XCI.—*Studies of Dynamic Isomerism. Part XXVI. Consecutive Changes in the Mutarotation of Galactose.*

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IN a paper on the "Dynamic Isomerism of the Reducing Sugars," recently contributed by one of us (*Z. physikal. Chem.*, Cohen Festband, p. 125), a detailed examination was made of the evidence for the unimolecular character of the mutarotation curves for glucose. The conclusion was reached that, even under the most diverse conditions of catalysis, the mutarotation of glucose and of tetramethyl glucose conforms strictly to the unimolecular law, within the limits of experimental error,* although transient perturbations

* Inflected curves have been observed, however, on two occasions when mutarotation was initiated by the addition of a drop of dilute acid or alkali to a solution of tetra-acetyl glucose in dry ethyl acetate.

during the initial stages of the action are not excluded by the experimental data there cited. The unimolecular character of the curves can, however, be reconciled with the existence of an indefinitely large proportion of an intermediate μ form of the sugar, provided that the velocity coefficients and optical rotations of the three forms are distributed symmetrically, since under these conditions the first stage of the transformation proceeds according to the unimolecular law, whilst the second stage (which would give rise to an inflected curve) is not accompanied by any marked change of rotatory power. The real existence of this hypothetical second stage was established by comparing the rate of change of rotatory power with the rate of increase of solubility of glucose in aqueous alcohol, since this comparison showed that the chemical changes last about twice as long as the mutarotation, and therefore continue for a period of several hours after the changes of rotatory power are complete.

In the analogous case of galactose it has been generally (but erroneously) assumed that the mutarotation also proceeds according to a unimolecular law. Evidence of the existence of consecutive chemical changes was found, however, by Riiber and his colleagues (*Ber.*, 1926, **59**, 2266; compare *Ber.*, 1922, **55**, 3136, 3142) in the fact that the dissolution of the α-sugar in water at 20° gives rise to an *expansion* during the first 15 minutes, followed by a *contraction*, which only becomes logarithmic after 50 minutes have elapsed. In the same way they found that the initial stages of mutarotation are accompanied by an *absorption of heat*, which lasts for about 13 minutes at 0°, whereas the later stages are accompanied by a *liberation of heat*. The mutarotation of α-galactose is therefore associated with two consecutive changes of structure, which give rise to energy changes and volume changes of opposite sign, as we should expect them to be if the intermediate μ-compound is related in a symmetrical manner to the stereoisomeric α- and β-sugars. No analogous indications of the complexity of the process were obtained, however, from their observations of mutarotation, which appeared to be accurately unimolecular.

Anomalies in the Mutarotation of α-Galactose.—The present paper originated in an attempt to establish a standard value for the velocity coefficient of galactose, as had already been done in the case of glucose (J., 1927, 1736), as a preliminary to the determination of a catalytic catenary for the sugar. We found, however, that our mutarotation curves made no approach to the unimolecular law, since the velocity coefficient fell progressively from $k_e =$ about 0·025 at 7 minutes to a limiting value of about 0·019. A survey of the literature confirmed the view that the mutarotation of galactose is not a simple unimolecular change. Thus, two of Urech's early experiments (*Ber.*, 1885, **18**, 3047) gave velocity coefficients ranging irregularly from 0·0092 to 0·0153 and from 0·0071 to 0·0122, but the third showed a progressive decrease from 0·0132 to 0·0048 in the course of 11 hours at 14°. Since this decrease was attributed to a secondary transformation of the sugar (similar to that which results from the action of alkalis; compare Lobry de Bruyn, *Rec. trav. chim.*, 1895, **14**, 201), Urech's observations were cited by Riiber and Minsaas, together with the more exact investigation of Osaka (*Z. physikal. Chem.*, 1900, **35**, 668), as evidence that the mutarotation of galactose "proceeds according to the simple logarithmic equation of a reaction of the first order." Osaka's conclusion, "that the course of the alterations of rotatory power of the sugars, on which observations have been made, can be expressed by the velocity-formula for a reaction of the first order," appears to have been justified for most of the eight sugars for which data had been given by Tollens and his colleagues (*Annalen*, 1890, **257**, 164; 1892, **271**, 60); but an inspection of the tables shows that his velocity coefficient for galactose decreased progressively from 0·0120 to 0·0088 at $c = 10{\cdot}20$ and from 0·0131 to 0·0076 at $c = 11{\cdot}08$; his average value was therefore derived from numbers which show a systematic variation of from 50 to 80% from the limiting value. In the same way, we found that the average value, $k = 0{\cdot}00479$ (logarithms to base 10), given by Mackenzie and Ghosh (*Proc. Roy. Soc. Edin.*, 1914, **35**, 22) for the velocity coefficient of a 2·175% solution of galactose at 12·5°, was based on data which showed a progressive decrease from $k = 0{\cdot}0080$ at 8 minutes to $k = 0{\cdot}0036$ at 166—323 minutes. The data of Riiber and Minsaas, on the other hand, gave steady values for the velocity coefficient of α-galactose; but, since their first value was based on readings taken 20 and 30 minutes after dissolution, it is not surprising that they should have overlooked an anomaly which is really conspicuous only during the first 10 minutes.

Although the earlier data thus confirmed unanimously the large deviations from the unimolecular formula which we had observed in the mutarotation of α-galactose, we took the precaution of repeating the observations with specially purified samples of the sugar, which was recrystallised for this purpose from acetic acid and from alcohol according to a method for which we are indebted to Professor Haworth; similar results were also obtained when the polarimeter tube was kept at 0·2°. Finally, since the velocity coefficients covered just the same range of values at concentrations of 2½, 5, 10, and 15 g. of galactose in 100 c.c. of solution, it was clear that the action could not be multimolecular; we therefore concluded that the mutarotation was probably of a type which could be expressed by means of an equation involving two or more consecutive unimolecular changes.

Anomalies in the Mutarotation of β-Galactose.—Although Riiber and Minsaas recorded a steady value for the velocity coefficient of β-galactose from 10—20 minutes and onwards, Hudson and Yanovsky (*J. Amer. Chem. Soc.*, 1917, **39**, 1022) had already observed the anomaly of a *minimum* rotation in a solution of α- and β-galactose in water, which had been diluted with alcohol to a concentration of 60%. We therefore made a fresh study of the mutarotation of β-galactose in order to see whether the anomaly which we had observed in α-galactose could be detected when mutarotation took place in the reverse direction. Our first sample, prepared by the method of Hudson and Yanovsky, gave $[\alpha]_{5461} = 66°$, whilst the second and third samples both gave $[\alpha]_{5461} = 63{\cdot}5°$, no further reduction of rotatory power being produced when the second sample was washed four times more with 80% alcohol. A rough estimate of the rotatory dispersion of galactose showed that Hudson's value for the β-sugar $[\alpha]_D = 52°$ would correspond with a specific rotation $[\alpha]_{5461} =$ about 61°. This rotation is 2° less than our minimum, but, if deduced by extrapolation to zero time, would be appreciably too low, in view of the slowness with which mutarotation takes place during the first few minutes. We therefore think it probable that our sample was substantially pure, and suggest that an initial rotation $[\alpha]_{5461} = 63{\cdot}5°$ may be accepted as a provisional standard. This rotatory power remained constant, within the limits of experimental error, during a period of about 4 minutes; the rotation then increased rapidly, giving rise to an inflected mutarotation curve, with a maximum slope at about 10 minutes. The velocity coefficient, on the other hand, increased progressively from zero to a limiting value which was identical with that finally reached by the α-sugar.

