Whether ionization is the primary step in the chemical action produced by α-particles and other corpuscular radiation or not, since it is approximately proportional to it for most reactions, it remains the most convenient means of comparative reference. The specific ionization is either known or can be calculated for most gases, and thus at least an approximate prediction may be made of the quantity of chemical action to be expected under a given set of conditions.

GOLDEN, COLORADO.

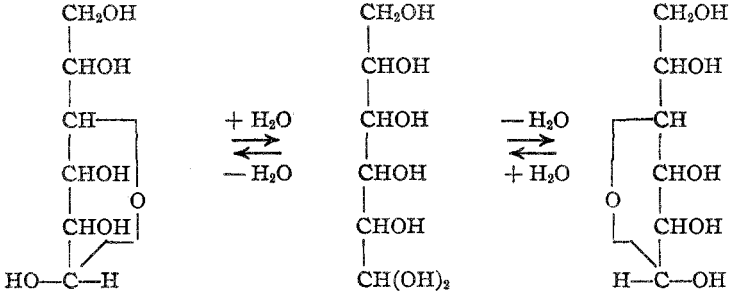
[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, ORGANIC CHEMISTRY, COLUMBIA UNIVERSITY. NO. 321.]

MUTAROTATION OF GLUCOSE AND FRUCTOSE.

BY J. M. NELSON AND FRANK M. BEEGLE.

Received January 2, 1919.

It is well known that a freshly prepared water solution of glucose gradually changes in optical rotatory power. This mutarotation is most commonly accounted for by considering that the dissolved sugar undergoes a transformation from one form to another, or from α- to β-glucose. The constitutions of these two forms are generally considered to be lactonic as represented in the formulas below. Various theories have been proposed for explaining the mechanism involved in this change. Among these might be mentioned that of Lowry who considers the intermediate formation of a hydrated aldehyde.



α-Glucose. Hydrated aldehyde. β-Glucose.

Since the aldehyde carbon is not asymmetric in the hydrated aldehyde, while in the other two forms it is, the disappearance and recurrence of the lactonic forms will tend to yield both the dextro and levo forms of this asymmetric group. In this way, if the dissolved glucose were originally α, part of it would go over into the intermediate and β forms until the equilibrium of the system was reached. Armstrong[1] objects to Lowry's view that the lactone bridge is opened up in the transformation, and believes that water adds to the lactone oxygen as an oxonium hydrate, instead of forming the intermediate hydrated aldehyde. When the water

[1] "The Simple Carbohydrates and Glucosides," 1912, p. 20.

is eliminated, an unsaturated compound results which then rearranges in either of two ways, yielding the α- and β-glucoses, respectively.

Urech[1] showed that the mutarotation was a monomolecular reaction, while Trey,[2] and Lowry,[3] found the rate of transformation to be influenced by temperature and the acidity of the solution. Hudson[4] found the velocity constant for the mutarotation of α-glucose, at 25° and a hydrogen ion concentration, ranging from 0.1 to 0.001 M to be 3.54×10^{-2} to 9.8×10^{-3}, and for a concentration of hydroxyl ion concentration between 2.2×10^{-6} and 6.6×10^{-6} molar to be 0.0326 to 0.0705. Similarly, in the mutarotation of fructose at 30° and a concentration of hydrochloric acid ranging between 0.0005 and 0.01 M, he found the velocity constant to vary from 0.128 to 0.196. It must be mentioned at this point, however, that Hudson's values for hydrogen ion concentration probably were calculated from conductivity tables and were not direct measurements. Fales and Nelson[5] have shown that this method of arriving at the hydrogen ion concentration of the solution is not exact enough, for this type of work, and that it is necessary to make direct measurements in each case.

There is a great variation in the literature concerning the values assigned to the specific rotation of α- and β-glucose and β-fructose and to the rotation, at equilibrium, for fructose. This is largely due, especially in the case of fructose, to lack of proper temperature control. Tollens and Parcus[6] give the specific rotation of β-fructose at 20° as —104°, and that it changes to —92° at equilibrium in a water solution. Hudson claims the specific rotation of α- and β-glucose as 25° to be +110° and +20°, respectively, and uses the value —140° at 30° for the specific rotation of β-fructose in some of his calculations. More recently,[7] however, he obtained at 20° +113.4° for the specific rotation of α-glucose, +19.7° for β-glucose and —133.5° for β-fructose, and —92° for the rotation of fructose at equilibrium.

The additional information supplied by the present investigation can be stated briefly as follows:

1. The relation between the rate of mutarotation of the three sugars, α- and β-*d*-glucose and β-*d*-fructose, and varying concentrations of hydrogen ion, which were measured directly, has been determined.

2. New values for the specific rotation of the three sugars have been obtained.

[1] *Ber.*, 16, 2270; 17, 1547; 18, 3059.
[2] *Z. phys. Chem.*, 22, 443, 448 (1897).
[3] *J. Chem. Soc.*, 83, 1314 (1903).
[4] THIS JOURNAL, 29, 1572 (1907); 30, 1576 (1908).
[5] *Ibid.*, 37, 2782 (1915).
[6] *Ann.*, 257, 167 (1890).
[7] THIS JOURNAL, 39, 1013 (1917).

3. The specific rotation of these sugars was found to be independent of the temperature between the limits studied.

4. The equilibrium rotation of glucose is not affected by temperature, while that of fructose varies with the temperature of the solution.

5. The mutarotation of glucose appears to be simply racemization, while that of fructose is not.

6. The mutarotation of glucose and fructose in the presence of each other, and in the presence of sucrose and invertase has been studied, and in each case was found to be independent of the other when present, except in the case of solutions containing fructose and sucrose when the rate of mutarotation and the rotation at equilibrium was affected.

