With the exception of the values marked with an asterisk, the data contained in the foregoing table have been compiled from the valuable summary of freezing-point data published by Noyes and Falk;<sup>1</sup> the values marked with an asterisk were taken from the tables published by Jones.<sup>2</sup>

The hypothesis advanced by Jones and the author<sup>3</sup> in explanation of this minimum in the freezing-point curve of a large number of electrolytes was that a certain portion of the solvent was removed from functioning as such owing to solvation of the dissolved substance. Should solvation tend to occur in solutions of hydrochloric acid, it is apparent that in a cell such as that indicated by the following scheme,

 $Hg - HgCl - 0.1 N HCl \parallel 1.0 N HCl - HgCl - Hg,$ 

the removal of an increasing amount of water from the rôle of solvent, with increasing concentration, would tend to cause an increase in the observed values of the electromotive force above those calculated by the Nernst equation, and therefore a corresponding increase in the values of the activity coefficient would occur. If the minima are due to solvation, we might reasonably expect a shift in the direction of increasing concentration as the temperature is raised. Such is actually found to be the case; the minima in the freezing-point curves occur at 0.2 molar concentration while those in the activity curves, based on measurements of electromotive force at 25°, occur at 0.5 molar concentration. While it is not claimed that the existence of similar minima in the 2 sets of curves is to be ascribed to solvation, or to any other common cause, it is suggested that such an explanation is not without the range of probability.

The author hopes to continue the investigation of this question in the near future.

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## A STUDY OF A DECOLORIZING CARBON.

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The use of finely divided carbon to decolorize solutions is universal. There are, however, comparatively few attempts recorded in the literature to use it for the removal of substances other than coloring matters. While working on the removal from blood of residual proteins (after heat coagulation) we tried a charcoal of vegetable origin. While this was found to remove proteins quantitatively, it also caused a lowering of the non-protein nitrogen. As there are numerous occasions where decolor-

<sup>1</sup> This Journal, 32, 1011 (1910).

<sup>2</sup> "Hydrates in Aqueous Solution," Carnegie Inst. Publication 60.

<sup>3</sup> Z. physik. Chem., 46, 286 (1903).

izing carbons are used in laboratory procedures, it was thought of interest to find out to what extent the decolorizing carbon removes nitrogenous and other constitutents from biological fluids. Urine was used in the majority of these experiments.

The carbon used in the present investigation was a vegetable carbon called "Norit." It is obtained from the manufacturer as a finely divided, intensely black powder, perfectly dry and of very low ash content. In most of the experiments it was used in this form, no attempt being made to utilize the finer particles only, although the investigations of A. B. Bradley<sup>1</sup> show a higher efficiency for the more finely divided (124-mesh sieve) carbon. Other conditions being equal, the material having the higher carbon content should give the better result. We compared the ash contents of Norit with that of animal charcoal (Merck, U. S. P.), assuming that the latter is very commonly used in the laboratory. One set of determinations was made on carbon which had been treated with dil. hydrochloric acid, filtered with suction, washed with water, treated with dil. alkali and then washed to a neutral reaction. Table I shows the analytical results obtained.

| TABLE | Т |
|-------|---|
| TUDUC |   |

Composition of Decolorizing Charcoal, in Percentages.

|       | 1                     | Norit.      | Animal ch     | arcoal. |
|-------|-----------------------|-------------|---------------|---------|
|       | As purchas            | ed. Washed. | As purchased. | Washed. |
|       | 1 4.87                | 2.20        | 73.35         | 17.16   |
| Anth  | 2 5.40                | 2.17        | 73.13         | 17.01   |
| Asu   | 3                     |             | 73.65         | 16.95   |
|       | Aver 5.13             | 2.18        | 73.34         | 17.04   |
| Diffe | rence as carbon 94.77 | 97.82       | 26.66         | 82.96   |

The procedure used in most of the experiments was as follows. A measured quantity of urine (100-200 cc.) was shaken with a weighed amount, usually 5%, of Norit, and then filtered. The shaking need not be very prolonged nor especially vigorous, as long as a good mixing and an even distribution of the substance throughout the liquid are accomplished.