Analysis of the Mutarotation Curves.—The view that "the interconversion of α- and β-glucose depends on the splitting of the oxide ring" and that "the aldehydic form of the sugar or its hydrate . . . is a necessary intermediate product in the conversion of α- into β-glucose or *vice versa*" (J., 1904, **85**, 1565) implies that the mutarotation of the α- or β-form of a reducing sugar depends on *two* consecutive unimolecular changes, as set out in the scheme

$$\underset{\alpha}{x} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\mu}{y} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \underset{\beta}{z}$$

Equations for an action of this type were therefore worked out at the request of one of us by Mr. H. Klugh in 1903, and a more complete analysis, in collaboration with Mr. W. T. John, was published in 1910 (J., **97**, 2634); but the only inflected mutarotation curves that have been studied hitherto (Lowry and Glover, J., 1913, **103**,

913) were too complex to be expressed by the preceding scheme; the data now recorded therefore provide the first opportunity that has arisen of completing this mathematical analysis.

Before giving an account of this investigation, however, we wish to make it clear that we are more concerned to demonstrate the *process* by which the analysis has been carried out than to attach a precise physico-chemical meaning to the *results* to which it leads, since these can only be regarded as valid when the fundamental assumptions on which the formulæ depend have been verified. In particular, the values deduced for the equilibrium concentration, y_∞, and the rotatory power, μ, of the intermediate sugar, depend on the hypothesis that only three sugars are concerned in the final equilibrium, *viz.*, the α- and β-sugars (6-ring oxides) and the intermediate (open-chain) μ-sugar, whereas we should prefer to postulate also the presence of a pair of γ-sugars (or 5-ring oxides), making 5 sugars in all. Whilst, therefore, our data can be represented completely by the empirical equations for 3 isomerides, we do not regard this as a proof that only *three* sugars are present in the final equilibrium, since we should then be obliged to admit the unimolecular form of the mutarotation curves of α- and β-glucose as evidence that only *two* isomerides are formed in an aqueous solution of glucose. Again, since a mathematical analysis is only practicable when the γ-sugars are ignored, we have not thought it necessary to discuss the limits of error of our empirical equations, and have therefore solved them as if the arbitrary constants which they contain were mathematically exact.

Empirical Equations for the Mutarotation Curves.

(*a*) *Numerical Data.*—The following data were available for the analysis of the mutarotation curves for aqueous solutions of α- and β-galactose at 20°.

TABLE I.

Mutarotation of α- and β-Galactose at 20°.

1. α-Galactose : first sample, recrystallised from 80% EtOH.

(*a*)	2½%	(4 dm.)	$\theta_0 = 16{\cdot}69$	$\theta_\infty = 9{\cdot}12$	$k_\infty = 0{\cdot}0187$
(*b*)	5%	(2 dm.)	$\theta_0 = 16{\cdot}55$	$\theta_\infty = 8{\cdot}92$	$k_\infty = 0{\cdot}0188$
(*c*)	10%	(2 dm.)	$\theta_0 = 31{\cdot}03$	$\theta_\infty = 17{\cdot}20$	$k_\infty = 0{\cdot}0189$
(*d*)	10%	(2 dm.)	$\theta_0 = 33{\cdot}09$	$\theta_\infty = 18{\cdot}15$	$k_\infty = 0{\cdot}0187$
(*e*)	15%	(2 dm.)	$\theta_0 = 45{\cdot}42$	$\theta_\infty = 24{\cdot}84$	$k_\infty = 0{\cdot}0186$
(*f*)	15%	(2 dm.)	$\theta_0 = 48{\cdot}88$	$\theta_\infty = 27{\cdot}20$	$k_\infty = 0{\cdot}0189$

2. α-Galactose : (*a*) second sample, recrystallised twice from 80% EtOH.
(*b*) third sample, recrystallised from acetic acid.
(*c*) fourth sample, recrystallised from acetic acid and 80% EtOH.

(*a*)	10%	(2 dm.)	$\theta_0 = 33{\cdot}63$	$\theta_\infty = 18{\cdot}80$	$k_\infty = 0{\cdot}0188$
(*b*)	10%	(2 dm.)	$\theta_0 = 34{\cdot}50$	$\theta_\infty = 18{\cdot}81$	$k_\infty = 0{\cdot}0189$
(*c*)	10%	(2 dm.)	$\theta_0 = 34{\cdot}71$	$\theta_\infty = 18{\cdot}91$	$k_\infty = 0{\cdot}0185$

3. β-Galactose: (a) precipitated by alcohol twice, and washed by 80% EtOH once.
(b) precipitated by alcohol twice, and washed by 80% EtOH twice.
(c) precipitated by alcohol twice, and washed by 80% EtOH six times.

(a) 5%	(2 dm.)	$\theta_0 = 6{\cdot}38$	$\theta_\infty = 9{\cdot}28$	$k_\infty = 0{\cdot}0191$
(b) 5%	(2 dm.)	$\theta_0 = 6{\cdot}35$	$\theta_\infty = 9{\cdot}34$	$k_\infty = 0{\cdot}0183$
(c) 7·7%	(2 dm.)	$\theta_0 = 9{\cdot}17$	$\theta_\infty = 14{\cdot}57$	$k_\infty = 0{\cdot}0192$
				0·0188

In this table θ_0 is deduced by extrapolating the rotation of the solution to zero time, and θ_∞ by direct observation of the final rotatory power, whilst k_∞ is the velocity coefficient calculated from the later part of the mutarotation.

(b) *Preliminary Survey.*—Before making use of the general equations of Lowry and John it is desirable to make a preliminary enquiry as to the cause of the deviations from the unimolecular equations, which are found to satisfy, at least approximately, the data for glucose, but not for galactose.

(i) Two consecutive reversible unimolecular actions can give rise to unimolecular mutarotation curves only when $k_1 = k_3$, $k_2 = k_4$, and $\alpha + \beta = 2\mu$. Under these conditions, the general equations of Lowry and John reduce to the very simple form:

$$\theta_\alpha = \tfrac{1}{2}(\alpha - \beta)e^{-k_1t} + \tfrac{1}{2}(\alpha + \beta)$$
$$\theta_\beta = -\tfrac{1}{2}(\alpha - \beta)e^{-k_1t} + \tfrac{1}{2}(\alpha + \beta)$$

The mutarotation then takes the form of a unimolecular change with velocity coefficient k_1, and covering a range of rotations from α or β to a final value $\frac{1}{2}(\alpha + \beta)$. Since k_2 does not enter into these equations at all, this statement is true for all concentrations of the intermediate sugar, which gives no indication whatever of its presence, in spite of the fact that it forms $100k_1/(k_1 + k_2)\%$ of the final equilibrium mixture, where this ratio may have any value from 0 to 100%.

