remained in suspension for a long time. The material in suspension was in a very finely divided form, whereas the portion which had settled was of 150 to 200 mesh. It was therefore considered worthwhile to carry out the determinations with the fine and the coarse portions separately.

The quantity of water taken in the cell was always 30 c.c. as this was found to be convenient.

The results obtained with the various specimens, which had not been completely washed, may be discussed under four heads, namely, (1) the effect of varying the initial pH of the water employed, (2) the effect of time, (3) the effect of varying the concentration of charcoal in the suspension, and (4) the effect of progressive washing of the specimen. These factors have been investigated in the light of the results given in the tables. In the following analysis of the results, the pH-value determined one minute after addition of the charcoal will be known as the *"instantaneous pH"* and the value obtained after a ten-minute interval, the *"final pH"* of the suspension. The term *"initial pH"* refers to the pH of pure water prior to addition of the charcoal. It may also be mentioned here that, except in the case of the original specimens, which were very impure, the pH of the suspension always attained a steady value in about ten minutes. Since with the impure specimens, the effect of concentration on the pH is considerable, especially at low concentrations, the values obtained at a concentration of about 500 mg./30 c.c. (Table II) have been taken for comparing the effects of time and washing.

1. *The effect of varying the initial pH of the water employed.*—(Table III) In all cases, an increase of the initial pH of the water raises both the instantaneous and the final pH-values of the suspensions.

2. *The effect of time.*—(Tables II and III) Except in the case of the coarse portion of Carboraffin, the pH of the suspension increases on keeping for a few minutes, until a steady value is reached in about ten minutes. It is also noteworthy that the difference between the instantaneous and the final pH-values for any given specimen, at a concentration of about 500 mg./30 c.c., is practically unaffected by variations of the initial pH of the water. This is shown by the figures in the last column of Table III.

## TABLE II

*pH of aqueous suspensions of charcoals, washed to different extents, at different carbon-concentrations*

