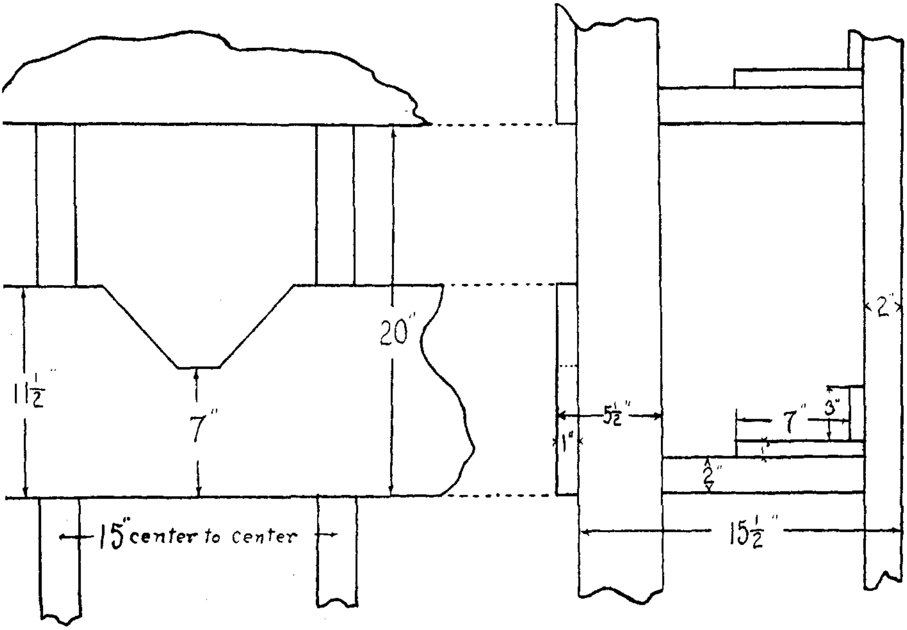
the bottle is placed in the rack, and the siphon inserted. A rubber tube leading from the distilled water tap is then connected to the lower end of the siphon and the bottle filled. The strong current of water entering at the deepest part of the solution acts as sufficient stirrer to thoroughly mix the solution and secure uniform density.



In this way a large number of bottles can be compactly stored and the solutions are easy of access. The framework structure allows the bottles to be cleaned without removing them from the rack, as they are exposed on all sides. All dirt can be brushed down into the inclined lead-lined drip trough at the base of the rack and flushed off. J. LORENZ SPORER.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPT. OF AGRICULTURE.]

IS THE HYDROLYSIS OF CANE SUGAR BY ACIDS A UNIMOLECULAR REACTION WHEN OBSERVED WITH A POLARISCOPE?

BY C. S. HUDSON.

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It may be recalled that in 1908 Julius Meyer[1] expressed the view that the hydrolysis of cane sugar by acids is accompanied by two simultaneous reactions, the mutarotation of glucose and fructose, and published experiments which seemed to show that the hydrolysis when observed

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[1] *Z. physik. Chem.*, 62, 59–88 (1908).

with the polariscope deviates slightly from the unimolecular order during the first 3 or 4 per cent. of the reaction. In the same year the author[1] showed that the hydrolysis of cane sugar by the enzyme invertase is certainly accompanied by these mutarotation reactions, but claimed that the acids catalyze the mutarotations so greatly that they are not of detectable influence in the hydrolysis of cane sugar by acids. Meyer's experiments, which seemed to show such an influence, were criticized on the ground that the possible errors in them were greater than Meyer had estimated and even greater than the deviation from the unimolecular order which he recorded. Essentially the same criticism has also been made by Bodenstein.[2] In a reply to these objections Meyer[3] has lately insisted on the great accuracy of his experiments and claims that he did indeed detect the mutarotation reactions during the hydrolysis of cane sugar by acids.[4] If the question were only a difference of opinion regarding the accuracy of Meyer's experiments the discussion could well be closed because all three parties are agreed on the principal point, namely, that the hydrolysis of cane sugar is not the simple reaction that it has heretofore been supposed to be, but is accompanied by two other important reactions. But Meyer goes further than this and claims[5] that he first proved experimentally the existence of these subsidiary reactions, and on account of this claim, which appears to me quite unwarranted, the following further criticism of Meyer's experiments is made. In it I will seek to show that Meyer has repeated portions of his measurements and found them to be entirely erroneous, that Armstrong and Caldwell made measurements similar to Meyer's four years in advance of him and found numbers which are different even in sign from Meyer's, that the deviation which Meyer claims he found is opposite in sign from that predicted by the very theory which he was testing, that certain obvious precautions which are necessary for the accuracy that Meyer attempted to reach were overlooked, and that his latest measurements contain certain self-evident errors of great size.

