

- III. "Researches on Lactin." By EDMUND J. MILLS, D.Sc., F.R.S., "Young" Professor of Technical Chemistry in Anderson's College, Glasgow, and JAMES HOGARTH. Received December 4, 1878.

Although lactin, or sugar of milk, has been investigated by numerous chemists, there are many problems connected with it which still await solution. We have accordingly undertaken a series of experiments in connexion with this remarkable compound, in the hope, not only of obtaining special results, but such as may be made available in studies of a more general nature. As our work throughout has been for the most part optical as well as chemical, we have first to state our methods of obtaining the constant of Jellett's polarimeter, the instrument employed in our investigations.

I. *Determination of the Polarimeter's Constant.*—*a.* By quinine sulphate. 5·5412 grms. of the sulphate were dissolved in water acidulated with hydric sulphate, and the solution made up to 100 cub. centims. The average of five readings gave a solution of $-25^{\circ}73$, equivalent to a specific rotatory power of $-232^{\circ}16$. De Gris and Alluard* give $-255^{\circ}6$, a number which is to our experimental number as 1·10096 to 1.

β. By cane sugar. Three sets of experiments on solutions containing respectively 16·3500, 8·1750, and 4·0875 grms. in 100 cub. centims., and embracing five, four, and four readings, gave a general mean reading $21^{\circ}74$, equivalent to a specific rotation $66^{\circ}48$.

This is to the generally accepted number ($73^{\circ}8$) as 1 to 1·11011.

γ. By salicin. Two sets of experiments with solutions containing respectively 4·9156 and 2·4578 grms. in 100 cub. centims., and each embracing three readings, gave a general mean reading $4^{\circ}92$, equal to a specific rotation $50^{\circ}046$. Bouchardat† gives $55^{\circ}832$, which is to the number got by Jellett's instrument as 1·11561 to 1.

The average of the three numbers, 1·10096, 1·11011, and 1·11561, gives 1·10889 as an experimental factor for converting our Jellett readings into ordinary readings.

The relation of the two scales may also be seen by examining the arc divided to read percentages of cane sugar with a solution containing 16·35 grms. in 100 cub. centims. In the Jellett instrument, an arc of $21^{\circ}666$ is divided into hundredths for this purpose; and as 16·35 grms. pure cannose read 100 on this scale, the specific rotation

* "Compt. rend.," lix, 201.

† "Compt. rend.," xviii, 298.

is $66^{\circ}256$, which is to $73^{\circ}8$ as 1 to 1.11386—a factor which differs from the above experimental one by 0.45 per cent.

All the specific rotations given by us are corrected by this factor, and are comparable with those in general use.

In all our experiments the specific rotation is calculated by the formula $[a] = \frac{aV}{lp}$. Where $[a]$ = specific rotation, a = the reading in degrees, V the volume of solution containing the weight p , and l = the length of the column in decimeters (in the above experiments, 2).

II. *Determination of the Permanent Specific Rotation of Lactin.*—The lactin was purified by filtration through animal charcoal, and two or three crystallizations, after which it left no sensible residue on ignition in air. Five sets of readings were made:—

(1.)	Average of 5 readings.	Specific rotation	52.84
(2.)	” ” ”	” ”	53.23
(3.)	” ” ”	” ”	53.37
(4.)	” 3 ”	” ”	53.04
(5.)	” ” ”	” ”	53.07

The general mean of these numbers is $53^{\circ}12$, which, multiplied by the factor 1.11386, gives $59^{\circ}17$ as the permanent specific rotation of lactin. The number given by Berthelot* is $59^{\circ}3$. In every experiment, care was taken that the rotatory power of the solution had become constant. Three different samples of lactin were employed. Experiments (1), (2), and (3), were on sample I, (4) on sample II, and (5) on sample III. As the samples were prepared at different times, and by a method varying slightly each time, the very small differences in the results show that the lactin contained little or no impurity.

III. *Examination of the Law for the Change of Rotation in a freshly prepared Solution of Lactin.*—If the rotatory power of an aqueous solution of lactin be examined at short intervals of time, it soon becomes apparent that a change is taking place, the angle through which the plane of polarization is rotated becoming gradually less. The object of the following experiments is to quantify the phenomenon in question.