7. The temperature coefficient of the mutarotation was also determined.

8. A new type of constant temperature bath for regulating the temperature of the polariscope tube has been devised.

Experimental.

Tables I–XII deal with the determination of the specific rotation of α-glucose, β-glucose and β-fructose. The hydrogen ion concentrations of the solutions were varied between $p_H{}^+ = 3.99$ and 5.0 for α- and β-glucose and $p_H{}^+ = 3.17$ and 3.4 for β-fructose, which values are within the limits of hydrogen ion concentration that give the minimum rate of mutarotation of the respective sugars.

Data used to Determine the Specific Rotation of α-Glucose.

TABLE I.

Temp. 0.15°. $p_H{}^+ = 3.98$.

Time in min. t.	Obs. rot. Degrees.	$k_1 + k_2 \times 10^5$.
4.3	11.02	(172)
23.3	10.86	84
43.0	10.65	84
67.0	10.44	80
131.0	9.86	80
206.0	9.34	76
276.0	8.84	77
356.0	8.35	78
427.0	8.12	73
572.0	7.48	73
636.0	7.25	74
698.0	7.02	75
764.0	6.75	78
1326.0	5.75	81
1488.0	5.64	79
1635.0	5.60	75
∞	5.25	..
		Av., 78

TABLE II.

Temp. 15°. $p_H{}^+ = 4.3$.

Time in min. t.	Obs. rot. Degrees.	$k_1 + k_2 \times 10^4$.
2.8	10.93	(51)
4.8	10.84	46
14.0	10.36	43
16.0	10.20	46
20.0	10.06	43
25.0	9.88	41
36.0	9.38	42
45.5	9.08	41
59.0	8.61	41
69.0	8.32	41
89.0	7.85	40
103.0	7.52	40
133.0	6.95	40
150.0	6.70	41
178.0	6.40	40
224.0	5.97	41
279.0	5.70	40
∞	5.25	..
		Av., 42

TABLE III.

Temp. 25°. $p_H^+ = 4.3$.

Time in min. t.	Obs. rot. Degrees.	$k_1 + k_2 \times 10^4$.
2.5	10.80	(97)
3.5	10.65	103
5.0	10.45	104
6.9	10.17	111
10.2	9.86	103
12.0	9.62	107
20.0	8.89	104
24.0	8.58	103
29.0	8.23	102
31.0	8.10	101
36.0	7.78	102
41.0	7.50	102
52.0	6.98	102
56.0	6.75	106
64.0	6.53	103
77.0	6.20	103
90.5	5.92	104
100.5	5.78	104
108.5	5.64	109
121.0	5.56	106
130.5	5.50	105
162.5	5.37	104
∞	5.25	...
		Av., 104

TABLE IV.

Temp. 37°. $p_H^+ = 3.99$.

Time in min. t.	Obs. rot. Degrees.	$k_1 + k_2 \times 10^4$.
2.0	10.36	301
3.0	10.10	(276)
4.2	9.72	282
6.7	8.98	294
8.4	8.58	293
11.1	7.98	299
12.8	7.66	302
15.0	7.30	304
17.5	6.95	303
19.9	6.67	310
21.1	6.48	309
24.5	6.30	308
26.5	6.18	296
28.7	6.00	314
36.5	5.70	303
50.5	5.44	305
61.5	5.35	309
∞	5.25	...
		Av., 302

Data Used for the Determination of the Specific Rotation of β-Glucose.

TABLE V.

Temp. 0.15°. $p_H^+ = 5.0$.

Time in min. t.	Obs. rot. Degrees.	$k_1 + k_2 \times 10^6$.
6.0	1.83	(210)
17.0	1.90	(120)
43.0	2.10	(110)
58.0	2.20	(100)
117.0	2.52	92
128.0	2.55	76
154.0	2.65	84
189.0	2.80	82
203.0	2.86	82
264.0	3.03	75
364.0	3.35	73
448.0	3.65	76
510.0	3.80	75
668.0	4.19	78
980.0	4.50	(68)
∞	5.25	...
		Av., 78

TABLE VI.

Temp. 15°. $p_H^+ = 4.7$.

Time in min. t.	Obs. rot. Degrees.	$k_1 + k_2 \times 10^4$.
3.3	1.90	(58)
5.7	1.95	(55)
10.9	2.13	46
19.5	2.34	41
33.5	2.75	41
44.0	2.92	40
68.0	3.36	39
81.0	3.60	40
105.5	3.95	41
128.0	4.14	39
174.0	4.55	40
219.0	4.80	40
∞	5.24	...
		Av., 41

TABLE VII.

Temp. 25°. $p_H^+ = 4.7$.

Time in min. t	Obs. rot. Degrees.	$k_1 + k_2 \times 10^4$.
2.8	2.00	115
5.3	2.14	97
8.8	2.40	101
11.0	2.59	108
15.5	2.83	103
18.5	3.04	108
22.9	3.25	106
30.5	3.58	104
37.5	3.84	105
44.0	4.01	102
50.5	4.16	100
56.0	4.32	103
62.5	4.46	103
75.0	4.60	97
88.0	4.79	100
116.0	4.98	96
∞	5.24	...
		—
		Av., 103

TABLE VIII.

Temp. 37°. $p_H^+ = 4.8$.