Initial pH of water = 7·0±00·5

| Original specimen | | | Litres of water employed for washing 1 g. of the original specimen | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 10 | | | 20 | | | 30 | | | 40 | | |
| Wt. of carbon mg./30 c.c. | pH | | Wt. of carbon mg./30 c.c. | pH | | Wt. of carbon mg/30 c.c. | pH | | Wt. of carbon mg./30 .c. | pH | | Wt. of carbon mg./30 c.c. | pH | |
| | 1 min. | 10 min. | | 1 min. | 10 min | | · min. | 10 min. | | 1 min. | 10 min. | | 1 min. | 10 min. |
| *Blood Charcoal* | | | | | | | | | | | | | | |
| 6 | 3·35 | .. | 3 | 3·39 | .. | 7 | 3·47 | .. | 3 | 3·35 | .. | 5 | 3·38 | .. |
| 12 | 3·28 | .. | 10 | 3·23 | .. | 14 | 3·42 | .. | 12 | 3·32 | .. | 17 | 3·37 | .. |
| 24 | 3·15 | .. | 17 | 3·14 | .. | 21 | 3·35 | .. | 47 | 3·32 | 3·40 | 36 | 3·36 | .. |
| 38 | 3·10 | 3·25 | 32 | 3·00 | 3·30 | 33 | 3·32 | 3·53 | 88 | 3·32 | 3·40 | 92 | 3·37 | 3·40 |
| 72 | 3·05 | 3·28 | 64 | 3·07 | 3·52 | 50 | 3·30 | 3·52 | 156 | 3·31 | 3·41 | 162 | 3·37 | 3·39 |
| 168 | 3·30 | 3·82 | 124 | 3·05 | 3·76 | 168 | 3·32 | 3·58 | 327 | 3·32 | 3·38 | 342 | 3·38 | 3·41 |
| 362 | 2·95 | 3·86 | 384 | 3·10 | 3·82 | 321 | 3·30 | 3·68 | 487 | 3·32 | 3·38 | 492 | 3·39 | 3·41 |
| 487 | 2·98 | 3·92 | 511 | 3·04 | 3·87 | 511 | 3·28 | 3·76 | .. | .. | .. | .. | .. | .. |
| *Carboraffin (Coarse)* | | | | | | | | | | | | | | |
| 8 | 3·24 | .. | 8 | 5·00 | 4·80 | 18 | 5·13 | .. | 4 | 5·14 | 5·06 | 9 | 5·15 | 5·10 |
| 194 | 3·16 | .. | 17 | 4·90 | 4·70 | 52 | 5·11 | .. | 18 | 5·14 | 5·06 | 21 | 5·14 | 5·12 |
| 344 | 3·04 | 3·42 | 40 | 4·85 | 4·70 | 173 | 5·09 | 4·96 | 164 | 5·13 | 5·04 | 172 | 5·14 | 5·12 |
| 414 | 3·02 | 3·50 | 265 | 4·60 | 4·32 | 248 | 5·04 | 4·92 | 388 | 5·12 | 5·03 | 403 | 5·13 | 5·13 |
| 508 | 3·01 | 3·56 | 481 | 4·50 | 4·20 | 526 | 4·99 | 4·87 | 540 | 5·10 | 5·00 | 546 | 5·13 | 5·12 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | *Carboraffin (Fine)* | | | | | | | | |
| .. | .. | .. | 5 | 3·34 | 3·58 | 7 | 3·16 | 3·40 | 3 | 3·09 | 3·09 | 6 | 3·05 | 3·05 |
| .. | .. | .. | 33 | 3·30 | 3·60 | 17 | 3·12 | 3·45 | 43 | 3·08 | 3·09 | 22 | 3·04 | 3·04 |
| .. | .. | .. | 143 | 3·26 | 3·65 | 129 | 3·09 | 3·46 | 143 | 3·06 | 3·10 | 167 | 3·04 | 3·06 |
| .. | .. | .. | 289 | 3·16 | 3·68 | 295 | 3·07 | 3·50 | 289 | 3·05 | 3·12 | 302 | 3·04 | 3·07 |
| .. | .. | .. | 442 | 3·14 | 3·74 | 450 | 3·07 | 3·52 | 460 | 3·05 | 3·12 | 470 | 3·05 | 3·07 |
| | | | | | | *Norit* | | | | | | | | |
| 24 | 8·27 | .. | 4 | 7·16 | .. | 5 | 6·67 | .. | 8 | 6·44 | .. | 16 | 6·25 | .. |
| 41 | 8·34 | .. | 9 | 7·17 | .. | 21 | 6·73 | .. | 27 | 6·53 | .. | 103 | 6·29 | .. |
| 77 | 8·66 | .. | 13 | 7·27 | 7·38 | 84 | 6·94 | 7·25 | 66 | 6·71 | .. | 245 | 6·30 | 6·33 |
| 89 | 8·95 | 9·32 | 34 | 7·27 | 7·42 | 113 | 7·03 | 7·35 | 88 | 6·76 | 7·00 | 420 | 6·32 | 6·35 |
| 145 | 9·05 | 9·40 | 83 | 7·39 | 7·64 | 180 | 7·06 | 7·48 | 119 | 6·80 | 7·07 | 590 | 6·34 | 6·38 |
| 169 | 9·06 | 9·48 | 137 | 7·51 | 7·77 | 448 | 7·24 | 7·60 | 225 | 6·86 | 7·09 | .. | .. | .. |
| 206 | 9·09 | 9·64 | 257 | 7·67 | 7·89 | .. | .. | .. | 501 | 6·94 | 7·15 | .. | .. | .. |
| 373 | 9·05 | 9·70 | 519 | 7·91 | 8·62 | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| 510 | 9·09 | 9·80 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | | | | | | *Darco* | | | | | | | | |
| 6 | 4·65 | .. | 17 | 5·55 | .. | 10 | 5·97 | .. | 8 | 5·82 | 5·85 | 14 | 5·90 | 5·92 |
| 16 | 4·31 | .. | 64 | 5·26 | .. | 23 | 5·87 | .. | 36 | 5·88 | 5·98 | 36 | 5·95 | 5·98 |
| 30 | 4·16 | .. | 107 | 5·04 | 5·53 | 30 | 5·83 | .. | 92 | 5·88 | 5·95 | 81 | 5·94 | 5·98 |
| 63 | 3·95 | 4·70 | 240 | 5·04 | 5·75 | 87 | 5·85 | 6·05 | 163 | 5·90 | 6·00 | 169 | 5·97 | 5·99 |
| 98 | 3·81 | 4·71 | 508 | 5·03 | 5·80 | 130 | 5·83 | 6·07 | 358 | 5·90 | 6·07 | 362 | 5·98 | 6·05 |
| 135 | 3·68 | 4·76 | .. | .. | .. | 245 | 5·83 | 6·12 | 501 | 5·92 | 6·12 | 520 | 5·98 | 6·00 |
| 189 | 3·58 | 4·92 | .. | .. | .. | 405 | 5·82 | 6·20 | .. | .. | .. | .. | .. | .. |
| 245 | 3·51 | 5·14 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| 301 | 3·46 | 5·22 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| 352 | 3·44 | 5·30 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| 421 | 3·42 | 5·40 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| 517 | 3·39 | 5·42 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |

## TABLE III

## *Variation of the pH of charcoal-suspension with the initial pH of the water employed*

Volume of suspension = 30 c. c. in each case.
Extent of washing is given as litres of wash-water per g. of specimen.