Five grms. of lactin were dissolved as rapidly as possible (time taken, 1 hour 15 minutes) in cold water, and the solution made up to 100 cub. centims. The polarimeter tube (2 decims. long) was filled with the liquid, and a first observation taken 15 minutes after complete solution, or $1\frac{1}{2}$ hour after first contact. Succeeding readings

* “Ann. Ch. Phys.,” [3], liv, 82; lx, 98.

Table I.—Results of Experiments on Lacti

Nature of Solution	Aqueous.			Containing 1 gramme Sod. Chlor. in 60 cc.			Containing 1 gramme Pot. Chlor. in 60 cc.			Aqueous.	
Average Temperature	10°3	10°6	11°0	12°2	10°1	12°8	12°2	10°5	12°1	11°3	10°1
<i>x</i> = 2	13·017	12·975	12·750	14·283	13·687	13·833	14·070	14·147	14·823	13·524	13·523
3	12·567	12·587	12·270	13·733	13·292	13·157	13·487	13·712	14·292	13·010	13·077
4	12·217	12·087	11·883	13·187	12·847	12·583	13·050	13·262	13·833	12·542	12·640
5	11·800	11·650	11·467	12·840	12·490	12·078	12·567	12·831	13·367	12·100	12·240
6	11·450	11·369	11·119	12·362	12·155	11·707	12 230	12·485	13·000	11·790	11·873
7	11·167	11·100	10·883	12·050	11·817	11·330	11·935	12·143	12·675	11·490	11·617
8	10·933		10·616	11·817	11·530	11·070	11·540	11·850	12·377	11·193	11·340
9		10·530									
10	10·540		10·225	11·327	11·110	10·683	11·133	11·405	11·810	10·763	10·933
11		10·025									
12	10·210		9·833	11·067	10·713	10·447	10·787	11·077	11·503	10 390	10·547
13		9·633									
14	9·850		9·517	10·825	10·392	10·213	10·547	10·727	11·117	10·190	10·257
Permanent Rotation.....	8·683	8·562	8·604	10·143	9·283	9·625	9·770	9·620	10·340	9·380	9·193
Extremes of Temperature	9·3 to 11°3	9°7 to 11°3	10°4 to 11°8	12°5 to 13°2	9°4 to 10°6	11°5 to 13°8	11°5 to 12°5	9°8 to 12°3	11°5 to 14°5	11°3 to 11°6	9°5 to 11°3
Number	1	2	3	4	5	6	7	8	9	10	11

No. 21.

<i>x</i> =	3	7	11	15	19	23
Rotation=	9·250	8·117	7·567	7·117	6·875	6·700

on Lactin.

Aqueous.		Containing 5 grammes Pot. Chlor. in 60 cc.			Containing 5 grammes Sod. Chlor. in 60 cc.			10 grammes Pot. Chlor.	10 grammes Sod. Chlor.
10°1	12°9	11°4	13°1	11°8	10°2	11°7	12°9	11°9	11°5
13·523	14·190	17·033	15·460	16·012	13·730	14·633	15·317	16·483	14·083
13·077	13·600	16·435	14·847	15·503	13·350	14·035	14·717	15·987	13·650
12·640	13·040	15·880	14·312	14·954	12·877	13·590	14·085	15·480	13·263
12·240	12·547	15·433	13·887	14·505	12·537	13·193	13·690	15·053	12·853
11·873	12·147	15·017	13·380	14·037	12·197	12·793	13·293	14·650	12·607
11·617	11·843	14·633	13·073	13·747	11·930	12·525	12·950	14·290	
11·340	11·567	14·270	12·737	13·333	11·667	12·253	12·650	13·943	12·063
10·933	11·147	13·768	12·220	12·857	11·172	11·833	12·223	13·320	11·600
10·547	10·733	13·273	11·820	12·453	10·785	11·463	11·852		11·210
10·257	10·583	13·000	11·477	12·167	10·513	11·140	11·560	12·533	10·873
9·193	9·893	11·783	10·667	11·083	9·332	10·140	10·789	10·923	9·567
9°5 to 11°3	12°5 to 13°3	11°3 to 11°8	12°1 to 14°3	11°6 to 12°0	9°8 to 10°3	11°5 to 12°4	12°5 to 13°2	11°3 to 12°3	11°3 to 11°7
11	12	13	14	15	16	17	18	19	20

	23	27	Permanent.
	6·700	6·550	6·417

were made at intervals of 2 hours, the results being given under Table I, No. 21.