Time in min. t.	Obs rot. Degrees.	$k_1 + k_2 \times 10^4$.
2.8	2.22	(225)
3.7	2.46	(266)
4.6	2.61	(266)
5.4	2.81	290
7.0	3.02	280
7.9	3.14	278
8.9	3.28	280
9.9	3.44	289
11.4	3.62	291
13.4	3.86	299
14.8	3.97	295
16.4	4.11	297
18.8	4.28	296
23.2	4.52	293
28.4	4.73	292
32.8	4.84	284
37.2	4.95	287
∞	5.25	...
		—
		Av., 290

The data in Table XIII, part *a*, are from experiments which were run on α-glucose at 37° to determine the shape of the curve, when hydrogen ion concentration, p_H^+, is plotted against the velocity constant $k_1 + k_2$ for mutarotation. The data in part *b* are from similar experiments which were run at 0.15° to determine whether the minimum rate of mutarotation falls within the same hydrogen ion concentration zone at this temperature as at 37°. The data in part *c* are from experiments on β-glucose at 0.15° and 37°, while the data in part *d* are from experiments on β-fructose at 0.15°, 15°, 25° and 37°.

An examination of the velocity constants $k_1 + k_2$ in Tables I–XII shows that mutarotation is directly proportional to the amount of unchanged sugar present at any given time. The velocity constant, which is the sum of the velocity coefficients for the two directions, was calculated by the formula

$$k_1 + k_2 = 1/t \log \rho_0 - \rho_\infty / \rho - \rho_\infty ,$$

$$\alpha\text{-glucose} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \beta\text{-glucose}$$

and

$$\alpha\text{-fructose} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \beta\text{-fructose.}$$

ρ_0 is the initial rotation, ρ_∞ that at equilibrium and ρ the rotation at the time t. The values of $k_1 + k_2$, when calculated by this formula are

practically constant for any one hydrogen ion concentration, between $p_H{}^+ = 1.0$ and 8.5.

Data Used for the Determination of the Specific Rotation of β-Fructose.

TABLE IX.

Temp. 0.15°. $p_H{}^+ = 3.17$.

Time in min. t.	Obs. rot. Degrees.	$k_1 + k_2 \times 10^4$.
3.3	—12.90	(79)
4.4	—12.82	87
8.6	—12.60	86
13.2	—12.42	79
15.7	—12.23	89
22.5	—11.92	91
26.1	—11.80	89
34.7	—11.53	88
40.3	—11.40	85
59.0	—10.95	87
66.0	—10.86	84
79.0	—10.68	83
85.0	—10.52	91
120.0	—10.30	84
∞	—10.00	..
		—
		Av., 86

TABLE X.

Temp. 15°. $p_H{}^+ = 3.3$.

Time in min. t.	Obs. rot. Degrees.	$k_1 + k_2 \times 10^4$.
1.5	—12.62	386
2.5	—12.38	366
3.5	—12.11	379
5.1	—11.73	389
6.4	—11.50	384
7.7	—11.25	390
9.9	—10.98	373
11.2	—10.77	383
16.1	—10.29	383
27.0	— 9.83	345
37.0	— 9.68	(302)
43.0	— 9.50	364
57.0	— 9.43	366
∞	— 9.40	...
		—
		Av., 373

TABLE XI.

Temp. 25°. $p_H{}^+ = 3.4$.

Time in min. t.	Obs. rot. Degrees.	$k_1 + k_2 \times 10^3$.
2.6	—11.45	80
3.3	—11.04	85
4.0	—10.75	85
4.4	—10.59	86
5.0	—10.38	87
5.6	—10.23	85
6.8	— 9.88	88
7.3	— 9.77	88
8.4	— 9.55	90
9.3	— 9.42	90
10.6	— 9.28	90
12.3	— 9.10	(94)
15.1	— 8.99	90
∞	— 8.80	..
		—
		Av., 87

TABLE XII.

Temp. 37°. $p_H{}^+ = 3.36$.

Time in min. t.	Obs. rot. Degrees.	$k_1 + k_2 \times 10^3$.
1.7	—10.50	187
2.8	— 9.53	194
4.0	— 8.89	200
4.7	— 8.62	209
5.9	— 8.42	202
7.1	— 8.30	197
8.0	— 8.23	198
9.6	— 8.15	209
11.6	— 8.13	191
8	— 8.10	...
		—
		Av., 199

The observed rotation in Table I-XII multiplied by 10 is equal to the specific rotation.

The error of observation is larger at the beginning of the reaction, because the change in the shade of color in the field of the polariscope is so rapid that the eye cannot make accurate comparison at any given moment. This error is more noticeable in the value of $k_1 + k_2$ at the start of the

reaction as can be seen in the tables, because at this stage of the experiment, the error which is large is divided by a small number of minutes, while later a small error is divided by a large number of minutes.[1] This is especially true at a concentration of hydrogen ion, p_{H^+}, > 2.0 and < 6.5. In the neighborhood of a hydrogen ion concentration, $p_{H^+} = 6.5$, the error is due to the speed of the rotation at the start and also to the action of the hydroxyl ion, which at this concentration is appreciable, causing the solution to darken, and hence making the readings less accurate toward the end of the experiment. β-Glucose was not run at a lower concentration of hydrogen ion than $p_{H^+} = 6.3$ at 37°, because the greatly increased coloration above this point made it impossible to obtain accurate readings.

TABLE XIII.

Velocity of mutarotation at different temperatures and hydrogen ion concentrations. $(k_1 + k_2) \times 10^2$ for

α-Glucose.

b.		a.	
p_H+.	0.15°.	p_H+.	37°.
1.33	0.242	1.0	11.86
2.38	0.091	1.72	5.00
3.05	0.079	2.06	3.76
3.98	0.079	2.53	3.26
5.07	0.077	2.73	3.20
5.35	0.077	3.36	3.00
6.84	0.092	3.99	2.99
7.51	0.22	5.58	3.05
..	...	5.95	2.98
..	...	6.37	3.22
..	...	6.50	3.43
..	...	6.55	3.30
..	...	6.75	5.17
..	...	7.27	8.67
..	...	7.55	11.81
..	...	8.50	22.05

β-Glucose.

c.			
p_H+.	0.15°.	p_H+.	37°.
1.33	0.210	1.72	4.86
2.02	0.093	2.60	3.13
4.80	0.078	2.93	3.00
6.00	0.076	4.82	3.00
6.43	0.078	5.90	3.04
6.70	0.080	6.30	3.25
7.51	0.186	..	..
8.00	0.330	..	..