(ii) If the rotatory power of the intermediate sugar is not the mean of the rotations of the α- and β-forms (although $k_1 = k_3$ and $k_2 = k_4$, as before), the equations become

$$\theta_\alpha = \frac{\alpha - \beta}{2}e^{-k_1t} + \left\{\frac{\alpha + \beta}{2} - \mu\right\}\frac{k_1}{k_1 + 2k_2}e^{-(k_1 + 2k_2)t} + \frac{1}{k_1 + 2k_2}\left\{(\alpha + \beta)k_2 + \mu k_1\right\}$$

$$\theta_\beta = -\frac{\alpha - \beta}{2}e^{-k_1t} + \left\{\frac{\alpha + \beta}{2} - \mu\right\}\frac{k_1}{k_1 + 2k_2}e^{-(k_1 + 2k_2)t} + \frac{1}{k_1 + 2k_2}\left\{(\alpha + \beta)k_2 + \mu k_1\right\}$$

The second exponential term (which vanishes only when $\alpha + \beta = 2\mu$) now persists; but since the coefficients of the two exponentials are the same in both equations, although different in sign, these two terms can be eliminated, one at a time, by adding or subtracting the two equations, thus :

$$\theta_a - \theta_\beta = (\alpha - \beta)e^{-k_1 t}$$

$$\theta_a + \theta_\beta - 2\theta_\infty = (\alpha + \beta - 2\mu)\frac{k_1}{k_1 + 2k_2}e^{-(k_1 + 2k_2)t}$$

since $$\theta_\infty = [(\alpha + \beta)k_2 + \mu k_1]/(k_1 + 2k_2).$$

If, therefore, the anomalous behaviour of galactose (as contrasted with glucose) were due exclusively to a deviation of the rotatory power of the intermediate sugar from the mean value for the α- and β-sugars, we could deduce a unimolecular coefficient for the *difference* of the rotatory powers of the α- and β-sugars, and so determine k_1, and then deduce a second unimolecular coefficient for the *average* of the rotatory powers, and so calculate the value of k_2 from the exponent $(k_1 + 2k_2)$. In this way we could obtain a complete solution of the problem, without making use of the general equations at all, and this simple test should obviously be applied in every case before the more complex procedure described below is adopted.

TABLE II.

Mutarotation of α- and β-Galactose.

(*a*) Difference. $\theta = \theta_a - \theta_\beta$; $k = 0{\cdot}0188$; $\log \theta = -0{\cdot}008163t + 1{\cdot}3337$ (correct at 10 min.).

(*b*) Average. $\theta = \frac{1}{2}(\theta_a + \theta_\beta) - \theta_\infty$; $k = 0{\cdot}0255$; $\log \theta = -0{\cdot}1108t + 0{\cdot}6386$ (correct at 5 min.).

t.	*θ* (obs.).	*θ* (calc.).	Diff.	*t*.	*θ* (obs.).	*θ* (calc.).	Diff.
2	20·90	20·76	+0·14	2	4·35	4·13	+0·22
5	19·71	19·61	+0·10	5	3·83	3·83	0·00
10	17·87	17·87	0·00	10	3·23	3·37	−0·14
15	16·21	16·27	−0·06	15	2·82	2·96	−0·14
20	14·69	14·80	−0·11	20	2·58	2·61	−0·03
30	12·18	12·27	−0·09	30	2·09	2·02	+0·07
40	10·09	10·17	−0·08	40	1·72	1·57	+0·12
50	8·34	8·43	−0·09	50	1·42	1·22	+0·20
60	6·95	6·98	−0·03	60	1·15	0·94	+0·21
70	5·81	5·78	+0·03	70	0·91	0·73	+0·18
80	4·79	4·79	+0·00	80	0·75	0·57	+0·18
90	4·00	3·97	+0·03	90	0·62	0·44	+0·18
100	3·30	3·29	+0·01	100	0·52	0·34	+0·18

When this test is applied to α- and β-galactose, as in Table II, it can be seen at once that, whilst the *differences* conform very nearly to the unimolecular law, the *averages* exhibit obvious systematic deviations, which are, however, also present in a less conspicuous form in the curve of differences. Whilst, therefore, the anomalous behaviour of galactose may be attributed in the first instance to the fact that the rotatory power of the intermediate sugar approximates to that of the β-sugar, instead of to the average of the α- and β-sugars, it is clear that the velocity coefficients are also unsymmetrical, but to an extent which can only be disclosed by a complete mathematical analysis, since the small deviations recorded in Table II give no indication of the actual magnitude of this anomaly.

(*c*) *General Equations.*—Since none of the simplifying assumptions is possible in the case of galactose, it is necessary to fall back on the general equations for two consecutive unimolecular reactions. The empirical equations for the mutarotation of the α- and β-sugars then have the general form

$$\theta_a = A_1e^{-m_1t} + B_1e^{-m_2t} + C; \quad \theta_\beta = A_2e^{-m_1t} + B_2e^{-m_2t} + C.$$

The number of exponential terms in these equations is equal to the number of consecutive changes which the sugars undergo; the identity of the exponents, and of the final constant C, expresses the fact that the sugars are undergoing the same series of changes (although in opposite directions) and give rise to the same final equilibrium mixture. It will be seen that these two equations, like the scheme on p. 669, include 7 arbitrary constants; if, therefore, equations of this type can be deduced for the mutarotation curves of the α- and β-sugars, it is theoretically possible to calculate from them the 7 fundamental constants of the original system, *viz.*, the four velocity coefficients k_1, k_2, k_3, k_4, and the rotatory powers α, μ, β, of the three sugars.

(*d*) *Initial Rotatory Power of α- and β-Galactose.*—The initial rotations of the α- and β-sugars are difficult to fix, since they depend, not only on the purity and dryness of the sugar, but on its homogeneity, *i.e.*, on the percentage of the α- and β-sugars which it contains; and even when the homogeneity of the material has been established, the initial rotations can only be deduced by extrapolation to a "zero-time," which is not very well defined, since there is always a little uncertainty as to the moment at which on the average the sugar entered into solution. We have therefore selected for α-galactose the value $[\alpha]_{5461} = 172{\cdot}5°$, and for β-galactose the value $[\alpha]_{5461} = 63{\cdot}5°$, as representing most closely the rotatory power of the sugars used in our experiments (compare Expts. 2*b* and 3*b* in Table I), although a slightly higher value for the initial and final rotations of α-galactose was given in Expt. 2*c*, where the concentration of the solution was perhaps a little greater. Since, however, the data for calculation were based on values for a 10% solution of the α-sugar in a 2 dm. tube or for a 5% solution of the β-sugar in a 4 dm. tube, the rotations in the empirical equation are one-fifth of the specific rotations. The initial rotations of the α-and β-sugars, which do not enter directly into the equations, therefore lead to the relations

$\alpha = A_1 + B_1 + C = 34{\cdot}5°$ or $A_1 + B_1 = 15{\cdot}7°$ (since $C = 18{\cdot}8°$, see below);

$\beta = A_2 + B_2 + C = 12{\cdot}7°$ or $A_2 + B_2 = -6{\cdot}1°$.