See Table I.

In order to increase the total change and lessen proportionally the error of experiment, it became necessary to use a stronger solution, to increase the length of column, and to reduce the interval elapsing between first contact and first observation as far as possible. To attain these conditions the following method was adopted:—About 10 grms. of powdered lactin were rubbed in a mortar with about 60 cub. centims. of water for half an hour, the solution filtered, and the first observation taken one hour after first contact. The metal tube belonging to the polariscope was also discarded, and a glass one constructed from a piece of tubing 17 millims. wide, by sealing on a side piece for the introduction of a thermometer, and grinding the ends carefully until it measured 242 millims., the greatest length admitted by the polarimeter. Two glass disks were cemented on the extremities, and the tube covered from end to end by a helix of thin tin tubing, through which a current of water might be passed to keep the temperature constant; to guard further from variations in temperature the tube was covered with cotton wadding. With these precautions three experiments were made (Table I, Nos. 1, 2, 3), the result being that the total change was nearly doubled. In all the other experiments the method was slightly varied, the lactin being placed in a bottle with a ground glass stopper, 60 cub. centims. water placed on it, and the whole shaken vigorously at intervals for half an hour, filtered, and the first observation taken as before. Each experiment extended over six hours, and included ten observations. For each observation three or four readings were made, and the average taken. In Nos. 4, 5, 6, 7, 8, 9, 13, 14, 15, 16, 17, 18, 19, 20, of the accompanying table, varying weights of sodic and potassic chloride were introduced. In every experiment the thermometer was read at the same time with the rotation; and the average temperature, as well as its extreme variation, is given in the table. That the different experiments might be compared, we have expressed them by the equation—

$$y = a + bx + cx^2,$$

in which y is the angle of rotation, x the time in half-hours, counting from the first contact of the lactin with water, and a , b , and c , are constants. The values of a , b , and c , were calculated by the method of least squares.

In Table II are given the equations, accompanied by the probable error of a single comparison of the calculated and experimental values of y . The sum of the \pm actual errors is in nearly all cases zero.

Table II.

Number.	Equation.	Probable error.
1	$y=13 \cdot 9002 - \cdot 48543x + \cdot 014330x^2$ $\cdot 0315$
2	$y=14 \cdot 1325 - \cdot 56919x + \cdot 017755x^2$ $\cdot 0423$
3	$y=13 \cdot 6284 - \cdot 49476x + \cdot 014629x^2$ $\cdot 0323$
4	$y=15 \cdot 4100 - \cdot 62775x + \cdot 021712x^2$ $\cdot 0316$
5	$y=14 \cdot 6188 - \cdot 49366x + \cdot 013833x^2$ $\cdot 0173$
6	$y=15 \cdot 0692 - \cdot 71727x + \cdot 026959x^2$ $\cdot 0519$
7	$y=15 \cdot 1537 - \cdot 60585x + \cdot 019943x^2$ $\cdot 0269$
8	$y=15 \cdot 1654 - \cdot 54298x + \cdot 016387x^2$ $\cdot 0232$
9	$y=15 \cdot 8792 - \cdot 58006x + \cdot 017402x^2$ $\cdot 0263$
10	$y=14 \cdot 5430 - \cdot 56770x + \cdot 018459x^2$ $\cdot 0229$
11	$y=14 \cdot 6154 - \cdot 56240x + \cdot 018388x^2$ $\cdot 0368$
12	$y=15 \cdot 3747 - \cdot 66860x + \cdot 023514x^2$ $\cdot 0380$
13	$y=18 \cdot 2142 - \cdot 65254x + \cdot 020109x^2$ $\cdot 0224$
14	$y=16 \cdot 6262 - \cdot 65155x + \cdot 020546x^2$ $\cdot 0313$
15	$y=17 \cdot 2230 - \cdot 64521x + \cdot 020448x^2$ $\cdot 0227$
16	$y=14 \cdot 6339 - \cdot 48232x + \cdot 013474x^2$ $\cdot 0177$
17	$y=15 \cdot 5954 - \cdot 56252x + \cdot 017796x^2$ $\cdot 0401$
18	$y=16 \cdot 4546 - \cdot 65417x + \cdot 022141x^2$ $\cdot 0455$
19	$y=17 \cdot 5923 - \cdot 58714x + \cdot 016131x^2$ $\cdot 0088$
20	$y=14 \cdot 9011 - \cdot 45421x + \cdot 012057x^2$ $\cdot 0255$