β-Fructose.

d.							
p_H+.	0.15°.	p_H+.	15°.	p_H+.	25°.	p_H+.	37°.
1.33	10.10	2.5	6.47	2.5	11.89	1.70	46.0
2.48	1.62	3.3	3.68	3.4	8.60	2.06	35.0
3.17	0.85	5.1	4.15	5.1	9.92	3.36	19.5
5.07	0.87	5.8	5.35	5.7	10.76	4.62	20.5
6.00	1.04	6.3	6.47	6.4	15.61	5.10	23.6
6.28	1.78	...	..	...	...	6.10	27.5
..	...	...	..	...	...	7.67	74.1

All the solutions of β-glucose were slightly turbid even after several recrystallizations from cold absolute alcohol. This turbidity could not

[1] These readings, marked by brackets were not included in taking the average.

be removed by filtration. It disappeared to a certain extent, however, as the reaction approached equilibrium.

Determination of the Specific Rotation of α- and β-Glucose and of β-Fructose.

When pure α- and β-glucose and β-fructose are dissolved, each at once starts to change into its other isomer and the rotation gradually changes until a constant value is reached. The rate of change depends upon the temperature of the solution and also upon the presence in the solution of salts,[1] acids and bases. On account of this change in rotatory power of the sugars immediately after going into solution, it is impossible to determine directly their specific rotation. Hudson calculated the specific rotation of α-glucose to be 110° from his experiments on the almost instantaneous hydrolysis of cane sugar by invertase at 0°. His calculations were based on the assumption that in weakly acid solutions the mutarotation of fructose is complete after 80 minutes. From the data from Table IX, it becomes apparent that the mutarotation of fructose in a weakly acid solution ($p_H^+ = 3.17$) at 0.15° even after 120 minutes is still incomplete, being —103°, and only approaches —100°, the rotation at equilibrium, after about 250 minutes. Therefore his value must be in error to a certain extent. Recently Hudson determined, by a solubility method, the specific rotation of α- and β-glucose and β-fructose and found them to be +113.4°, +19.7 and —133.5°, respectively, in water solution at 20°. When the values given in Table I, on α-glucose in water solution, at 0.15°, are plotted practically a straight line is obtained, which on extension to zero time gives

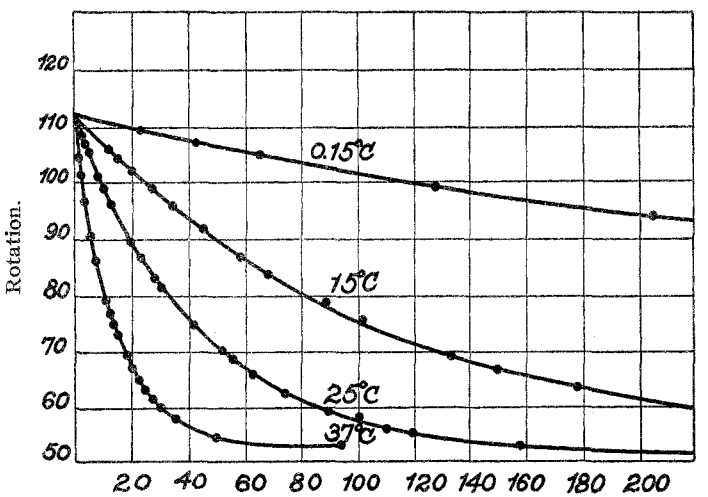


Fig. 1.

[1] Levy, *Z. Phys. Chem.*, **17**, 325 (1895); Trey, *Ibid.*, **22**, 424 (1897).

a value of 111.2° for the specific rotation of α-glucose. The results in Tables II, III and IV, at 15°, 25° and 37°, respectively, when plotted, as represented in Fig. 1 and extended in the same way as those of Table I give the same value, 111.2°.

This shows that the specific rotation of α-glucose does not vary with change in temperature and therefore the value obtained by extending the curve from Table I is very likely close to the true specific rotation of α-glucose.

The same is true for β-glucose as is evident when the results in Tables V–VIII are plotted in the same manner. In this way the specific rotation of β-glucose was found to be +17.5°. This is graphically represented in Fig. 2. The rotation at final equilibrium for both α- and β-glucose was

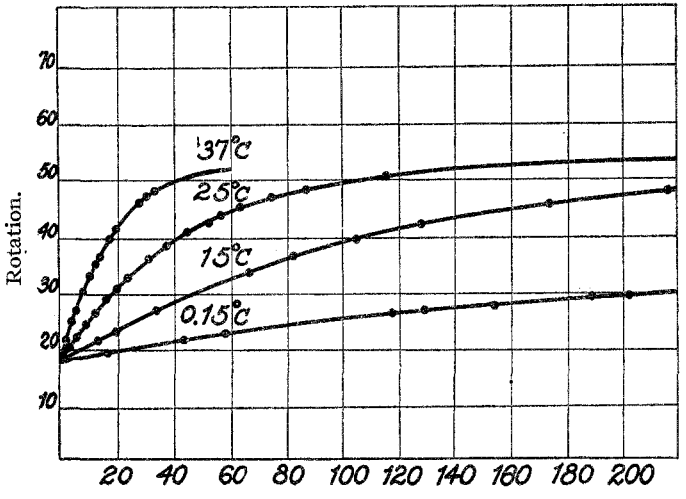


Fig. 2.

found to be 52.5° at all temperatures and concentrations at which the mutarotation was studied. This is in harmony with the work of Dubrunfaut and Mateqozeh,[1] who found that the final rotation of glucose undergoes no perceptible change between 0° and 100°.

