The true freezing point of benzene may then be safely taken as 5.483°. This is only 0.001° different from the result of Barry, and 0.003° different from the latest and best trials of Davis.

The wide deviations of others are probably to be referred chiefly to doubtful thermometry, for benzene is evidently not very difficult to obtain in a pure state.

These experiments show that the freezing point of pure benzene, 5.483°, is attained so easily that it may be used as a very satisfactory fixed point in thermometry; and taken in connection with the freezing point of water, about 5.5° below, may afford an excellent means of fixing two points on a Beckmann thermometer.

The authors are glad to express indebtedness to the Carnegie Institution of Washington for generous support in this investigation.

Summary.

The results of this research may be summed up as follows:

(1) Benzene pure enough for the purpose in hand is not difficult to prepare.

(2) With due precautions in the thermometric measurements a very definite freezing point is given by benzene. The true value is determined by constancy after repeated fractional crystallization.

(3) The freezing point of benzene is 5.483° ± 0.002° on the international hydrogen scale.

(4) This fixed temperature may be advantageously used, in connection with the ice point of water, for calibrating Beckmann thermometers. Especial attention must be paid to the temperature of the exposed column in correcting this interval for use at other temperatures.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

ON THE ABSORPTION OF GLUCOSE BY BONE-BLACK.

[PRELIMINARY COMMUNICATION.]

BY HAROLD A. MORTON.

In connection with a study of the mutarotation and specific rotatory power of the sugars, I have been obliged to purify a considerable quantity of glucose. Using bone-black as a decolorizer, I observed that a surprisingly large quantity of the sugar was extracted by the bone-black from the aqueous solution. It appeared interesting to investigate the phenomenon systematically, the question being whether the partition of the sugar does not follow some simple principle, like the distribution law.

Preliminary experiments soon indicated that at ordinary temperatures the process of absorption is exceedingly slow, and that, to obtain results within a reasonable time, it would be best to employ a temperature of about 80°. In the experiments described below, a Freas constant temperature oven was employed. The tubes containing the mixtures were kept within the oven in a large bath of water covered with a layer of oil. In this manner it was possible, throughout the experiments, to maintain a temperature of 80.6°, the variations from which at no time exceeded 0.2°. The glass tubes in which the experiments were carried out had a capacity of about 35 cc. Into each tube was introduced a carefully weighed amount (about 3.5 g.) of bone-black and a measured volume (in most cases 23 cc.) of sugar solution. The tube was then sealed off, the bone-black more or less evenly distributed throughout the solution by gentle tapping, and the tube placed horizontally in the bath. In some cases two, in others three, tubes of the identical make-up were used, to permit of testing the attainment of equilibrium by abandoning the tubes for different lengths of time. Preliminary experiments had indicated that as 80° equilibrium is not attained in less than six days, and consequently, as the tables show, none of the tubes were removed for examination in less than this time. In most cases equilibrium was attained after about ten days of heating.

Ordinary distilled water was employed without further purification. The sugar was purified by recrystallization of pure anhydrous glucose from water at ordinary temperatures; the resulting monohydrate, after being air-dried, was used as such for making up solutions of approximately the desired strength. The exact strength of the solutions was then determined polarimetrically on the basis of Tollens's measurements.[1]

Preliminary experiments having indicated that no commercial bone-black could be relied on to be sufficiently pure, Kahlbaum's best bone-black was subjected to a somewhat laborious process of purification. It was first stirred for several hours in a large volume of nearly boiling 2% nitric acid, then the process was repeated with a fresh lot of nitric acid, next the bone-black was similarly treated with 2% solutions of sodium carbonate, and finally all soluble salts were thoroughly washed out by stirring with large amounts of distilled water. On filtering off the last wash-water, the mass was carefully dried.

After the requisite time of heating in the thermostat, each tube was opened and its contents filtered through a layer of asbestos in a Gooch crucible, care being taken not to lose any of the filtrate, which was weighed. In this manner it was learned what weight had been lost by absorption in the bone-black. The filtrate being thereupon analyzed polarimetrically, it further became clear how much sugar and also how much water had been taken up by the bone-black. The method is obviously not very precise, for in spite of all effort a certain amount of the solution was partly lost, partly retained mechanically by the bone-black, but fortunately the inaccuracy has not been such as to obscure the law which apparently

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[1] Tollens, *Ber.*, 9, 1535 (1876).

TABLE I.