| Specimen | Wash-water L./g. | Wt. of charcoal mg. | Initial pH of water | pH of suspension | | pH variation in |
|---|---|---|---|---|---|---|
| | | | | 1 min. | 10 min. | 10 mins. |
| Blood Charcoal | Original specimen | 442 | 5·60 | 2·64 | 3·56 | +0·92 |
| | | 450 | 6·05 | 2·77 | 3·69 | 0·92 |
| | | 441 | 6·28 | 2·82 | 3·76 | 0·94 |
| | | 448 | 6·87 | 2·98 | 3·90 | 0·92 |
| | 10 | 427 | 5·61 | 2·76 | 3·56 | +0·80 |
| | | 448 | 5·95 | 2·82 | 3·60 | 0·78 |
| | | 437 | 6·30 | 2·90 | 3·66 | 0·76 |
| | | 451 | 6·90 | 3·02 | 3·86 | 0·84 |
| | 20 | 445 | 5·64 | 2·92 | 3·50 | +0·58 |
| | | 439 | 6·00 | 2·95 | 3·54 | 0·59 |
| | | 449 | 6·26 | 3·05 | 3·60 | 0·55 |
| | | 502 | 6·91 | 3·14 | 3·74 | 0·60 |
| | 30 | 455 | 5·66 | 3·35 | 3·38 | +0·03 |
| | | 467 | 5·98 | 3·36 | 3·39 | 0·03 |
| | | 479 | 6·32 | 3·34 | 3·40 | 0·06 |
| | | 489 | 6·89 | 3·34 | 3·40 | 0·06 |
| | 40 | 477 | 5·63 | 3·36 | 3·37 | +0·01 |
| | | 486 | 6·10 | 3·37 | 3·38 | 0·01 |
| | | 499 | 6·30 | 3·37 | 3·39 | 0·02 |
| | | 506 | 6·95 | 3·37 | 3·39 | 0·02 |
| Carboraffin | Original specimen | 432 | 5·67 | 2·74 | 3·30 | +0·56 |
| | | 426 | 5·97 | 2·87 | 3·41 | 0·54 |
| | | 443 | 6·26 | 2·90 | 3·45 | 0·55 |
| | | 452 | 6·85 | 2·94 | 3·50 | 0·56 |
| Carboraffin (Coarse) | 10 | 451 | 5·64 | 4·24 | 3·90 | −0·34 |
| | | 438 | 6·00 | 4·46 | 4·14 | 0·32 |
| | | 442 | 6·28 | 4·50 | 4·20 | 0·30 |
| | | 437 | 6·86 | 4·56 | 4·25 | 0·31 |
| | 20 | 499 | 5·60 | 4·66 | 4·50 | −0·16 |
| | | 502 | 5·99 | 4·72 | 4·54 | 0·18 |
| | | 447 | 6·29 | 4·81 | 4·62 | 0·19 |
| | | 480 | 6·90 | 4·94 | 4·80 | 0·14 |
| | 30 | 497 | 5·62 | 5·10 | 5·08 | −0·02 |
| | | 490 | 5·98 | 5·12 | 5·09 | 0·03 |
| | | 496 | 6·30 | 5·12 | 5·10 | 0·02 |
| | | 503 | 6·92 | 5·13 | 5·10 | 0·03 |
| | 40 | 468 | 5·60 | 5·11 | 5·10 | −0·01 |
| | | 497 | 6·05 | 5·13 | 5·11 | 0·02 |
| | | 479 | 6·27 | 5·13 | 5·12 | 0·01 |
| | | 490 | 6·93 | 5·14 | 5·12 | 0·02 |

## TABLE III (*Contd.*)

| Specimen | Wash-water L./g. | Wt. of charcoal mg. | Initial pH of water | pH of suspension | | pH variation in |
|---|---|---|---|---|---|---|
| | | | | 1 min. | 10 min. | 10 mins. |
| Carboraffin (Fine) | 10 | 437 | 5·68 | 3·05 | 3·45 | +0·40 |
| | | 443 | 6·01 | 3·09 | 3·55 | 0·46 |
| | | 444 | 6·30 | 3·12 | 3·64 | 0·52 |
| | | 430 | 6·88 | 3·14 | 3·72 | 0·58 |
| | 20 | 499 | 5·63 | 3·05 | 3·32 | +0·27 |
| | | 501 | 5·95 | 3·06 | 3·38 | 0·32 |
| | | 500 | 6·29 | 3·06 | 3·42 | 0·36 |
| | | 497 | 6·88 | 3·08 | 4·48 | 0·40 |
| | 30 | 456 | 5·66 | 3·04 | 3·07 | +0·03 |
| | | 449 | 6·10 | 3·04 | 3·09 | 0·05 |
| | | 470 | 6·30 | 3·05 | 3·10 | 0·05 |
| | | 499 | 6·88 | 3·06 | 3·13 | 0·07 |
| | 40 | 467 | 5·69 | 3·03 | 3·06 | +0·03 |
| | | 479 | 6·02 | 3·03 | 3·07 | 0·04 |
| | | 480 | 6·32 | 3·05 | 3·08 | 0·03 |
| | | 498 | 6·96 | 3·04 | 3·08 | 0·04 |
| Norit | Original specimen | 479 | 5·62 | 8·18 | 8·96 | +0·78 |
| | | 469 | 6·01 | 8·46 | 9·16 | 0·70 |
| | | 499 | 6·27 | 8·64 | 9·30 | 0·66 |
| | | 502 | 6·80 | 9·00 | 9·80 | 0·80 |
| | 10 | 443 | 5·70 | 7·06 | 7·84 | +0·78 |
| | | 428 | 5·94 | 7·20 | 7·98 | 0·78 |
| | | 495 | 6·25 | 7·32 | 8·13 | 0·81 |
| | | 501 | 6·82 | 7·84 | 8·60 | 0·76 |
| | 20 | 487 | 5·62 | 6·59 | 6·95 | +0·36 |
| | | 477 | 5·96 | 6·80 | 7·02 | 0·22 |
| | | 469 | 6·28 | 6·94 | 7·27 | 0·33 |
| | | 501 | 6·80 | 7·20 | 7·54 | 0·34 |
| | 30 | 487 | 5·63 | 6·40 | 6·56 | +0·16 |
| | | 485 | 6·00 | 6·62 | 6·82 | 0·20 |
| | | 493 | 6·30 | 6·76 | 6·94 | 0·18 |
| | | 498 | 6·87 | 6·90 | 7·10 | 0·20 |
| | 40 | 490 | 5·67 | 6·27 | 6·31 | +0·04 |
| | | 501 | 6·04 | 6·28 | 6·34 | 0·06 |
| | | 470 | 6·29 | 6·29 | 6·34 | 0·05 |
| | | 493 | 6·97 | 6·34 | 6·38 | 0·04 |
| Darco | Original specimen | 470 | 5·65 | 3·00 | 4·62 | +1·62 |
| | | 488 | 5·92 | 3·16 | 4·74 | 1·58 |
| | | 500 | 6·24 | 3·24 | 4·86 | 1·62 |
| | | 507 | 6·84 | 3·39 | 5·40 | 2·01 |
| | 10 | 507 | 5·62 | 4·75 | 5·26 | +0·51 |
| | | 497 | 5·96 | 4·80 | 5·39 | 0·59 |
| | | 487 | 6·26 | 4·88 | 5·48 | 0·60 |
| | | 477 | 6·82 | 5·00 | 5·75 | 0·75 |