The results in Tables IX–XII, for β-fructose are shown graphically in Fig. 3. The specific rotation obtained by extending the curve obtained from the data at the temperature 0.15° is —130.8°. This value, for concentration of 5% is constant for all temperatures between 0.15° and 37°. It is to be noted, however, that fructose differs from glucose in that its rotation at equilibrium varies with temperature and was found to be —100°, —94°, —88° and —81° at 0.15°, 15°, 25° and 37°, respectively.

[1] Browne, *Handbook of Sugar Analysis*, 1912, p. 180; Mackenzie, "Sugars and their Simple Derivatives," 1913, p. 68.

It might be interesting at this point to compare the above values. for the specific rotation of fructose at equilibrium for different temperatures,

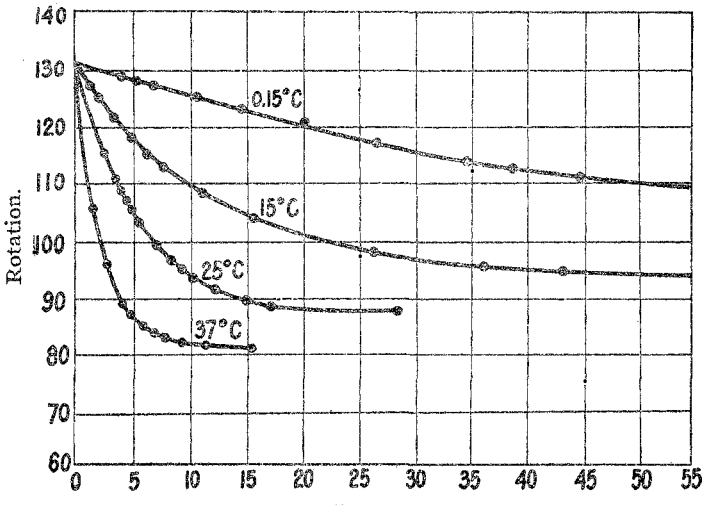


Fig. 3.

with the values given by one of the various temperature correction formulas which have been proposed. The formulas of Honig and Jesser[1]

$$[\alpha]^t_D = -103.92 + 0.681t(t + 10^\circ \text{ to } 40^\circ)$$

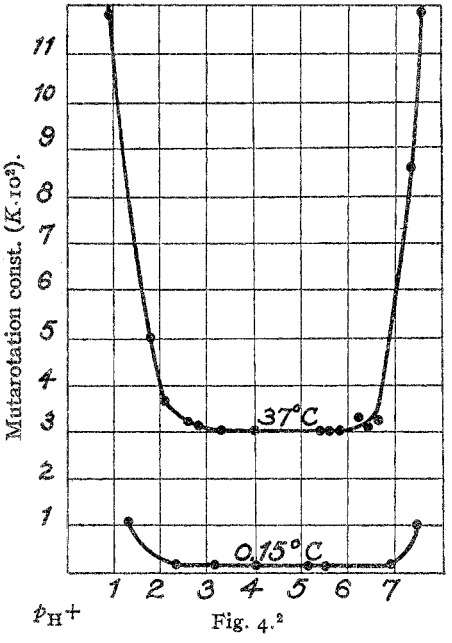


Fig. 4.[2]

gives the calculated rotation of fructose at equilibrium as, $[\alpha]^{15^\circ}_D = 93.85^\circ$, $[\alpha]^{25^\circ}_D = 87.14^\circ$ and $[\alpha]^{37^\circ}_D = 79.09^\circ$.

The Effect of Hydrogen Ion Concentration on the Rate of Mutarotation.

By inspection of the data in Table XIII, and Fig. 4, it becomes apparent that both α- and β-glucose have a zone of hydrogen ion concentration between $p_H{}^+ = 3.6$ and 6.0 at 37°, and between 2.6 and 6.9 at 0.15° in which the speed of mutarotation is the slowest. It is apparent also that when the values for the velocity of

[1] *Z. Deut. Zuckerind*, 38, 1028 (1888).

[2] The K in Figs. 4 and 5 is given as $k_1 + k_2$ in the Tables.

mutarotation of $k_1 + k_2$ for α- and β-glucose as given in Table XIII are plotted, as in Fig. 4, the curves at each temperature are superimposable, which is what would be expected for a true catalyst in the case of a reversible reaction. This also agrees with the observations of Hudson.[1]

The zone of hydrogen ion concentration which exhibits the minimum rate of mutarotation appears to be wider at 0.15° than at 37°. This is probably due to the fact that while there is the same percentage change in velocity at 0.15° as at 37° for a small change in hydrogen ion concentration, still this change from $p_H{}^+ = 3.6$ to 2.6 and from 6.0 to 6.9 at 0.15° does not alter the velocity enough, where the speed of the reaction is so slow, to make a perceptible change in the calculated value of $k_1 + k_2$. Since the zone of hydrogen ion concentration for the minimum speed of mutarotation is approximately the same at 0.15° and 37°, it can safely be assumed that this zone would hold for all intermediate temperatures. The data in Table XIII for β-fructose show that it also has a zone of hydrogen ion concentration, at which mutarotation proceeds the slowest. The zones at 0.15°, 15°, 25°, and 37° are represented graphically in Fig. 5. The zone at 37° is the narrowest, $p_H{}^+ = 3.4$–4.6, and it gradually widens out to $p_H{}^+ =$ 3.2–5.1 at 0.15°. This difference in width of the zones at the various temperatures may be explained in the same way as in the case of the glucoses. Fig. 5 shows that the zone of hydrogen ion concentration, in which the minimum speed of mutarotation occurs, will apply at any temperature between 37° and 0.15°. Furthermore, this zone is much more restricted for fructose than for glucose. This in harmony with the results of Hudson,[2] who found that he could vary the acidity less with