(*e*) *Rotatory Power of the Equilibrium Mixture.*—The final specific rotations of the 12 solutions set out in Table I are as follows :

1. $[\alpha]_{5461} = 91°, 89°, 86°, 91°, 83°, 91°.$
2. $[\alpha]_{5461} = 94°, 94°, 95°$
3. $[\alpha]_{5461} = 93°, 93°, 95°$

$\left.\begin{array}{l} 2. \\ 3. \end{array}\right\}$ Mean 94°.

The first six values are irregular and low, perhaps on account of the presence of a variable proportion of alcohol in the first sample of the recrystallised sugar; but three further samples of α-galactose, and three samples of β-galactose give a uniform value $[\alpha]_{5461} = 94°$. The constant term in the two equations, which represents the final rotation of the solutions, has therefore the value $C = 18{\cdot}8°$.

(*f*) *Final Velocity Coefficients of α- and β-Galactose.*—Apart from the initial and final rotations, the easiest quantity to determine in these equations is the limiting value of the unimolecular velocity coefficient. Trustworthy values are obtained by ignoring the first half of the mutarotation of the α-sugar (where the coefficients are abnormally high), and the first third of the mutarotation of the β-sugar (where they are abnormally low), and treating the observations as if they had been begun 30 or 40 minutes after making up the solution (see col. 6 in Tables VI and VII). Since, as is shown below, the influence of the second term dies out after about ½ hour, this is a logical method for determining the value of the smaller exponent. It will also be recalled that Riiber and Minsaas obtained a constant unimolecular velocity coefficient (and therefore failed to discover the anomalous character of the mutarotation curves) as a result of adopting a similar procedure. In the present instance, the limiting value of the velocity coefficient, as deduced from the 12 experiments set out in Table I, is $m_1 = 0{\cdot}0188$, and this value can be inserted immediately in the equations as the exponent of the first term. When the true initial rotation of the α-sugar was used in calculating the unimolecular velocity coefficients, however, a slightly higher (but less trustworthy) limiting value was found, namely $k = 0{\cdot}0192$ (see col. 5 in Tables VI and VII), which agrees exactly with the mean of six values deduced from a study of three different properties of the two sugars by Riiber and Minsaas, *viz.*,

	k.	k_s.
Mutarotation of α-galactose	0·00834	0·0190
„ „ β- „	0·00837	0·0193
Volume changes of α-galactose	0·00836	0·0192
„ „ β- „	0·00845	0·0195
Refractivity of α-galactose	0·00822	0·0189
„ „ β- „	0·00843	0·0194
	k_s at 20° =	0·0192

(*g*) *Initial Velocity Coefficient of* β-*Galactose.*—Since the rotatory power of β-galactose remains constant for about 4 minutes, $d\theta/dt = 0$, when $t = 0$; and since at this stage the only transformation is from the β-sugar to the intermediate (aldehydic) form, it follows that the rotatory power of these two sugars must be nearly the same, so that $\beta = \mu$ (approximately). This condition is, however, not sufficiently well-defined to be utilised in order to fix at once the value of the unknown rotatory power, μ, of the intermediate sugar (which is one of the objects of this research) and can only be used as evidence of the *approximate* equality of the rotatory power of the two sugars.

(*h*) *Initial Velocity Coefficient of* α-*Galactose.*—Although the initial stage of the mutarotation is obviously unimolecular rather than multimolecular, the velocity coefficients calculated by the ordinary method change so rapidly that it is not practicable to deduce a trustworthy initial value by extrapolating to zero time. Such a value can, however, be obtained by calculating from the rotations themselves an intermediate " end-point," to which the first stage of the mutarotation would lead if the second stage could be suspended. For this purpose we have used a formula given by Smith (*Phil. Mag.*, 1926, **1**, 496), *viz.*,

$$\alpha_\infty = \alpha_1 - (\alpha_1 - \alpha_2)^2/(2\alpha_2 - \alpha_1 - \alpha_3),$$

where α_1, α_2, α_3 are readings at equal increments of time, and α_∞ is the hypothetical end-point.

Four successive groups of three rotations at intervals of 2 minutes, read from a curve on which the readings for the first 10 minutes of Expt. 1*d* had been plotted, were found by this method to give

$$\alpha_\infty = 22{\cdot}5,\ 28{\cdot}0,\ 26{\cdot}7,\ 25{\cdot}4;\ \text{mean } 25{\cdot}6°. \quad [\alpha]_{5461} = 132{\cdot}5°.^*$$

A more accurate series of 5 sets of 3 readings, covering a total period of 7 minutes only, in Expt. 2*b* gave

$$\alpha_\infty = 28{\cdot}1,\ 27{\cdot}6,\ 26{\cdot}9,\ 26{\cdot}3,\ 24{\cdot}5;\ \text{mean } 26{\cdot}7°. \quad [\alpha]_{5461} = 133{\cdot}5°.$$

A third series of 4 sets of three readings (Expt. 2*c*), covering a period of 7½ minutes, gave

$$\alpha_\infty = 26{\cdot}9,\ 26{\cdot}4,\ 27{\cdot}8,\ 27{\cdot}9;\ \text{mean } 27{\cdot}25. \quad [\alpha]_{5461} = 136{\cdot}2°.$$

* This value has been calculated by deducing the strength of the solution from its final rotatory power on the assumption that $[\theta_\infty] = 94°$.

The last two series give a very uniform value for the end-point, $\alpha_{\infty} = 27°$, from which we can deduce that the specific rotatory power of the solution on completion of the first stage of the transformation would be $[\alpha]_{5461} = 135°$, as contrasted with the final equilibrium value $[\alpha]_{5461} = 94°$ at the end of the second stage.

This rotatory power is of the same order of magnitude as that assigned by Riiber and Minsaas to the intermediate sugar, *viz.*, $[\alpha]_D = 135°$, whence $[\alpha]_{5461}$ = about 153°; but it cannot be interpreted in this way, since, as we have seen, the intermediate form has nearly the same rotatory power as the β-sugar, whereas this is nearly equal to that of the α-sugar. A more plausible view, which we have not yet confirmed by mathematical analysis, is that the intermediate end-point, $[\alpha]_{5461} = 135°$, represents the rotatory power, not of the μ-sugar, but of an equilibrium mixture, $\alpha \rightleftharpoons \mu$, from which only the β-sugar is excluded.

By making use of this intermediate end-point, we obtain the velocity coefficients shown in Table III. The second of these series is not so consistent as the first, where the velocity coefficient is exceptionally uniform; but in both cases the data show clearly that the early stages of the mutarotation of α-galactose can be expressed quite satisfactorily as a unimolecular change, with velocity coefficient 0·064, and tending towards an end-point at $[\alpha]_{5461} = 135°$.

TABLE III.