TABLE III (*Contd.*)

| Specimen | Wash-water L./g. | Wt of charcoal mg. | Initial pH of water | pH of suspension | | pH variation in |
|---|---|---|---|---|---|---|
| | | | | 1 min. | 10 min. | 10 mins. |
| Darco | 20 | 496 | 5·61 | 5·70 | 6·09 | +0·39 |
| | | 479 | 6·03 | 5·74 | 6·12 | 0·38 |
| | | 495 | 6·29 | 5·76 | 6·12 | 0·36 |
| | | 489 | 6·83 | 5·81 | 6·15 | 0·34 |
| | 30 | 500 | 5·67 | 5·84 | 6·03 | +0·19 |
| | | 490 | 6·01 | 5·87 | 6·05 | 0·18 |
| | | 497 | 6·28 | 5·88 | 6·05 | 0·17 |
| | | 501 | 6·87 | 5·90 | 6·09 | 0·19 |
| | 40 | 499 | 5·65 | 5·95 | 5·98 | +0·03 |
| | | 485 | 6·10 | 5·96 | 5·98 | 0·02 |
| | | 501 | 6·32 | 5·96 | 5·98 | 0·02 |
| | | 503 | 6·93 | 5·97 | 6·00 | 0·03 |

3. *The effect of varying the concentration of charcoal in the suspension.*—This effect also is specific for the specimen of charcoal, and it appears to depend entirely on the nature and quantity of the impurities present. With Darco washed with *more* than 20 litres of water per gram and also with Norit, both the instantaneous and the final pH-values increase with the concentration. With Carboraffin (coarse) both these values decrease with the concentration. In the case of the remaining specimens, namely blood charcoal, Carboraffin (fine), Carboraffin (original) and Darco washed with *less* than 20 litres per gram, an increase of concentration raises the final pH-values although the instantaneous pH-values are lower.

4. *The effect of washing.*—Progressive washing of the specimen alters the instantaneous and the final pH-values showing thereby the dependence of the pH on the nature and amount of the impurity, left after each stage of washing. Washing with pure water increases the instantaneous as well as the final pH-values in the case of Carboraffin (coarse) and also with Darco up to 20 L./g., whereas both these values are steadily reduced in the cases of Norit and Carboraffin (fine). When, however, blood charcoal is washed with water, the instantaneous pH is raised and the final pH lowered. Darco behaves in the same way as blood charcoal in this respect when the quantity of water employed for washing exceeds 20 L./g.

The results further reveal that exhaustive washing with water considerably reduces the changes in the pH of the suspension produced by allowing the freshly formed suspension to stand for a few minutes, or by varying the concentration of the specimen or the initial pH of the water employed, so that ultimately these effects are hardly noticeable. In the case of blood charcoal, for instance, the difference between the instantaneous and the final pH-values, at a concentration of about 500 mg./30 c.c. is 0·94 for the original specimen (*vide* Table II), but this difference steadily diminishes in the order 0·83, 0·48, 0·06 and 0·02, as the specimen is washed with 10, 20, 30 and 40 litres of water respectively. At the same time, the instantaneous pH-values of the suspensions of blood charcoal (formed with water of initial pH = 7) decrease from 3·35 to 2·98 in the case of the original specimen, as the concentration of the solid in suspension is increased from about 5 to 500 mg./30 c.c. Over the same range of concentrations, the variation of the instantaneous pH-values is diminished in the order 0·35, 0·19, 0·03 and 0·01, as the specimen is progressively washed with water. Finally, the changes in the instantaneous and the final pH-values produced by varying the initial pH of water from 5·6 to 7 (*vide* Table III) diminish from 0·34 for the original specimen of blood charcoal to 0·01 when the same specimen is washed with 40 litres of water per gram. The variations in the instantaneous and the final pH values with time, concentration and the initial pH of water are thus reduced so that in the thoroughly washed samples these variations fall well within the limits of experimental error. A complete analysis of the results, carried out on these lines for all the specimens at different stages of washing, is given in Table IV.