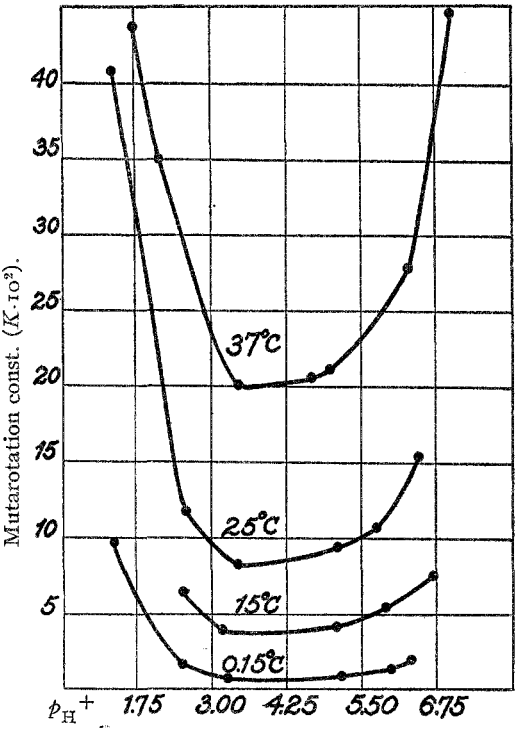


Fig. 5.

[1] *Z. physik Chem.*, 44, 487 (1903). and Meyer, *Ibid.*, 62, 71 (1908).

[2] THIS JOURNAL, 30, 1576 (1908).

fructose than with glucose without getting an increasing in the rate of mutarotation.

The Effect of Temperature on the Rate of Mutarotation.

The velocity of mutarotation is affected greatly by the temperature of the solution in which the reaction is taking place. Thus the velocity of mutarotation constant, $k_1 + k_2$, for α- and β-glucose at 0.15° is 0.00078, at 25° is 0.0104 and at 37° is 0.030. While the velocity increases greatly with temperature, the increase per degree rise in temperature, between 0.15° and 37°, is not constant. This variation is shown by the curves in Fig. 6 which were obtained by plotting the velocity constant in the zone of hydrogen ion concentration for minimum rate of mutarotation, against temperature. These curves can also serve to give the value of the velocity constant $k_1 + k_2$ at any intermediate temperature.

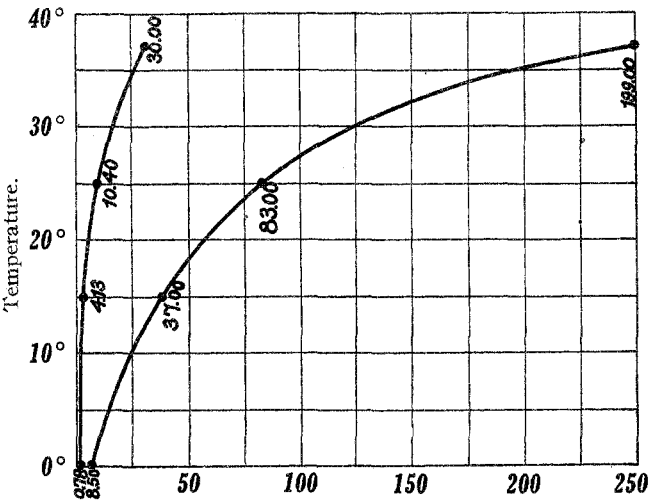


Fig. 6.

(After the article had gone to press it was noticed that the last point (199.0) on the lower curve (fructose) is two of the above divisions too far to the right.)

It might be mentioned at this point that since the specific rotations of the two isomeric glucoses 111.2° and 17.5° and the rotation at equilibrium, 52.5°, are independent of temperature, the heat of the mutarotation reaction is zero. This is easily seen from the van't Hoff relationship. $d \log K/dT = Q/RT^2$, where K is the equilibrium constant. Since K does not vary with a change in temperature, then $d \log K/dT = 0$, and consequently Q must be zero. The mutarotation of glucose therefore appears to be similar to racemization of many optically active compounds, like the malic acids, and does not involve any change in the chemical

constitution, other than spacial. This is also in accord with the generally accepted view of the difference between the two isomeric *d*-glucoses indicated by the structural formulas given for α- and β-glucoses in the first part of the article.

It, however, is contrary to the speculations of Anderson[1] and the views of Nef,[2] who have proposed that the difference between the two isomeric glucoses is in the position of the lactone bridges in the lactonic structure as given in the formula referred to above.

Berthelot[3] claims to have determined the heat of mutarotation of glucose.

$$\alpha\text{-glucose} \longrightarrow \text{equilibrium glucose} = 1.55 \text{ cal.}$$
$$\beta\text{-glucose} \longrightarrow \text{equilibrium glucose} = 0.67 \text{ cal.}$$

He brought about the transformation of α- and β-glucose into the equilibrium mixture by adding first a solution of sodium hydroxide, equivalent to 2 g. sodium hydroxide per 400 g. of sugar solution, and measuring the heat liberated, then adding more sodium hydroxide and measuring the additional heat liberated. It is well known that alkali affects glucose chemically and in the course of this investigation it was found that even a concentration of hydrogen ion, $p_{H^+} = 8.0$, which is an infinitely less concentration of hydroxyl ion than the solution Berthelot used, caused a chemical change in the solution of α- or β- glucose which was accompanied by a darkening of the solution, sufficient to interfere with the reading of the polariscope. From a consideration of these facts, it is more probable that the heat changes measured by Berthelot were due to some other change of glucose than that of mutarotation.