The results are presented in the following tables. It will be seen from Table II that the total nitrogen is considerably decreased, the loss amount-

|                  | TABLE II.            |          |           |
|------------------|----------------------|----------|-----------|
|                  | Effect of Norit on 1 | Urine.   |           |
| 100 Cc. c        | of Urine Treated wit | h 5 G. c | of Norit. |
| Untreated urine. | Treated.             |          | Loss. %.  |
|                  | Total Nitrogen.      | G.       |           |
| 13.265           | 10.773               |          | 18.8      |
| 4.900            | 4.162                |          | 15.0      |
| 9.576            | 8.232                |          | 12.9      |
| 7.140            | 6.066                |          | 15.0      |
| 5.894            | 4.858                |          | 15.8      |

<sup>1</sup> A. B. Bradley, J. Soc. Chem. Ind., 38, 396 (1919).

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|                  | TABLE II (continued). |          |
|------------------|-----------------------|----------|
| Untreated urine. | Treated.              | Loss. %. |
|                  | Ammonia Nitrogen. G.  |          |
| 0.6126           | 0.3199                | 4.59     |
| 0.4880           | 0.4550                | 0.67     |
| 0.5450           | 0.3560                | 3.47     |
| 0.3530           | 0.3050                | 1.57     |
|                  | Urea Nitrogen. G.     |          |
| 4.368            | 4.004                 | 8.35     |
| 4.630            | 4.250                 | 8.20     |
| 7.490            | б.650                 | 11.21    |
|                  |                       |          |

ing to about 15%, the decrease in ammonia and urea nitrogen being proportional.

A much larger decrease will be noted in the creatinine results, the loss amounting to from 50 to 90%.

### TABLE III.

# Effect of Norit on Urine.

| Untreated urine. | Treated.       | Loss. %. |
|------------------|----------------|----------|
|                  | Creatinine. G. |          |
| 1.154            | 0.437          | 62.13    |
| 1.300            | 0.610          | 53.07    |
| 0.850            | 0.095          | 88.82    |
| 0.855            | 0.170          | 80.11    |
| 1.501            | 0.600          | 60.03    |
| 1.470            | 0.558          | 62.04    |
| 1.316            | 0.210          | 84.04    |
| 0.675            | 0.035          | 91.85    |
|                  | Uric Acid. G.  |          |
| 0.655            | Trace          | • • •    |
| 0.520            | Trace          | • • •    |
| 0.122            | Trace          |          |
| 0.557            | 0.018          | • • •    |
| 0.375            | None           | • • •    |
| 0.313            | None           |          |
|                  |                |          |

Uric acid is almost quantitatively removed. In the cases where "trace" is reported, the color<sup>1</sup> in a liquid column of about 120 mm. or over was a faint blue. Where "none" is reported the color was that of the "blank" determination.

As indicated in Table IV, phosphates are decreased in amounts varying from 12 to 39%, whereas only a small percentage of chlorides is removed.

<sup>1</sup> The Benedict-Hitchcock method was used for the determination of uric acid, J. *Biol. Chem.*, 20, 619 (1913).

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|                  | TABLE IV.                                      |           |
|------------------|--|-----------|
| 1                | Effect of Norit on Urine.                      |           |
| roo Cc. of       | Urine Treated with 5 G.                        | of Norit. |
| Untreated urine. | Treated.                                       | Loss. %.  |
|                  | Phosphates. G. P <sub>2</sub> O <sub>5</sub> . |           |
| 0.960            | 0.716  | 25.41     |
| I.345            | 0.965  | 28.25     |
| 1.470            | 0.970  | 34.01     |
| 3.170            | 2.760  | 12.93     |
| 2.950            | 2.520  | 14.58     |
| 1.780            | 1.090  | 38.76     |
|                  | Chlorides. G. NaCl.                            |           |
| 4.85             | 4.75   | 2.06      |
| 9.90             | 9.90   | 0.00      |
| 7.00             | 6.90   | I.42      |
| 9.60             | 9.40   | 2.08      |
| 7.00             | 6.60   | 5.71      |
| 12.20            | 12.10  | 0.81      |
|                  |  |           |