	Series I. Tube No.			Series II. Tube No.		Series III. Tube No.		Series IV. Tube No.		
	I.	II.	III.	I.	II.	I.	II.	I.	II.	III.
Weight of bone-black	3.51	3.51	3.46	3.50	3.50	3.52	3.51	3.52	3.51	3.49
Original weight of solution	28.14	27.75	23.32	24.30	24.26	24.66	24.73	25.15	25.24	25.03
Original angle a (circular degrees)	4.976	4.976	4.976	14.898	14.898	20.232	20.232	26.258	26.258	26.258
Original percentage glucose in solution	4.630	4.630	4.630	13.338	13.338	17.748	17.748	22.507	22.507	22.507
Original weight of glucose in solution	1.303	1.285	1.080	3.242	3.236	4.377	4.389	5.661	5.681	5.634
Time of heating (hours)	144	174	262	171	265	172	266	148	196	269
Final weight of solution	24.8	23.6	19.2	20.3	20.5	20.6	20.3	21.2	20.8	20.4
Final angle a (circular degrees)	4.039	4.022	3.856	13.108	12.673	18.477	17.745	24.537	24.157	23.356
Final percentage of glucose in solution	3.771	3.756	3.603	11.818	11.444	16.320	15.716	21.171	20.876	20.243
Final weight of glucose in solution	0.935	0.886	0.692	2.399	2.346	3.362	3.190	4.488	4.342	4.130
Final weight of glucose per 1 g. solution (c_1)	0.0377	0.0375	0.0360	0.1182	0.1144	0.1632	0.1572	0.2117	0.2088	0.2024
Total weight of glucose in bone-black	0.368	0.399	0.388	0.843	0.890	1.015	1.199	1.173	1.339	1.504
Weight of glucose per 1 g. bone-black (c_2)	0.105	0.113	0.112	0.241	0.254	0.288	0.341	0.333	0.381	0.431
$\frac{\text{Weight of glucose per 1 g. solution}}{\text{Weight of glucose per 1 g. bone-black}} = \frac{c_1}{c_2}$	....	0.33	0.32	....	0.45	....	0.46	....	....	0.47

	Series V. Tube No.			Series VI. Tube No.		Series VII. Tube No.		
	I.	II.	III.	I.	II.	I.	II.	III.
Weight of bone-black	3.51	3.53	3.52	3.51	3.51	3.52	3.52	3.52
Original weight of solution	26.49	26.42	26.58	27.43	27.62	28.21	28.49	28.37
Original angle a (circular degrees)	42.635	42.635	42.635	57.837	57.837	68.312	68.312	68.312
Original percentage of glucose in solution	34.417	34.417	34.417	44.327	44.327	50.578	50.578	50.578
Original weight of glucose in solution	9.117	9.093	9.148	12.159	12.243	14.268	14.410	14.349
Time of heating (hours)	149	237	262	150	245	151	243	285
Final weight of solution	22.2	21.5	21.6	21.7	22.0	22.4	22.1	22.3
Final angle a (circular degrees)	39.242	39.145	38.661	54.409	52.772	64.505	62.916	62.860
Final percentage of glucose in solution	32.062	31.994	31.653	42.183	41.145	48.361	47.410	47.376
Final weight of glucose in solution	7.118	6.879	6.837	9.154	9.052	10.833	10.478	10.565
Final weight of glucose per 1 g. solution (c_1)	0.3206	0.3199	0.3165	0.4218	0.4115	0.4836	0.4741	0.4738
Total weight of glucose in bone-black	1.999	2.214	2.311	3.005	3.191	3.435	3.932	3.784
Weight of glucose per 1 g. bone-black (c_2)	0.570	0.627	0.656	0.856	0.909	0.976	1.117	1.075
$\frac{\text{Weight of glucose per 1 g. solution}}{\text{Weight of glucose per 1 g. bone-black}} = \frac{c_1}{c_2}$	....	....	0.48	....	0.45	....	0.42	0.44

governs the results. The analyses were carried out with the aid of an excellent Lippich saccharimeter made by Schmidt and Haensch. The Ventzke degrees originally read off were changed into circular degrees, and, further, all angles given in the tables are based on readings obtained with a 2 decimeter tube.

The concentrations of the seven series of glucose solutions studied ranged from 4.63% to 50.58%, so that the regularity exhibited by the results can hardly be accidental. The results are fully reproduced in the tables, which will explain themselves.

The results of Series I to VII in Table I would seem to indicate that the absorption of glucose from aqueous solution follows a principle very like the distribution law. In these preliminary experiments, it was not possible to undertake a determination of the specific volume of the bone-black after it had taken up sugar, in order to ascertain the volume-concentration of sugar in the bone-black. The distribution law in its ordinary form could, therefore, not be tested. On the other hand, it was possible to compare the ratios of the weight of sugar per gram of solution to that per gram of bone-black in the several experiments. The results are summarized in Table II, which shows that *those ratios are practically equal for the entire range of concentrations studied.* Thus the distribution law seems to hold true here in some approximate form.

TABLE II.