In Table IV, the instantaneous and the final pH-values of the suspensions (columns 3 and 4), obtained at a charcoal-concentration of 500 mg./30 c.c. and with pure water of initial pH = 7, are reproduced from Table II. The pH-variation in ten minutes, given in column (5), is the difference between the figures in columns (3) and (4). Columns (6) and (7) give the changes in the instantaneous and the final pH-values, brought about by varying the initial pH of the water employed from 5·6 to 7. These figures are derived from Table III. The figures in columns (8) to (11) are deduced from Table II, which deals with suspensions formed with water of

## TABLE IV

*Effect of progressive washing of specimens on the pH of charcoal-suspensions showing its variation with time, concentration and initial pH*

| Specimen | Wash-water L./g. | pH of suspension (concn. = 500 mg./30 c.c. Initial pH = 7) | | pH variation in 10 mins. | pH variation with change of initial pH of water from 5·6 to 7 | | pH variation with concentration of charcoal | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Inst. pH | Finl. pH | | Inst. pH | Finl. pH | concn. range mg./30 c.c. | change in Inst. pH | concn. range mg./30 c.c. | change in Finl. pH |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Blood charcoal | 0 | 2·98 | 3·92 | +0·94 | 0·34 | 0·34 | 5 to 500 | −0·37 | 30 to 500 | +0·67 |
| | 10 | 3·04 | 3·87 | 0·83 | 0·26 | 0·30 | | 0·35 | | 0·57 |
| | 20 | 3·28 | 3·76 | 0·48 | 0·22 | 0·24 | | 0·19 | | 0·23 |
| | 30 | 3·32 | 3·38 | 0·06 | 0·01 | 0·02 | | 0·03 | | 0·02 |
| | 40 | 3·39 | 3·41 | 0·02 | 0·01 | 0·02 | | 0·01 | | 0·01 |
| Carboraffin (Coarse) | 10 | 4·50 | 4·20 | −0·30 | 0·32 | 0·35 | 18 to 500 | −0·40 | 170 to 500 | −0·30 |
| | 20 | 4·99 | 4·87 | 0·12 | 0·28 | 0·30 | | 0·14 | | 0·06 |
| | 30 | 5·10 | 5·00 | 0·10 | 0·03 | 0·02 | | 0·04 | | 0·04 |
| | 40 | 5·13 | 5·12 | 0·01 | 0·03 | 0·02 | | 0·01 | | 0·00 |
| Carboraffin (Fine) | 10 | 3·14 | 3·74 | +0·60 | 0·09 | 0·27 | 5 to 500 | −0·20 | 5t o 500 | +0·16 |
| | 20 | 3·07 | 3·52 | 0·45 | 0·03 | 0·16 | | 0·09 | | 0·12 |
| | 30 | 3·05 | 3·12 | 0·07 | 0·02 | 0·06 | | 0·04 | | 0·03 |
| | 40 | 3·05 | 3·07 | 0·02 | 0·01 | 0·02 | | 0·00 | | 0·02 |
| Norit | 0 | 0·09 | 9·80 | +0·71 | 0·82 | 0·84 | 20 to too | +0·82 | 80 to 500 | +0·48 |
| | 10 | 7·91 | 8·62 | 0·71 | 0·78 | 0·76 | | 0·64 | | 0·98 |
| | 20 | 7·24 | 7·60 | 0·36 | 0·61 | 0·59 | | 0·57 | | 0·35 |
| | 30 | 6·94 | 7·15 | 0·21 | 0·50 | 0·54 | | 0·41 | | 0·15 |
| | 40 | 6·34 | 6·38 | 0·04 | 0·07 | 0·07 | | 0·09 | | 0·05 |
| Darco | 0 | 3·39 | 5·42 | +1·03 | 0·39 | 0·78 | 10 to 500 | −1·26 | 100 to 500 | +0·71 |
| | 10 | 5·03 | 5·80 | 0·77 | 0·25 | 0·49 | | −0·52 | | 0·27 |
| | 20 | 5·82 | 6·20 | 0·38 | 0·11 | 0·06 | | −0·15 | | 0·15 |
| | 30 | 5·92 | 6·12 | 0·20 | 0·06 | 0·06 | | +0·10 | | 0·15 |
| | 40 | 5·98 | 6·00 | 0·02 | 0·02 | 0·02 | | +0·08 | | 0·02 |

initial pH = 7. Column (9) gives the difference in the instantaneous pH-value brought about by varying the concentration of the charcoal between the limits indicated roughly by the corresponding figures in column (8). Similarly, the variation of the final pH-values over the concentration-range specified in column (10) is given in column (11). The extent of washing is given in column (2) in terms of litres of wash-water employed per gram of the original specimen.