The decrease in glucose, Table V, is comparatively small where sugarcontaining urines are concerned. If, however, pure solutions containing small amounts of glucose are treated with Norit, the removal of sugar may amount to over 25%.

|   | TABLE V.               |          |  |  |  |
|---|------------------------|----------|--|--|--|
| Effect of Norit on Urine and Pure Sugar Solution. |                        |          |  |  |  |
| Untreated urine.                                  | Treated with 5% norit. | Loss. %. |  |  |  |
|   | Glucose. Per cent.     |          |  |  |  |
| 3.30  | 3.12                   | 5.45     |  |  |  |
| 1.98  | I.94                   | 2.02     |  |  |  |
| 1.77  | 1.77                   | 0.00     |  |  |  |
| 3.57  | 3 54                   | 0.84     |  |  |  |
| 1.97  | r.95                   | 1.01     |  |  |  |
| I.79  | I.74                   | 2.79     |  |  |  |
| 3.07  | 3.03                   | 1.30     |  |  |  |
| Pure glucose sol.                                 |                        |          |  |  |  |
| 0.41  | 0.32                   | 21.95    |  |  |  |
| 0.30  | 0.22                   | 26.66    |  |  |  |
| 0.37  | 0.30                   | 23.33    |  |  |  |
| 0.77  | 0.64                   | 16.88    |  |  |  |

It should be mentioned in this connection that lactose is removed to about the same extent from milk as glucose is from urine. The milk was diluted with water, acidified and heated. Norit was then added and the mixture filtered. Perfectly clear filtrates were obtained which showed, however, a considerable decrease in lactose as compared with samples with which another method of protein removal was employed.

The effects of adding various amounts of carbon are shown in Table VI. The loss is proportional to the amount of Norit used in all cases except that of uric acid. It is, however, impossible to obtain colorless

filtrates with 3% and in cases of deeply colored urines with 4% additions of Norit.

|             | TAB        | LE VI.           |                    |           |
|-------------|------------|------------------|--------------------|-----------|
| Effect of V | /arious Am | ounts of Norit o | on Urine.          | 1-        |
|             | Untreated  |                  | Jo cc. treated wit |           |
| And         | urine.     | 3% Norit.        | 4% Norit.          | 5% Norit. |
| Total N     | 7.140      | 6.328            | 6.202              | 6.066     |
| Urie acid   | 0.375      | Trace            | None               | None      |
| Creatinine  | 0.850      | 0.286            | 0.172              | 0.095     |

In all cases, we used the carbon as obtained from the manufacturer. A comparison between effectiveness of such material and washed Norit is shown in Table VII. The differences in the results are rather small, but are, of course, in favor of the purified product.

|                           | 1                  | l'able VII.   |             |                  |                 |          |
|---------------------------|--------------------|---------------|-------------|------------------|-----------------|----------|
| Comparison of the E       | ffect of C         | Commercial    | and Wash    | ed Norit         | on Urin         | e.       |
|                           | Total<br>nitrogen. | Uric<br>acid. | Creatinine. | Phos-<br>phates. | Chlo-<br>rides. | Glucose. |
| Untreated urine           | 8.008              | 0.313         | 0.764       | 1.13             | 8.55            | 1.98     |
| Treated with com'l Norit  | 7.280              | None          | 0.139       | 0.98             | 8.40            | I.94     |
| Treated with washed Norit | 7.056              | None          | 0.123       | 0.96             | 8.55            | I.94     |

A short attempt was also made to test the behavior of Norit toward bacteria. Bouillon cultures of 2 organisms were shaken with Norit for a few seconds, then allowed to stand for 3 or 4 minutes. While sterilization was by no means complete, there was a very marked decrease in bacterial count. It may be possible, as has been claimed by one European observer, to effect complete sterilization in this way. The matter will be further investigated.