In Meyer's first article the mutarotation of fructose was found to have the velocity coefficients 0.017 at 18° and 0.027 at 25°. In response to a letter from me he has measured these values again and now finds 0.18 at 18° and 0.32 at 25°, values which are tenfold greater than his former

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[1] THIS JOURNAL, 30, 1160–6 (1908).

[2] *Z. Elektrochem.*, 15, 413 (1909).

[3] *Z. physik. Chem.*, 72, 117–23 (1910).

[4] In replying to my criticism Meyer has made an arithmetical error (p. 119) in which he confuses 3 per cent. with three-tenths of 1 per cent. and this difference refutes his own argument. It will be sufficient time to discuss the bearing of this portion of the reply after he publicly corrects this error. He has also confused α- and β-fructose on pp. 117 and 122.

[5] *Z. physik. Chem.*, 72, 117 (1910).

ones. Although he thus admits that one set of his measurements was entirely incorrect, he insists that another set of a similar though not identical kind, namely that in which the minute deviation was supposedly detected, contains no error greater than about one-tenth of 1 per cent. The experiments were made under the same conditions, and great accuracy is claimed for one set and great error admitted for the other; comment would hardly seem necessary.

In 1904 Armstrong and Caldwell[1] made polariscopic measurements to test whether the hydrolysis of cane sugar by acids follows the unimolecular order and came to the conclusion that it does not, and that the velocity-coefficient of the reaction *increases* slightly during the inversion instead of remaining constant as is required by the theory. Meyer's measurements lead him to the conclusion that the velocity-coefficient *decreases* during the inversion. Meyer has not mentioned this work of Armstrong and Caldwell, nor the older work of O'Sullivan and Tompson,[2] who were the first to show that the mutarotation of glucose accompanies the inversion of cane sugar by invertase, nor the work of the author,[3] which shows that the mutarotation of both glucose and fructose follows slowly on the hydrolysis by invertase. It would seem that he should at least discuss the cause of the disagreement between his detection of the *decreasing* coefficient and Armstrong and Caldwell's of an *increasing* one, particularly in view of the fact, which I shall immediately explain, that a *decreasing* coefficient is not in agreement with the theory which Meyer was testing.

Meyer supposes that the mutarotation of glucose and fructose following the inversion of cane sugar would cause the reaction as measured by the polariscope to show a decreasing coefficient, and as he found a decreasing one in his experiments he claims that he has proved experimentally the correctness of the theory. The mutarotation of fructose proceeds so much faster than that of glucose that the influence of the former may be neglected in comparison with that of the latter. The glucose which is first formed is known to be α-glucose, of specific rotation 110°, and it subsequently passes to the stable mixture of α- and β-glucoses, of specific rotation 52°. If now the mutarotation of glucose is comparable in rate with the inversion of cane sugar, the glucose resulting from the hydrolysis will contain an excess of α-glucose and have a specific rotation higher than the stable mixture, 52°. As it is assumed in calculating the velocity-coefficient of the hydrolysis from the polariscopic readings that the glucose has the specific rotation 52°, the presence of an excess of α-glucose, due to the comparative slowness of the mutarotation reaction, must cause

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[1] *Proc. Roy. Soc. London*, 74, 195–201 (1904).

[2] *J. Chem. Soc.*, **57**, 834–931 (1890).

[3] THIS JOURNAL, **30**, 1160–6, 1564–83 (1908); **31**, 655–64 (1909).

the inversion to appear slower than it really is. During the further progress of the inversion the excess of α-glucose diminishes and therefore the polariscopic readings in the late stages of the reaction give a true measure of the extent of the hydrolysis. Such a reaction, in which there is an error of this kind causing it to apparently go slower in its initial stages than it really does, must give an *increasing* velocity-coefficient during its progress. Meyer found however a *decreasing* coefficient, which is thus quite at variance from the theory which he claims he has proved by detecting such a coefficient. It would seem to the author that this point should be a conclusive objection to Meyer's claim that he proved the existence of the mutarotation reactions in the hydrolysis of cane sugar.