From all these observations the fundamental fact emerges that, while the pH of a partially washed charcoal-suspension varies with the time, the concentration of the specimen and the initial pH of the water, the same sample after very thorough washing with conductivity water gives a *constant* pH-value, which is characteristic of the particular specimen. Since the obvious effect of washing is the removal of soluble impurities, the variability of the pH of impure specimens could be ascribed mainly to such sources of contamination in the charcoal.

The variation of the pH of the suspension with washing as well as with other factors in the system, namely, time, concentration and initial pH, depends naturally on the nature and quantity of the impurities involved at each stage of the operation. Beyond this broad generalisation, it is difficult to account for all the variations observed. This is so because the effect of impurities is in most cases very complicated, and a chemical examination of the specimen will not be helpful. It is known that the impurities that occur in charcoal may be acidic and basic substances present either as active acids and alkalis, or sparingly soluble polar adsorbents such as the zeolites and other silicates and aluminates. The pH-value obtained with charcoal, therefore, represents the joint effect of the active carbon itself in the specimen and that of the impurities associated with it. With progressive washing, the soluble impurities are eliminated until finally the pH-effect of the insoluble adsorbent itself is exhibited. By comparing the pH-values given by the specimens at various stages of washing, the nature of the soluble impurities may be deduced without recourse to chemical analysis of the specimen.

The coarse portion of Carboraffin when washed completely with water yielded a specimen with an invariable pH-value of 5·13 (Tables II and III). Specimens of this charcoal washed partially gave considerably lower pH-values in instantaneous as well as final observations. This indicates that the impurity, eliminated by washing, is wholly acidic in character, a view which is supported by the observation (Table IV) that the pH of the suspension decreases on standing, or when the concentration is increased. Similarly, in the case of Norit it can be concluded that the contamination is alkaline, because the pH-values obtained with incompletely washed specimens increase with time and concentration and decrease with washing.

The results obtained with the fine portion of Carboraffin, blood charcoal and Darco are more complicated and suggest the simultaneous existence of acidic as well as basic impurities. In the case of blood charcoal, for instance, the instantaneous pH-values for the original specimen and the specimens washed with 10, 20 and 30 litres of water are, respectively, 2·98, 3·04 and 3·32. These are lower than the value, 3·4, which is obtained with the specimen washed with 40 L./g. This set of observations establishes the presence of acidic impurities in the carbon and that these impurities are removable by water. The corresponding values taken with the same specimens after a ten-minute interval are 3·92, 3·87 and 3·76. These are bigger than the value 3·4 for the purest specimen, thus proving the presence of basic impurities which, however, are not very soluble. Since it follows that both acidic and basic materials occur in blood charcoal, the instantaneous and the final pH-values must vary with concentration and progressive washing in a manner opposed to each other. Since the effect of the acidic impurity is noticed first it follows that it is the more soluble. From the fact that the final pH-values always show the effect of the basic impurity, it can be concluded that this occurs to a larger extent and also that it is the less soluble.

The case of Darco is likewise complicated. Increase in pH with time indicates the preponderance of alkaline impurities. The initial lowering of the pH-values points to an acidic impurity, which is readily soluble and therefore easily eliminated by further washing. The alkaline impurity is less soluble and is probably present in greater concentration than the acidic material.

Partially washed specimens of Carboraffin (fine) give instantaneous and final pH-values which are higher than the value, 3·05, obtained after thorough washing. The pH-value determined immediately after addition of the specimen *increases* with time. Both the instantaneous and the final pH-values are steadily lowered as a result of repeated washing, until the value, 3·05, is reached in the limit. The final pH-values show, moreover, an increase with the concentration. All these observations indicate predominant alkaline impurity. Since it is observed that the instantaneous pH-values of potentially washed specimens decrease as the concentration rises, and since this variation of the instantaneous pH is minimised by repeated washing (Table IV), it appears that a soluble acidic constituent is also present.

Finally, in the original specimen of Carboraffin, before separation into coarse and fine portions, the pH of the suspension increases with time. With increasing concentrations the instantaneous pH-values decrease, but the final values increase. This is evidence of both acidic and basic impurities and that the former is more soluble, but present in smaller proportion than the alkaline contamination.

In conclusion, it may be stated that the pH-values of charcoal suspensions containing soluble impurities vary with repeated digestion with water, until at last a *constant* value is obtained under conditions of exhaustive washing. This value is unaffected by the concentration of the charcoal or by the initial pH of the water in the system. The pH of the suspension of a thoroughly washed sample attains an equilibrium value almost instantaneously and maintains this value when kept out of contact with air. It may therefore be concluded that this constant value represents the *characteristic pH-value* of the specimen, that is, of the carbon itself and of any insoluble impurity present in it. The characteristic pH-values of the various specimens, after washing with 40 litres of conductivity-water are noted below in Table V. Each of these denotes the resultant effect of the carbon and of such insoluble mineral constituents as would behave as hydrolytic or zeolitic adsorbents.