Velocity Coefficients in the Early Stages of Mutarotation of α-Galactose.

t (min.).	$k_e \times 10^4$.	t (min.).	$k_e \times 10^4$.
2·15 + 0·95	640	2·65 + 0·95	624
+ 1·45	640	+ 1·30	602
+ 1·83	637	+ 1·93	611
+ 2·20	649	+ 2·37	624
+ 2·70	650	+ 2·78	643
+ 3·25	632	+ 3·23	645
+ 3·83	643	+ 3·68	639
+ 4·42	654	+ 4·17	650
+ 5·08	644	+ 4·67	650
+ 5·95	649	+ 5·17	648
+ 6·67	649	+ 5·68	651
+ 7·35	645	+ 6·25	658
Mean k_e = 0·0644		Mean k_e = 0·0637	

(*i*) *Calculations of Exponents and Coefficients.*—In order to determine the values of the coefficients A_1, B_1, A_2, B_2 of the empirical equations, and the unknown exponent m_2, we may notice that the velocity coefficients in the initial stages of the mutarotation of α- and β-galactose are given by

$$-d\theta/dt = A_1m_1 + B_1m_2 \text{ and } - d\theta/dt = A_2m_1 + B_2m_2.$$

If expressed as the velocity coefficient of a unimolecular action, with C as the limiting value, these quantities become

$$\frac{A_1m_1 + B_1m_2}{A_1 + B_1} \text{ and } \frac{A_2m_1 + B_2m_2}{A_2 + B_2}$$

Since the initial stages of the mutarotation of the α-sugar can be expressed as a unimolecular action with a velocity coefficient 0·064, and a range of 172°—135° = 37° (instead of 172° − 94° = 78°, when referred to the equilibrium value), the first of these expressions has the value $0{\cdot}064 \times 37 \div 78 = 0{\cdot}030$, whilst the second is approximately zero (see p. 675). Thus for the α-sugar we have

$$A_1 + B_1 = 15{\cdot}70 \text{ and } A_1m_1 + B_1m_2 = 15{\cdot}70 \times 0{\cdot}030 = 0{\cdot}48,$$

whilst for the β-sugar

$$A_2 + B_2 = -6{\cdot}1 \text{ and } A_2m_1 + B_2m_2 = 0 \text{ (approximately)},$$

where in each equation $m_1 = 0{\cdot}0188$. If therefore m_2 were known, we could now calculate the four remaining coefficients, A_1, B_1, A_2, B_2, of the empirical equations from these four relationships. Alternatively, we can eliminate m_2, B_1, and B_2 from these relations and so obtain

$$0{\cdot}115A_1 - 0{\cdot}181A_2 - 2{\cdot}91 = 0 \quad . \quad . \quad (1)$$

Since only the ends of the mutarotation curves have been used hitherto, the additional datum that is required to complete the analysis can be brought in most easily by reading off the values of θ for each sugar at a time (*e.g.*, 20 minutes) when mutarotation is less than half-complete. Thus since $\theta_\alpha = 28{\cdot}68$ and $\theta_\beta = 13{\cdot}99$ when $t = 20$ (and consequently $e^{-m_1t} = 0{\cdot}6865$) we can write :

$$0{\cdot}6865A_1 + B_1e^{-m_2t} + C = 28{\cdot}68$$
$$0{\cdot}6865A_2 + B_2e^{-m_2t} + C = 13{\cdot}99$$

or, since $B_1 = 15{\cdot}70 - A_1$, $B_2 = -6{\cdot}10 - A_2$, $C = 18{\cdot}80$, we can eliminate m_2 and obtain

$$-0{\cdot}622A_1 + 0{\cdot}898A_2 + 15{\cdot}2 = 0 \quad . \quad . \quad (2)$$

Similar equations can be deduced from the values of θ_α and θ_β at any other values of t, but, when t is large, the ratios involved approximate to zero and therefore become of very little value.

Equations (1) and (2) can now be combined to give A_1 and A_2, and hence B_1, B_2, and m_2. Unfortunately, these eliminations result in an exaggeration of the experimental errors which make it almost a matter of accident whether they yield a plausible solution of the problem or not. The combination of data which we happened to use gave values for the coefficients which required very little adjustment to make them fit the curves, the adjusted values being

$m_2 = 0{\cdot}146$, $A_1 = 14{\cdot}3$, $B_1 = 1{\cdot}4$, $A_2 = -7{\cdot}13$, $B_2 = 1{\cdot}03$; but as a different selection of data gave $B_2 = 0$ (in which case the mutarotation curve of the α-sugar would have been unimolecular), we think it desirable to describe an alternative procedure, which does not depend on the selection of a single pair of readings but is based upon a general average of a series.

Table IV.

Determination of Coefficients.

t.	θ_α.	A_1.		θ_β.	A_2.	
2	33·60	15·48		12·70	−6·33	
5	32·49	15·04		12·78	−6·61	
10	30·97	14·69		13·10	−6·88	
15	29·73	14·49		13·52	−7·00	
20	28·68	14·40		13·99	−7·01	
30	26·95	14·33		14·80	−7·03	
40	25·57	14·36		15·48	−7·04	−7·1
50	24·39	14·31	14·31	16·05	−7·04	
60	23·43	14·30		16·48	−7·16	
70	22·62	14·25		16·86	−7·23	
80	—	—		17·16	−7·29	

Table V.

Mutarotation of α- and β-Galactose.

t.	θ_α (obs.).	θ_α (calc.).	Diff.
0	34·50*	14·30 + 1·40 + 18·80 = 34·50	0·00
2	33·60	13·77 + 1·05 + 18·80 = 33·62	−0·02
5	33·49	13·02 + 0·67 + 18·80 = 32·49	0·00
10	30·97	11·84 + 0·32 + 18·80 = 30·96	+0·01
15	29·73	10·78 + 0·16 + 18·80 = 29·74	−0·01
20	28·68	9·81 + 0·07 + 18·80 = 28·68	0·00
30	26·98	8·13 + 0·02 + 18·80 = 26·95	+0·03
40	25·57	6·74 + — + 18·80 = 25·54	+0·03
50	24·39	5·59 + — + 18·80 = 24·39	0·00
60	23·43	4·63 + — + 18·80 = 23·43	0·00
70	22·62	3·83 + — + 18·80 = 22·63	−0·01
80	21·95	3·18 + — + 18·80 = 21·98	−0·03
100	20·97	2·18 + — + 18·80 = 20·98	−0·01
t.	θ_β (obs.).	θ_β (calc.).	Diff.
0	12·70*	−7·13 + 1·03 + 18·80 = 12·70	0·00
2	12·70	−6·87 + 0·77 + 18·80 = 12·70	0·00
5	12·78	−6·46 + 0·50 + 18·80 = 12·84	−0·06
10	13·10	−5·91 + 0·24 + 18·80 = 13·13	−0·03
15	13·52	−5·38 + 0·12 + 18·80 = 13·54	−0·02
20	13·99	−4·89 + 0·06 + 18·80 = 13·97	+0·02
30	14·80	−4·06 + 0·01 + 18·80 = 14·75	+0·05
40	15·48	−3·33 + — + 18·80 = 15·48	0·00
50	16·05	−2·79 + — + 18·80 = 16·02	+0·03
60	15·48	−2·31 + — + 18·80 = 16·51	−0·03
70	16·86	−1·91 + — + 18·80 = 16·89	−0·03
80	17·16	−1·59 + — + 18·80 = 17·21	−0·05
100	17·67	−1·01 + — + 18·80 = 17·69	−0·02

* By extrapolation.