The data in Tables IX–XII are represented graphically in Fig. 3 and shows that the specific rotation of β-fructose is the same for any temperature between the limits 0.15° and 37°, but the rotation at equilibrium varies. The fact that the value for the velocity constant of mutarotation $k_1 + k_2$, for all temperatures, is constant throughout the reaction when the specific rotation —130.8° and the observed equilibrium angle for the particular temperature, are employed to calculate $k_1 + k_2$, may be regarded as additional evidence for the specific rotation of β-fructose being independent of the temperature.

Since the equilibrium point in the mutarotation of fructose is effected by change in temperature, it is logical to assume that the transformation is accompanied by a heat of reaction, and that heat is absorbed as β-fructose is changed into the α-isomer. This difference in the effect of change in temperature on the equilibrium point of fructose and glucose suggests that the mutarotation of fructose is a more complicated change

[1] *J. Phys. Chem.*, **20**, 269(1916).
[2] *Ann.*. **403**, 273 306 (1914).
[3] *Ann. chim phys.*, [7] **7**, 571 (1896).

in the sugar molecule than that in the mutarotation of glucose. Haworth and Law,[1] among others have also come, by an entirely different way, to the same conclusion, that the mutarotation of fructose is more complicated than that of glucose.

The Effect of Invertase on the Rate of Mutarotation.

It is well known that the addition of glucose or fructose to a solution of cane sugar retards its rate of hydrolysis by invertase. It was therefore thought desirable to ascertain whether invertase had any influence on the mutarotation of these two sugars and thereby affecting the concentration of some of the reactants and resultants in the reaction solution, and hence affecting the velocity in this way.

It was found that the presence of a relatively large quantity of invertase in solutions of either α-glucose, β-glucose, β-fructose or a mixture of α-glucose and β-fructose does not affect either the rate of mutarotation or the equilibrium rotation, at 37°, in the zone of hydrogen ion concentration corresponding to the minimum velocity of mutarotation. For this purpose 2.5 g. samples of the pure sugar were placed in 50 cc. volumetric flasks and then dissolved by adding a strong solution of invertase, at 37°, of such a concentration of hydrogen that when the solution was made up to volume, the hydrogen ion concentration of the resulting solution fell within the desired limits.

TABLE XIV.

	Velocity coefficient, $(k_1 + k_2)$, for mutarotation of:			Rotation at equilibrium for:		
	α-Glucose.	β-Glucose.	β-Fructose.	α-Glucose.	β-Glucose.	β-Fructose.
With invertase....	0.30	0.029	0.184	52.5°	52.5°	81.0°
Without invertase.	0.030	0.030	0.188	52.5°	52.5°	81.0°

These results agree with those of Hudson,[2] who also found that invertase does not affect the velocity of mutarotation of glucose. The work was repeated in order to be more certain as to the exact hydrogen ion concentration.

The Effect of Sucrose on the Mutarotation of the Hexoses.

Since glucose and fructose retard the hydrolysis of cane sugar by invertase it was thought advisable also to ascertain whether sucrose affects the mutarotation of these hexoses.

For this purpose 2.5 g. each of the different hexoses were placed in 50 cc. flasks and various weights of sucrose added. The flasks containing the sugars then were suspended in the constant temperature bath until they had acquired the temperature of the bath. Then water, at 37°, containing sufficient acid or alkali, so that the resulting sugar solution would have a hydrogen ion concentration within the zone for minimum

[1] *J. Chem. Soc.*, 109, 1315 (1916).

[2] THIS JOURNAL, 30, 1577 (1908).

rate of mutarotation, was added to dissolve the sugar and also to bring the solution to the desired volume. The results obtained showed that the rate of mutarotation and the rotation at equilibrium of α- and β-glucose was affected very little, if any, by the presence of sucrose. Thus the rotation at equilibrium of glucose, 5 g. per 100 cc., in the presence of sucrose is as follows:

TABLE XV.

G. sucrose per 100 cc.	5	10	15	20
G. glucose per 100 cc.	5	5	5	5
Calc. rotation for sucrose	6.65°	13.30°	19.95°	26.60°
Calc. rotation for glucose	5.25°	5.25°	5.25°	5.25°
Calc. total rotation	11.80°	18.55°	25.30°	31.85°
Obs. total rotation	11.89°	18.52°	25.20°	31.84°

Similarly in the case of a mixture of glucose and fructose, the mutarotation of each proceeds independently of the other, at 37°, when the hydrogen ion concentration is that for the minimum rate of mutarotation. The equilibrium rotation of a solution of 2 g. glucose and 4 g. fructose in 100 cc., in three cases was —4.37°, —4.37° and —4.40°. The calculated rotation due to the glucose was +2.10° and due to the fructose —6.48°, making the theoretical value for the above mixture —4.38°, while the average observed was —4.38°.

A solution containing 5 g. of fructose per 100 cc. and varying amounts of sucrose, unlike in the case of glucose mentioned above, does not give observed rotations equal to the sum of the rotations corresponding to the concentrations of the two sugars (Table XVI). If it is assumed that it is the specific rotation of the fructose which is affected, then by plotting the grams of sucrose as abscissas and the corresponding change in the rotation of the fructose as ordinates, a straight line is obtained and hence the variation is directly proportional to the amount of sucrose present.

TABLE XVI.

Rotation at equilibrium of Fructose. 5 g. of fructose per 100 cc. in the presence of varying amounts of sucrose. Temperature 37°.