TABLE V

| Specimen | Characteristic pH |
|---|---|
| Blood charcoal .. | 3·4 |
| Carboraffin (Coarse) .. | 5·1 |
| Carboraffin (Fine) .. | 3·1 |
| Darco .. .. | 6·0 |
| Norit .. .. | 6·3 |

## Discussion

It has been shown conclusively by King (*loc. cit.*) that activated carbon, even when free from ash-forming inorganic constituents, alters the pH of water to a value that is determined by the conditions of activation. The origin of the excess of either hydrogen or hydroxyl ions in the aqueous medium has been the subject of much speculation in recent years. The investigations of King have gone a long way to establish many of the salient features of the phenomenon. In the first place, he showed, by working with ash-free sugar-charcoal of great purity, that the change of pH was not due to the dissolution of impurities previously contained in the specimen. The observations recorded in the present paper also point to the same conclusion.

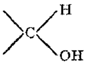
While the pH-values obtained with unwashed specimens containing appreciable amounts of soluble impurities, vary with the concentration of the charcoal in suspension and the initial pH of water and also on standing, these variations become less and less on progressive washing until, finally, they become negligible. These observations record not only the variations caused by impurities, but also show that specimens which have been completely freed from soluble matter give constant values. This establishes the fact that carbon can affect the pH of water without the aid of soluble impurities, which may be in the nature of electrolytes. On the basis of the present results, it can also be seen that the ash-free activated carbon in contact with pure water (save for a trace of carbonic acid) develops a characteristic equilibrium pH which is constant, irrespective of changes in the concentration of the carbon and the initial pH of water. The characteristic pH is reached almost immediately after addition of the carbon to water and this value is maintained for a considerable time, if the suspension is preserved out of contact with air.

A number of theories have been proposed from time to time to explain the effect of carbon on the pH of water as a fundamental property of activated carbon, quite independent of the influence of impurities. Most of these theories postulate a non-equivalent adsorption of the ions of water, whereby the hydrogen or the hydroxyl ion is adsorbed in preference, leaving an excess of one of the ions in solution. However, no reasons have been given for such behaviour.

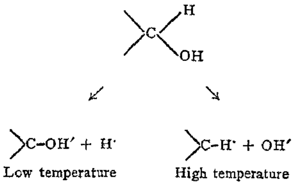
Bohn (*Biochem. Z.,* 1926, **178**, 119) investigating the adsorption of hydrogen and hydroxyl ions by carbon, has suggested that the surface-energy of activated carbon is sufficient to split the water-molecule into its constituent ions. The resulting hydrogen and hydroxyl ions are taken up with unequal force on the surface of the adsorbent. A kind of electrical double layer is then built up around the solid particle, the ion that is more strongly adsorbed constituting the inner layer. The carbon, together with this adsorptively held $H^{\cdot}OH'$ ion-pair assumes a positive or negative charge with respect to the surrounding medium, according as the hydrogen or the hydroxyl ion is preferentially attached to the carbon. This accounts for the electrokinetic behaviour of the carbon-particle in aqueous media. Bohn proceeds further to regard charcoal in aqueous systems as an ampholoid, since it manifests both acidic and basic properties. Each sample of activated carbon, even when absolutely free from ash, has a characteristic *"iso-electric pH"*. If the charcoal is brought into contact with an aqueous medium of the same pH as the iso-electric point of the charcoal, no change in the reaction is produced. If, however, the solution has a pH-value higher than the iso-electric point, the charcoal behaves as an acid, lowering the pH of the medium. On the other hand, in media with a pH lower than the iso-electric point, the same charcoal exhibits its basic character by increasing the pH. Bohn thus explains the pH-change that follows when charcoal is added to water or any aqueous medium as a manifestation of its property to shift the pH of the medium nearer to the iso-electric point. This property is in turn traced to the non-equivalent or unequal adsorption of ions on the surface of carbon.

Non-equivalent adsorption of electrolytes on polar adsorbents, such as the zeolites, is usually associated with the exchange of equipolar ions between the adsorbent and the solution. Since the surface of pure carbon does not contain any ion (other than probably hydrogen or hydroxyl) that could go into solution in exchange for the $H^{\cdot}$ or $OH'$ ion that is adsorbed from the solution, the theory of preferential adsorption, as given by Bohn, does not explain the ionic-equilibrium in water. It may be assumed, however, that the carbon-particle with its adsorbed ions comprises in itself a massive ion-complex in equilibrium with the ions that are left behind in solution. This would help to preserve the electrical neutrality of the system as a whole, although it would also suggest that the pH-effect of the carbon will be felt only as long as it remains in the system, and that if by any means it is removed from contact with water, the pH of the latter will return to the normal. It is very difficult to check this by direct experiment as any attempt to separate the carbon from the water would introduce complications due to contamination, and the results would be inconclusive.

King (*loc. cit.*) found that the pH-effect that is produced when activated carbon comes in contact with water is intimately connected with the conditions of activation, such as time and temperature, and he therefore ascribed the origin of the phenomenon to the oxide layer on carbon. This layer may have either acidic or basic properties depending upon the temperature of its formation and may accordingly lower or raise the pH of water. Representing the oxide layer on carbon arbitrarily by the formula:



King explained the phenomenon by postulating a selective dissociation or desorption of either the $H^{\cdot}$ or the $OH'$ ion. In carbons produced at temperatures lower than 700° C. the $H^{\cdot}$-ion is labile while in those obtained at higher temperatures the $OH'$-ion is labile. From the former, therefore, an acid solution is obtained and from the latter an alkaline solution:



Here again the charged particle is to be regarded as a non-molecular ion in equilibrium with the ions in solution.