This procedure depends upon the fact that one exponential dies out before the other, after which the mutarotation becomes unimolecular and gives rise to steady velocity coefficients. We can therefore extrapolate back to a hypothetical initial value at zero time, on the assumption that the second exponential is not present, and so obtain values of A_1 or A_2 from the expressions

$$A_1 = (\theta_\alpha - \theta_\infty)/e^{-0\cdot0188t};\ A_2 = (\theta_\beta - \theta_\infty)/e^{-0\cdot0188t}.$$

TABLE VI.

Mutarotation of α-Galactose in Water at 20°.

(*a*) Second sample (recryst. HAc), 10 g./100 c.c. in 2 dm. tube.

$$\theta_\alpha = 13\cdot62e^{-0\cdot0188t} + 1\cdot21e^{-0\cdot146t} + 18\cdot80.$$

	θ_{5461}.				
t (min.).	obs.	calc.	Diff.	*k*.	k_e.
2·15	32·80	32·78	+0·02		
2·70	32·58	32·56	+0·02	0·0285	
3·10	32·44	32·41	+0·03	0·0274	
3·60	32·26	32·24	+0·02	0·0272	
3·98	32·13	32·12	+0·01	0·0267	
4·35	31·99	31·99	0·00	0·0271	
4·85	31·82	31·83	−0·01	0·0269	
5·40	31·67	31·65	+0·02	0·0259	
5·98	31·47	31·48	−0·01	0·0260	
6·57	31·27	31·29	−0·02	0·0262	
7·23	31·10	31·10	0·00	0·0255	
8·10	30·85	30·87	−0·02	0·0252	
8·82	30·66	30·67	−0·01	0·0248	
9·50	30·50	30·49	+0·01	0·0244	
10·70	30·16	30·19	−0·03	0·0244	
12·30	29·78	29·81	−0·03	0·0239	
13·22	29·59	29·60	−0·01	0·0235	
15·15	29·16	29·17	−0·01	0·0232	
17·00	28·77	28·80	−0·03	0·0229	
19·83	28·24	28·25	−0·01	0·0223	
22·15	27·81	27·83	−0·02	0·0220	
24·28	27·46	27·47	−0·01	0·0217	
26·97	27·02	27·02	0·00	0·0215	
30·17	26·55	26·53	+0·02	0·0211	
33·23	26·10	26·08	+0·02	0·0210	
36·55	25·65	25·65	0·00	0·0208	0·0191
40·15	25·21	25·20	+0·01	0·0206	0·0188
43·28	24·85	24·84	+0·01	0·0204	0·0187
47·35	24·40	24·39	+0·01	0·0203	0·0188
54·67	23·67	23·67	0·00	0·0201	0·0189
63·00	22·96	22·97	−0·01	0·0196	0·0183
70·17	22·45	22·40	+0·05	0·0198	0·0188
82·28	21·71	21·70	+0·01	0·0196	0·0188
92·15	21·21	21·21	0·00	0·0196	0·0187
105·95	20·65	20·64	+0·01	0·0195	0·0189
122·73	20·14	20·15	−0·01	0·0195	0·0189
150·00	19·63	19·61	+0·02	0·0191	0·0186
∞	18·80	18·80	0·00		

(*b*) Third sample (recryst. HAc and EtOH), 10 g./100 c.c. in 2 dm. tube.

$$\theta_a = 14{\cdot}33e^{-0{\cdot}0188t} + 1{\cdot}40e^{-0{\cdot}146t} + 18{\cdot}81.$$

t (min.).	θ_{5461} obs.	θ_{5461} calc.	Diff.	k.	k_e.
2·65	33·36	33·40	−0·04		
3·60	33·01	33·03	−0·02	0·0257	
3·95	32·90	32·89	+0·01	0·0250	
4·58	32·68	32·68	0·00	0·0247	
5·02	32·52	32·52	0·00	0·0252	
5·43	32·36	32·38	−0·02	0·0257	
5·88	32·21	32·23	−0·02	0·0255	
6·33	32·08	32·09	−0·01	0·0250	
6·82	31·91	31·94	−0·03	0·0252	
7·32	31·76	31·78	−0·02	0·0250	
7·82	31·62	31·63	−0·01	0·0247	
8·33	31·47	31·47	0·00	0·0245	
8·90	31·30	31·31	−0·01	0·0245	
9·48	31·14	31·15	−0·01	0·0243	
10·20	30·95	30·96	−0·01	0·0240	
11·47	30·62	30·62	0·00	0·0237	
12·38	30·38	30·39	−0·01	0·0236	
13·53	30·11	30·11	0·00	0·0232	
15·37	29·70	29·68	+0·02	0·0228	
17·75	29·19	29·18	+0·01	0·0224	
20·33	28·67	28·66	+0·01	0·0220	
22·62	28·23	28·23	0·00	0·0218	
26·03	27·64	27·62	+0·02	0·0214	
30·35	26·94	26·92	+0·02	0·0210	
36·05	26·12	26·09	+0·03	0·0206	
44·47	25·06	25·02	+0·04	0·0202	0·0186
53·87	24·05	24·01	+0·04	0·0199	0·0187
61·85	23·29	23·29	0·00	0·0199	0·0190
77·83	22·11	22·13	−0·02	0·0197	0·0190
89·25	21·49	21·49	0·00	0·0195	0·0189
101·75	20·91	20·93	−0·02	0·0195	0·0190
112·52	20·51	20·54	−0·03	0·0195	0·0191
∞	18·81	18·81	0·00		

The data set out in Table IV give for A_1 the trustworthy value 14·3; B_1 must then have the value 1·4, since $A_1 + B_1 = 15{\cdot}7$. Moreover, since $14{\cdot}3 \times 0{\cdot}0188 + 1{\cdot}4m_2 = 0{\cdot}48$, it follows at once that $m_2 = 0{\cdot}148$, in close agreement with the value 0·146 which we had already found to fit the curves. The extrapolated values for A_2 vary very little after the first 10 minutes; a long series of values is then obtained with an average $A_2 = -7{\cdot}1$, which agrees closely with the coefficient −7·13 which we had found to fit the curves. Since $A_2 + B_2 = -6{\cdot}1$, the value of B_2 must be 1·0 approximately, but a slight adjustment is needed to get the inflexion into the right position, and this adjustment leads to a small negative value (instead of an exact zero value) for $d\theta/dt$ for the β-sugar when $t = 0$.