#### Summary.

(1) Norit removes, from urine, ammonia-nitrogen, chlorides and glucose slightly; urea, total nitrogen and phosphates considerably; creatinine very largely, and uric acid completely.

(2) Adsorption from solution by solids is specific and selective. This unfortunately means only that we are as yet ignorant of relations which undoubtedly do exist between the degree of adsorption, on the one hand, and the physical and chemical properties of adsorbent and adsorbed substance on the other.

(3) Freundlich's simple adsorption formula holds good for the two cases of total nitrogen and creatinine, given in Table VI. In the case of pure glucose, Table V, the experimental errors in determining such small quantities of glucose are necessarily too large to test the adsorption formula. Nevertheless, Tests 1, 2 and 4 in this series indicate that the formula holds, as has already been established by Herzog and others.

(4) When several solutes are present in a solution, each one of them is adsorbed less than when they are present separately. This is well shown in Table V, where the amount of glucose adsorbed, when present alone in quantities of 2 to 3% would be much larger than 0.05%, since 0.09% is adsorbed at an initial concentration of 0.46%.

We wish to express our thanks to Mr. W. Leitch, of Joseph Bakers, Ltd., White Plains, N. Y., for his help in procuring the Norit. We also wish to thank Mr. Robert Whymper, Bermondsey, London, S. E., for his kind and valued advice.

MILWAUKEE, WISCONSIN.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF ILLINOIS.]

# DETERMINATION OF THE ELECTROLYTIC POTENTIAL AND OVERVOLTAGE OF ARSENIC.

BY VINCENT B. MARQUIS. Received May 18, 1920.

### 1. Electrolytic Potential.

The electrolytic potential of arsenic, or the potential between an arsenic electrode and a solution normal with respect to arsenious ions, has never been accurately determined because of the difficulty of determining the arsenious ion concentrations. In aqueous solution arsenious salts are strongly hydrolyzed and the metal ion concentration cannot be determined by conductivity measurements because of the presence of the acid which is formed by the hydrolysis. The conductivity of arsenious trichloride and hydrochloric acid solutions were measured by Zawidzki<sup>1</sup> with results as shown in the following table, in which V is the number of liters containing one mol and  $\Lambda$  the equivalent conductivity.

| V. | $ \begin{array}{c} \Lambda. \\ HCl + As(OH)_{3}. \\ I/ohm. \end{array} $ | HCl.<br>1/ohm, | $\Lambda' - \Lambda.$<br>1/ohm. |
|----|--|----------------|---------------------------------|
| 16 | 366.3  | 368.5          | +2.2                            |
| 32 | 374.2  | 375.3          | +1.0                            |
| 64 | 379.6  | 379.2          | 0.6                             |

These results show clearly why conductivity measurements do not help in the determination of arsenious ion concentration. The ability of arsenious chloride to form arsenious cations has, however, been demonstrated by Kahlenberg and Lincoln<sup>2</sup> by measuring the conductivity of solutions of arsenious chloride in ethyl aceto-acetate and nitrobenzene.

The potential between an arsenic electrode and a normal solution of arsenious chloride was measured by B. Neumann<sup>3</sup> and found to be 0.550 volt. From this value it has been estimated by Abegg that the electrolytic potential of arsenic is  $\pm 0.27$  volt, using the scale in which hydro-

<sup>2</sup> Kahlenberg and Lincoln, J. Phys. Chem., 3, 28 (1899).

<sup>3</sup> Neumann, Z. physik. Chem., 14, 220 (1894).

<sup>&</sup>lt;sup>1</sup> Zawidzki, Ber., 36, 1434 (1903).