An important point of difference between the theory of preferential adsorption of ions and that of selective desorption or dissociation as formulated by King is that in the former an enhancement of the ionisation of water is assumed whereas in the latter no change in the ionic product is suggested. In reviewing both theories it is essential to bear in mind that a pH-measurement involves the determination of the *activity* of the *H·-ion*. The potential of a hydrogen-electrode (to which category the glass-electrode belongs) is not directly affected by the activity of the OH′-ion and a measure of the latter is derived indirectly from the H·-ion activity and the ionic product of water.

According to the mechanism suggested by King, the low temperature oxide-layer of carbon dissociates in contact with water, and H·-ions pass into solution. The activity of the H·-ions in solution is thereby increased and this is registered by a fall in the pH-value. On the other hand, when the high temperature carbon reacts with water OH′-ions are sent into solution. This mechanism will not, however, explain the observation that a specimen of charcoal freed from soluble impurities registers in water a pH which is unaffected by changes in the concentration of charcoal or in the initial pH of water.

On the other hand, it is possible to modify the theory of preferential adsorption to account for the observed results. It may be assumed that the carbon, with its oxide layer as such, adsorbs either H·- or OH′-ions preferentially but not exclusively. It should then be expected that the ionisation of water will increase to such an extent as is required by the adsorption-equilibrium between the adsorbent and the $H^{\cdot}$- and $OH'$-ions and by the mutual affinity between the two ions. Since preferential adsorption is possible only if the affinity between the adsorbent and the ion in question is greater than the mutual affinity between the two ions, we should expect to find in the solution (water) that one of the ions is of smaller activity (on account of preferential adsorption) and the other ion of greater activity (on account of increased ionisation) than is obtained normally in pure water. If the $H^{\cdot}$-ion is preferentially adsorbed from water, then the activity of the $H^{\cdot}$-ion will be reduced in the solution and consequently a pH-value greater than 7 will be registered. On the other hand, if the $OH'$-ion is preferentially adsorbed, then the $H^{\cdot}$-ion will be left in excess and, due to enhanced ionisation, the activity of the $H^{\cdot}$-ion will be greater than $10^{-7}$; in other words the pH will be lower than 7.

True equilibrium conditions between the carbon and the ion that is preferentially adsorbed by it cannot be expected because of the mutual affinity between $H^{\cdot}$- and $OH'$-ions. The ions, therefore, tend to distribute themselves between the absorbent and the solution in a manner determined by the affinity between the adsorbent and the ions and that between the ions themselves. There is, therefore, a triple equilibrium between the carbon and the $H^{\cdot}$- and $OH'$-ions which can be represented as follows:—

$$(1)\ C + H^{\cdot} \rightleftharpoons C\ldots H^{\cdot}$$
$$(2)\ C + OH' \rightleftharpoons C\ldots OH'$$
$$(3)\ H^{\cdot} + OH' \rightleftharpoons H_2O$$

The three reversible reactions are concurrent, and the increase of ionisation resulting from the first two reactions is counteracted by the third. A critical limit is therefore set on the degree of enhanced ionisation depending almost entirely on the first two reactions, that is to say, depending on the adsorptive power of carbon. It follows, in consequence, that the $H^{\cdot}$-ion activity in water in equilibrium with pure activated carbon is maintained at a particular critical value, depending almost wholly on the selective adsorptive power of the carbon. This explains why in the purified specimens the pH of the suspension varies very slightly, if at all, with variations in the concentration of carbon or of the initial pH of water.

The equilibrium pH of carbon suspensions being characteristic of the carbon, it varies with the conditions of carbon-activation. At low temperatures (*i.e.*, below 700°) exposure of carbon to air or oxygen produces marked acidic properties and hydroxyl ions are preferentially taken up by such carbons. At higher temperatures the carbon develops a basic character, adsorbing hydrogen ions in preference. Hence the observation that carbons air-activated at moderate temperatures give acid solutions, while those prepared at elevated temperatures give alkaline solutions. It may once again be emphasised that the hydrogen ion activity in an aqueous suspension of carbon can be influenced by two factors:

(1) a non-equivalent adsorption of the ions, and

(2) an increase in the degree of ionisation of water.

This admits the possibility of a low temperature carbon exercising equal affinity for $H^{\cdot}$- and $OH'$-ions (or acids and bases respectively) and yet give an acid reaction with water through enhanced ionisation. For precisely the same reason, a carbon possessing greater affinity for the hydrogen-ion may give a neutral solution with a pH-value of 7.

## Summary

1. The pH-values of aqueous suspensions of commercial activated charcoals, at different stages of washing with water, are determined with a glass-electrode. A convenient glass-electrode arrangement is described.

2. In the case of the partially washed specimens, the pH of the suspension varies with time, concentration and initial pH of water. The values obtained with the same specimens after thorough washing are found to be constant.

3. The influence of various acidic and basic substances present in charcoal are discussed.

4. The pH-effect of active carbon is explained on the basis of a non-equivalent adsorption of $H^{\cdot}$- and $OH'$-ions and an increased ionisation of water.

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