Original concentration of aqueous solution. Per cent.	c_1 (in liquid).	c_2 (in solid).	c_1/c_2.
4.63	0.0360	0.112	(0.32)
13.34	0.1144	0.254	0.45
17.75	0.1572	0.341	0.46
22.51	0.2024	0.431	0.47
34.42	0.3165	0.656	0.48
44.33	0.4115	0.909	0.45
50.58	0.4738	1.075	0.44
			Mean, 0.46

The distribution constant 0.46 expresses the curious fact that when equilibrium has been attained the amount of sugar contained in a gram of bone-black is more than twice as great as that contained in a gram of solution, which would scarcely be expected.

But the data contained in the above tables indicate further that the bone-black had taken from the solutions, not only part of their glucose, but also part of the water. That the solution is not taken up by the bone-black without change, is shown by the observed change in rotation of the solutions. Table III shows the relative amounts of glucose and water in the bone-black and in the aqueous solution. The weight of glucose per 1 g. water in the bone-black is denoted by the symbol c'_1; the weight of glucose per 1 g. of water in the solution is denoted by c'_2. Leaving out of account the most dilute solution (Series I), the ratios c'_2/c'_1, shown by the last horizontal line in the table, may probably be considered as constant within the errors of experiment. However this be, the value of the ratio indicates that the solution within the bone-black is at least twice as concentrated as the outside solution.

TABLE III.

	Series No.						
	I.	II.	III.	IV.	V.	VI.	VII.
Grams glucose in final solution	0.691	2.334	3.191	4.129	6.836	9.053	10.566
Grams water in final solution	18.5	18.1	17.1	16.3	14.8	12.95	11.73
Glucose per gram of water in the solution (c'_1)	0.037	0.129	0.186	0.254	0.463	0.699	0.900
Grams glucose in bone-black	0.389	0.902	1.193	1.499	2.320	3.182	3.799
Grams water in bone-black	3.71	3.00	3.21	3.10	2.68	2.42	2.30
Glucose per gram of water in the bone-black (c'_2)	0.105	0.301	0.372	0.484	0.865	1.316	1.65
$\frac{\text{Glucose per gram of water in bone-black}}{\text{Glucose per gram of water in solution}} = \frac{(c'_2)}{(c'_1)}$	(2.8)	2.3	2.0	1.9	1.9	1.9	1.8

It finally seemed interesting to inquire whether bone-black does not take up water according to some principle similar to that followed by its absorption of glucose. Table IV shows this to be the case.

TABLE IV.

W_c. Grams water per 1 g. of bone-black.	W_s. Grams water per 1 g. of solution.	W_c/W_s.
1.07	0.96	1.1
0.86	0.89	1.0
0.91	0.84	1.1
0.89	0.80	1.1
0.76	0.68	1.1
0.69	0.59	1.2
0.65	0.52	1.2
		Mean, 1.1

It is my hope to continue these experiments under conditions permitting of greater precision of measurement, and to extend them to a number of other substances.

It is a pleasure to express my gratitude to Professor M. A. Rosanoff for a number of helpful suggestions in connection with this work. Indirectly my thanks are also due to the National Academy of Sciences, for the use of instruments placed at the disposal of Professor Rosanoff and his students by the Committee of the Bache Fund.

WORCESTER, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE VOLUMETRIC ESTIMATION OF TITANIUM BY MEANS OF FERRIC CHLORIDE.

BY T. R. BALL AND G. MCP. SMITH.

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The tedious operations involved in the quantitative separation of titanium from iron, aluminium, etc., render it desirable to find a convenient and reliable volumetric process for the direct determination of this element in the presence of the above mentioned substances.

With this end in view, various processes have been proposed for the volumetric estimation of titanium. All of these are based upon the fact that titanic salts are under certain conditions capable of being reduced quantitatively to salts of trivalent titanium, which, in turn, may readily be oxidized back to the tetravalent condition; as oxidizing agents for this purpose have been proposed, potassium permanganate, methylene blue, and ferric salts.

Owing to the difficulty experienced in titrating with permanganate in the presence of ferrous iron and hydrochloric acid, Wells and Mitchell[1] reduce the iron in sulfuric acid solution with hydrogen sulfide, and then titrate the iron alone with potassium permanganate. In the resulting solution they reduce the iron and the titanium with zinc, after which both metals are titrated with potassium permanganate. The titanium is, of course, gotten by difference. According to the authors, the results are always somewhat low.

In accordance with Wells and Mitchell, Newton[2] reduces the two metals in sulfuric acid solution with zinc, in an atmosphere of hydrogen. Then, however, in order to lessen as much as possible the oxidizing action of air on the solution during the subsequent operations, he adds an excess of ferric sulfate solution. In this way, the titanous sulfate present is at once oxidized at the expense of an equivalent quantity of the ferric iron, and the total ferrous iron in the resulting solution is titrated with potassium permanganate.[3]

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[1] THIS JOURNAL, 17, 878 (1895).

[2] *Am. J. Sci.*, 25, 130 (1908).

[3] According to either of these methods, it is necessary to correct for any iron which may be contained in the zinc. No such correction has to be made in the case of the methylene blue and ferric salt titration methods.