(*j*) *Empirical Equations for the Mutarotation of α- and β-Galactose.*—The empirical equations as finally adjusted are

$$\theta_\alpha = 14{\cdot}30e^{-0{\cdot}0188t} + 1{\cdot}40e^{-0{\cdot}146t} + 18{\cdot}80$$
$$\theta_\beta = -7{\cdot}13e^{-0{\cdot}0188t} + 1{\cdot}03e^{-0{\cdot}146t} + 18{\cdot}80.$$

The extent of the agreement with the interpolated values for the rotatory powers of the two sugars at equal increments of time is shown in Table V. This table also shows how the influence of the second exponential disappears after about 30 minutes, when the curves assume a unimolecular form, as Riiber and Minsaas observed. The agreement between the original readings and values calculated from the equations is shown in Tables VI and VII.

TABLE VII.

Mutarotation of β-Galactose in Water at 20°.

(*a*) First sample (washed once), 5 g./100 c.c. in 2 dm. tube.

$$\theta_\beta = -3{\cdot}20e^{-0{\cdot}0188t} + 0{\cdot}30e^{-0{\cdot}146t} + 9{\cdot}28.$$

	θ_{5461}.				
t (min.).	obs.	calc.	Diff.	k.	k_e.
1·75	6·51	6·41	+0·10		
2·53	6·48	6·44	+0·04		
3·13	6·48	6·45	+0·03		
3·73	6·48	6·47	+0·01		
4·82	6·48	6·51	−0·03		
5·73	6·52	6·54	−0·02		
7·23	6·56	6·59	−0·03	0·0053	
8·08	6·58	6·62	−0·04	0·0057	
9·23	6·64	6·67	−0·03	0·0079	
10·47	6·67	6·71	−0·04	0·0081	
12·33	6·75	6·79	−0·04	0·0096	
13·87	6·82	6·85	−0·03	0·0099	
16·47	6·93	6·96	−0·03	0·0119	
18·28	6·99	7·03	−0·04	0·0122	
20·23	7·09	7·10	−0·01	0·0133	
22·25	7·18	7·18	0·00	0·0140	
24·35	7·27	7·26	+0·01	0·0147	
26·38	7·33	7·33	0·00	0·0147	
29·20	7·45	7·43	+0·02	0·0155	
32·35	7·55	7·54	+0·01	0·0157	0·0192
37·33	7·69	7·69	0·00	0·0159	0·0184
41·53	7·82	7·81	+0·01	0·0160	0·0188
45·28	7·93	7·91	+0·02	0·0168	0·0192
49·73	8·06	8·02	+0·04	0·0173	0·0198
54·85	8·16	8·14	+0·02	0·0173	0·0193
59·53	8·27	8·23	+0·04	0·0177	0·0196
69·13	8·42	8·41	+0·01	0·0175	0·0190
80·88	8·58	8·58	0·00	0·0175	0·0187
89·20	8·71	8·68	+0·03	0·0182	0·0190
117·42	8·95	8·93	+0·02	0·0185	0·0194
∞	9·28	9·28	0·00		

(*b*) Second sample (washed twice), 5 g./100 c.c. in 2 dm. tube.

$$\theta_\beta = -3{\cdot}56e^{-0{\cdot}0188t} + 0{\cdot}51e^{-0{\cdot}146t} + 9{\cdot}34.$$

t (min.).	θ_{5461} obs.	θ_{5461} calc.	Diff.	k.	k_s.
1·92	6·31	6·29	+0·02		
2·48	6·31	6·30	+0·01		
2·88	6·32	6·30	+0·02		
3·32	6·31	6·30	+0·01		
3·90	6·31	6·32	−0·01		
4·42	6·32	6·33	−0·01		
4·95	6·35	6·34	+0·01		
5·83	6·35	6·36	−0·01		
6·53	6·36	6·38	−0·02		
7·60	6·40	6·42	−0·02	0·0053	
8·80	6·46	6·46	0·00	0·0074	
9·95	6·51	6·51	0·00	0·0085	
11·50	6·54	6·55	−0·01	0·0082	
12·37	6·59	6·59	0·00	0·0093	
14·10	6·68	6·68	0·00	0·0107	
16·00	6·76	6·75	+0·01	0·0114	
18·03	6·86	6·84	+0·02	0·0124	
20·33	6·95	6·94	+0·01	0·0129	
22·43	7·04	7·02	+0·02	0·0134	
24·53	7·13	7·10	+0·03	0·0140	
26·68	7·22	7·19	+0·03	0·0144	
28·58	7·28	7·26	+0·02	0·0145	
29·43	7·32	7·30	+0·02	0·0147	
32·12	7·43	7·44	−0·01	0·0153	
35·32	7·52	7·51	+0·01	0·0153	0·0184
39·15	7·64	7·63	+0·01	0·0152	0·0182
42·85	7·76	7·75	+0·01	0·0159	0·0185
47·00	7·88	7·87	+0·01	0·0162	0·0193
51·17	7·98	7·98	0·00	0·0163	0·0190
58·78	8·16	8·16	0·00	0·0166	0·0184
64·23	8·27	8·27	0·00	0·0167	0·0179
69·27	8·35	8·37	−0·02	0·0166	0·0173
77·92	8·50	8·51	−0·01	0·0169	0·0182
90·72	8·67	8·69	−0·02	0·0170	0·0181
109·17	8·85	8·86	−0·01	0·0170	0·0178
∞	9·34	9·34	0·00		

Evaluation of the Fundamental Constants.

The empirical equations set out above provide a complete summary of the experimental data, and it is impossible to deduce from these data anything that is not contained in the equations. Whilst, however, it is easy to work out the seven constants of the empirical equations when the seven fundamental constants of the system are known, it is not easy to carry out the converse process, on account of the complex form in which the fundamental constants appear in the equations. (i) The simplest relationships are found in the exponents, which depend only on the velocity coefficients of the sugars, and not on their optical rotations. These relationships can be summarised most concisely by means of the two following equations :

$$k_1+k_2+k_3+k_4=m_1+m_2=0{\cdot}0188+0{\cdot}146=0{\cdot}1648 \quad . \quad . \quad (3)$$
$$k_2k_3+k_1k_3+k_1k_4=m_1m_2=0{\cdot}0188\times 0{\cdot}146=0{\cdot}002745 \quad . \quad . \quad (4)$$

(ii) The coefficients of the empirical equations* are more complex functions, since they depend on the rotations as well as the velocity coefficients of the sugars. They may, however, be summarised as follows :

$$C = \alpha x_\infty + \mu y_\infty + \beta z_\infty = 18{\cdot}80$$

$$A_1 = -\frac{m_2}{m_2-m_1}C + \frac{m_2}{m_2-m_1}\alpha - \frac{k_1}{m_2-m_1}(\alpha-\mu) = 14{\cdot}30$$

$$B_1 = \frac{m_1}{m_2-m_1}C - \frac{m_1}{m_2-m_1}\alpha + \frac{k_1}{m_2-m_1}(\alpha-\mu) = 1{\cdot}40$$

$$A_2 = -\frac{m_2}{m_2-m_1}C + \frac{m_2}{m_2-m_1}\beta - \frac{k_3}{m_2-m_1}(\beta-\mu) = -7{\cdot}13$$

$$B_2 = \frac{m_1}{m_2-m_1}C - \frac{m_1}{m_2-m_1}\beta + \frac{k_3}{m_2-m_1}(\beta-\mu) = 1{\cdot}03$$