It is to be objected to the experiments of both Meyer and Armstrong and Caldwell that a source of considerable error was not considered, namely the fact that the specific rotation of fructose increases with its concentration; thus in the hydrolysis of a 20 per cent. cane sugar solution the fructose increases in concentration from zero to about 10 per cent., which involves according to the measurements of Hammerschmidt[1] and others, an increase of 2 per cent. in the specific rotation of fructose. If the progress of the inversion is calculated from the polariscopic readings under the assumption that the specific rotation of fructose remains constant during the reaction, the velocity coefficient must be expected to increase. The changing concentrations of glucose and cane sugar also involve similar corrections, but they are small in comparison with that for fructose. This error would affect the velocity coefficient in the same manner that the mutarotation of glucose would, and until it is accurately investigated it cannot be claimed that an *increasing* coefficient proves the occurrence of the mutarotation during the hydrolysis of cane sugar by acids; and of course the claim of Meyer, who found a *decreasing* coefficient, is quite unreasonable.

Lastly, as an illustration of the inaccuracies which occur in Meyer's measurements, and in refutation of his insistence that both Bodenstein and the author have done him the injustice of underestimating the accuracy of his work, it may be mentioned that he records[2] as the final rotations of two fructose solutions of the same concentration, prepared from the same sample, and measured in tubes of the same length, —14.40° at 25° and —14.41° at 18°. It is well known that fructose has one of the largest temperature coefficients of rotation ever found, namely 0.007° per degree of rotation per degree rise of temperature.[3] Other observers, including Dubrunfaut, Zecchini, Dafert, Hönig and Jesser, Jungfleisch and Grimbert, Wiley, Borntraeger, and Ost,[4] have invariably detected

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[1] *Z. Ver. d. Zuckerind.*, 41, 157.

[2] *Z. physik. Chem.*, 72, 122 (1910).

[3] Wiley, *Am. Chem. J.*, 18, 81.

[4] Lippmann's "Chemie der Zuckerarten," ed. 1904, Vol. I, pp. 823–5.

a change of rotation for such solutions of (14.40) (0.007) (7) = 0.69°, or over half a degree, but Meyer did not find any appreciable difference at the two temperatures. With this error of half a degree plainly visible in his published work it is impossible to agree with him that such readings as 40.45° and 40.41° differ beyond his experimental error; and yet the deviation from the unimolecular order which he found the inversion of cane sugar by acids to show, depends on the reality of the difference between such measurements.[1]

The rates of the inversion of cane sugar and the mutarotation of glucose at different temperatures and acid strengths have been measured by various investigators, and it is possible to calculate from them the deviation which is to be expected from the unimolecular order due to the mutarotation of the glucose. The author has made such a calculation and finds the deviation to be, under the most favorable conditions of temperature and acidity, a very small quantity only about a tenth of 1 per cent. It agrees in magnitude and sign with the deviation which Armstrong and Caldwell found and it is quite possible that the mutarotation reaction is responsible for a portion of their deviation, but the change in the specific rotation of fructose which has been mentioned, causes a deviation in the same direction and the two possible causes of the deviation leave the matter still in doubt as to whether Armstrong and Caldwell's deviation is due to mutarotation, change of rotation of fructose, or a true exception to the law of mass-action, which latter view is the one that Armstrong and Caldwell hold. But there can be no reasonable further doubt regarding the cause of Meyer's deviation—it was due to experimental errors alone, and is opposite in sign to the deviation predicted by theory.

A REVIEW OF DISCOVERIES ON THE MUTAROTATION OF THE SUGARS.[2]

By C. S. Hudson.

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Dubrunfaut[3] discovered in 1846 that the specific rotation of a freshly prepared cold solution of crystalline glucose decreases from an initial value of about 110° to become constant at 52°. This phenomenon he named *birotation* but later discoveries have shown the name to be inappropriate and the better term *mutarotation*, which was introduced by Lowry[4] in 1899, has generally replaced it, though the word *multirotation*

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[1] See *Z. physik. Chem.*, 62, 59–88 (1908).

[2] Presented at the Second Decennial Celebration of Clark University, Worcester, Mass., Sept. 15, 1909.

[3] *Ann. chim. phys.*, 18, 99–107 (1846); 21, 178–80 (1847); *Compt. rend.*, 23, 38–44 (1846).

[4] *J. Chem. Soc.*, 75, 212–5 (1899).