G. sucrose per 100 cc.	1	3	5	7	10
Obs. combined rotation	—6.84°	—4.25°	—1.65°	+0.98°	+ 4.90°
Calc. rotation due to sucrose	+1.33°	+3.99°	+6.65°	+9.31°	+13.30°
Difference due to fructose	—8.17°	—8.24°	—8.30°	—8.33°	— 8.40°
Obs. rotation of fructose alone	—8.10°	—8.10°	—8.10°	—8.10°	— 8.10°
Change in rotation due to presence of sucrose	0.07°	0.14°	0.20°	0.23°	0.30°

These results were confirmed by triplicate experiments and agreed to ±0.01°.

Procedure.—The velocity of mutarotation was determined by allowing the change to take place in a 200 mm. polariscope tube, using a Schmidt

and Haensch polarimeter, sensitive to 0.01°. The ordinary jacketed polariscope was found unsatisfactory for obtaining constant temperature throughout the course of the experiment. In order to overcome this difficulty, a large 50 liter constant temperature water bath was constructed so that one end fitted between the analyzer and polarizer of the polariscope. By means of a specially constructed arm extending from the polariscope stand into the bath, the tube was held in position between the polarizer and analyzer, and at the same time immersed in the bath. Windows of plate glass were placed in the walls of the bath opposite the ends of the tube. The bath was provided with a motor stirring device and a mercury electric constant temperature regulator which permitted a constant temperature to be maintained that did not vary more than ±0.01°. In this way no difficulty was experienced in obtaining duplicate results which checked very well.

All the work was done on a 5% sugar solution. The solution in which the sugar was to be dissolved was prepared by adding sufficient dil. hydrochloric acid or sodium hydroxide solution to distilled water to bring the sugar solution, when made up, to approximately the desired hydrogen ion concentration. The flask, containing the components of the solutions, were all suspended in the constant temperature bath for about an hour before mixing in order to avoid, as far as possible, a different initial temperature when the mutarotation commenced. The time of mixing the water and sugar was recorded by means of a stop watch, and the length of time required for the finely pulverized sugar to dissolve was about 20 seconds at 25° and 37°, and from 40 to 80 seconds at 0.15°. The flasks were kept immersed in the bath during the process of solution. The liquid was transferred to the polariscope tube, immediately after the sugar was dissolved and readings recorded as soon as possible.

The polariscope was adjusted to zero, daily and very often between successive experiments, by filling the tube with water instead of sugar solution. It was found necessary, at the lower temperatures, 0.15°–15°, to determine the zero point of the instrument with each individual tube used, by filling it with distilled water and then applying the correction to each set of readings of the sugar solution in this tube. At the end of the reaction the tube was filled with distilled water and the zero point redetermined to see if any change had taken place. If any change had occurred that set of determinations was discarded. The sugar solution left after filling the polariscope tube was always saved for the determination of the hydrogen ion concentration of the solution.

The α-glucose,[1] β-glucose,[2] and β-fructose[3] were purified according to

[1] Hudson and Yanovsky, THIS JOURNAL, 39, 1017 (1917).

[2] Hudson and Dale, *Ibid.*, 39, 323 (1917).

[3] Hudson and Yanovsky, *Ibid.*, 39, 1024 (1917).

the methods of Hudson. Before using, all the sugars were dried, at 50°, to constant weight *in vacuo* over conc. sulfuric acid.

The hydrogen ion concentration was measured, by a combination of electrometric and colorimetric methods, as described by Nelson and Vosburgh.[1] The determinations were made at the same temperature as that of the sugar solution studied. In order to do this, it was necessary first to measure the temperature coefficient of the saturated calomel cell. This work will be described in another paper by Fales and Beegle.

NEW YORK CITY.

RELATION BETWEEN INTENSITY OF TYNDALL BEAM AND SIZE OF PARTICLES.[2]

BY RICHARD C. TOLMAN, ROSCOE H. GERKE, ADIN P. BROOKS, ALBERT G. HERMAN, ROBERT S. MULLIKEN AND HARRY DEW. SMYTH.

Received January 17, 1919.

I. Introduction.

In a previous article[3] a simple Tyndallmeter has been described for measuring the strength of Tyndall beam in smokes and suspensions. The strength of the Tyndall beam has been shown to be directly proportional to the concentration of a smoke or of a suspension,[4] and it is the purpose of this article to show the relation between the strength of Tyndall beam and the size of particles. Work along this line on suspensions of colloidal sulfur has already been performed by Mecklenburg.[5] Mecklenburg's, results show that for particles in the range of size which he examines, the Tyndall beam became more intense the larger the particles, concentration remaining uniform. It has already been pointed out, however, in our article[6] on "The Disappearance of Smoke in a Confined Space," that at a given concentration the intensity of Tyndall beam became larger with finer particles. For this reason a further investigation of the subject seemed necessary and a determination, if possible, of the exact relation between strength of Tyndall beam and size of particle. The general results of the work are to show that for the range of particles in actual smokes (5×10^{-6} to 10^{-4} cm.) and for particles in suspensions 10^{-4} cm. in diameter up, the Tyndall beam becomes more intense at a given concentration the greater the sub division. Mecklenburg's results were all for particles below 10^{-4} cm. Nevertheless at that size of particle his results

[1] THIS JOURNAL, 39, 810 (1917).

[2] The work described in this article was carried out by the Dispersoid Section, Research Division, Chemical Warfare Service and has been approved for publication by Major-General William L. Sibert, Director of Chemical Warfare Service, U. S. A.

[3] THIS JOURNAL, 41, 297 (1919).

[4] *Ibid.*, 41, 300 (1919).

[5] *Kolloid-Z.*, 16, 97 (1915).

[6] THIS JOURNAL, 41, 304 (1919).