If we add these equations in pairs we merely get the former relations $A_1 + B_1 + C = \alpha$; and $A_2 + B_2 + C = \beta$. If, however, we subtract them we get

$$A_1 - B_1 = \frac{m_2+m_1}{m_2-m_1}(\alpha - C) - \frac{2k_1}{m_2-m_1}(\alpha-\mu) = 12{\cdot}9$$

$$A_2 - B_2 = \frac{m_2+m_1}{m_2-m_1}(\beta - C) - \frac{2k_3}{m_2-m_1}(\beta-\mu) = -8{\cdot}16$$

or

$$k_1(\alpha-\mu) = \tfrac{1}{2}(m_2+m_1)(\alpha-C) - \tfrac{1}{2}(m_2-m_1)\,12{\cdot}9 = 0{\cdot}4732 \quad (5)$$
$$k_3(\beta-\mu) = \tfrac{1}{2}(m_2+m_1)(\beta-C) + \tfrac{1}{2}(m_2-m_1)\,8{\cdot}16 = 0{\cdot}01634 \quad (6)$$

where numerical values for $k_1(\alpha-\mu)$ and $k_3(\beta-\mu)$ have been deduced by inserting $m_2 + m_1 = 0{\cdot}1648$, $m_2 - m_1 = 0{\cdot}1272$, $\alpha - C = 15{\cdot}7$, $\beta - C = -6{\cdot}1$.

(iii) The fifth relation that is required to give the four unknown velocity coefficients and the unknown rotation μ, is supplied by

$$\theta_\infty = \alpha x_\infty + \mu y_\infty + \beta z_\infty$$

or

$$C = \frac{\alpha k_2k_3 + \mu k_1k_3 + \beta k_1k_4}{k_2k_3 + k_1k_3 + k_1k_4}$$

whence $\quad (\alpha - C)k_2k_3 + (\mu - C)k_1k_3 + (\beta - C)k_1k_4 = 0$

* The coefficients for $\theta\beta$ are got by substituting k_3 for k_1 and β for α, since the m's are reversible functions of the k's.

or, dividing by k_1k_3,

$$\mu = C - (\alpha - C)\frac{k_2}{k_1} - (\beta - C)\frac{k_4}{k_3} = 18{\cdot}8 - 15{\cdot}7\frac{k_2}{k_1} + 6{\cdot}1\frac{k_4}{k_3} \quad . \quad (7)$$

(iv) The simplest way of proceeding from this point is to assume a value of μ, and then to deduce k_1 and k_3 from (5) and (6). Substitution in (3) gives $k_2 + k_4$, which can be combined with (7) (after a similar substitution) to give k_2 and k_4. The sum of the products in (4) can then be evaluated and compared with the observed value $m_1m_2 = 0{\cdot}002745$. By this method of trial and error, we find that μ has the value 11·67, and that, if we alter it only to 11·65, an erroneous value (0·002726 instead of 0·002745) is obtained for m_1m_2. We can therefore assign to the intermediate sugar the specific rotation $[\alpha]_{5461} = 58°$ if we accept the validity of the three-sugar scheme. The corresponding values of the velocity coefficients are :

$$\begin{array}{rlcrl} k_1 &= 0{\cdot}0207 & \qquad & k_3 &= 0{\cdot}0159 \\ k_2 &= 0{\cdot}0494 & & k_4 &= 0{\cdot}0788 \\ \hline k_1 + k_2 &= 0{\cdot}0701 & & k_3 + k_4 &= 0{\cdot}0947 \end{array}$$

Equilibrium Concentrations and Rotations.

The equilibrium concentrations deduced from the velocity coefficients of the three-sugar scheme are

$$x_\infty = 28{\cdot}5\%\,; \; y_\infty = 12{\cdot}0\%\,; \; z_\infty = 59{\cdot}5\%.$$

These can be compared with the values deduced by Riiber and Minsaas, *viz.*,

$$x_\infty = 6{\cdot}61\%\,; \; y_\infty = 27{\cdot}35\%\,; \; z_\infty = 66{\cdot}04\%.$$

A similar comparison of the optical rotations of the three sugars gives

		α.	μ.	β.
	$[\alpha]_{5461}$ =	173°	58°	63·5° (Lowry and Smith)
	$[\alpha]_D$ =	144·5°	135·0°	52·2° (Riiber and Minsaas)
or	$[\alpha]_{5461}$ =	173·4°	162°	62·6°

if we increase the values of $[\alpha]_D$ by 20%* to allow for the change of wave-length.

Since Riiber and Minsaas did not detect any anomalies in the mutarotation curves, their estimate of the rotatory power of the intermediate sugar is based on less direct evidence than our own, and is obviously incorrect in making this rotation approximate to that of α-galactose, whereas actually it does not differ much from

* This is greater than the observed increment, but has been selected because it gives the best agreement in the case of the α- and β-sugars.

that of β-galactose. Their equations also lead to an abnormally *slow* mutarotation of α-galactose in the early stages (corresponding to the small change of rotation from α to μ), whereas in fact the mutarotation is exceptionally *fast* at this stage.

On the assumption that only 3 isomerides are present, our estimate of the percentages of the three sugars in the equilibrium mixture is probably correct to within a few units, since it is based on data in which the effects of the third sugar are very obvious. It has the advantage of raising the proportion of the α-sugar to a more reasonable figure than that given by Riiber and Minsaas, namely 28·5% instead of only 6·6%. The proportion of the intermediate open-chain sugar, on the other hand, is reduced from 27% to 12% of the total. The two estimates concur, however, in making the β-sugar the predominant constituent, forming 60 to 66% of the equilibrium mixture.

Since the equilibrium proportion of α-galactose in anhydrous methyl alcohol is about 1/2 of the total (J., 1904, **85**, 1557), the ratio β/α cannot be greater than unity in this solvent; it is therefore surprising to find a ratio $\beta/\alpha > 2/1$ in water. This wide difference may be due to a selective action of water in promoting the formation of β-galactose at the expense of the α-sugar; but, on the other hand, it may be merely a proof that the equilibrium in aqueous solutions is too complex to be represented by the simple system which must be postulated if a mathematical analysis of the data is to be carried out. Whilst, therefore, we have sought to make the fullest possible use of this mathematical analysis, and to follow up all the consequences which flow from its application to our data, our positive assertions do not go beyond the simple facts set out in the following summary, *viz.*, that: (i) The mutarotation data for galactose cannot be interpreted on a 2-sugar scheme, but can be expressed by a 3-sugar scheme; (ii) a third sugar must therefore be formed in substantial quantities in solution; (iii) this sugar must be related unsymmetrically to the α- and β-sugars, in rotation or in velocity of formation and reversion, or in both; (iv) since the mutarotation of β-galactose proceeds only very slowly during the first few minutes, and gives rise to inflected curves, the initial product of change must have a similar rotation to the β-sugar.

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