By the aid of these equations we can now calculate the initial specific rotation of lactin, or the rotation when $x=0$ calculated to unit of weight. When $x=0$, $y=a$; and the permanent rotation being known, the initial specific rotation = $\frac{a \times 59 \cdot 17}{\text{permanent rotation}}$. The following are the values found, the chloride experiments being averaged by themselves.

Average of Nos. 1, 2, 3, 10, 11, 12.....	93° 98
„ „ Nos. 4, 5, 6	91° 90
„ „ Nos. 7, 8, 9	91° 97
„ „ Nos. 13, 14, 15	91° 87
„ „ Nos. 16, 17, 18.....	91° 37
Single experiment, No. 19	95° 30
„ „ No. 20	92° 16
Average of the twenty experiments, 92° 63.	

On differentiating the equations, putting $\frac{dy}{dx}=0$, and calculating the values of x and y , we find that the values of y thus got do not correspond to the permanent rotation, but are always greater; showing that the change in rotatory power does not progress according to the

same law throughout, but that, at the point referred to, a new reaction begins. This value of y is proportional to the amount of lactin in solution, indicated by the permanent rotation; and the specific rotation calculated from it in the different experiments is practically constant, its average value (from twenty experiments) being $64^{\circ}8$.

The following are the values of x and y when $\frac{dy}{dx}=0$.

Table III.

No.	x .	y .	Specific rotation.
1	16.937	9.789	66.71
2	16.029	9.571	66.14
3	16.910	9.445	64.95
4	14.456	10.872	63.42
5	17.843	10.214	65.11
6	13.308	10.298	63.31
7	15.189	10.552	63.91
8	16.567	10.667	65.63
9	16.666	11.045	63.22
10	15.388	10.178	64.20
11	15.292	10.315	66.39
12	14.217	10.622	63.53
13	16.225	12.920	64.88
14	15.855	11.461	63.57
15	15.776	12.133	64.78
16	17.898	10.319	65.41
17	15.804	11.149	65.06
18	14.772	11.622	63.79
19	18.199	12.250	66.36
20	18.836	10.624	65.71

This break in the change seems to point to the dual nature of lactin mentioned by Fudakowski,* whose experiments show that lactin, like cannose, gives two glucoses—lacto glucose and galactose.

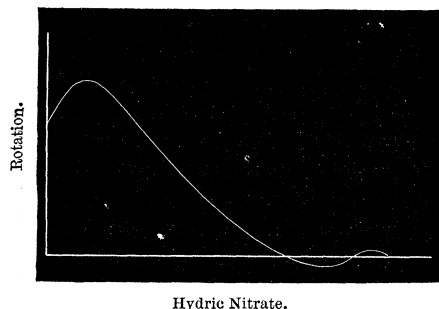
An increase of temperature evidently hastens the change; but the exact relation of temperature to the rate of change has not been discovered.

The presence of sodic or potassic chloride increases the amount of lactin in solution, but has no apparent effect on the rate of change.

IV. *Action of Hydric Nitrate on Lactin.*—We made an attempt to trace this action, but did not succeed in overcoming experimental difficulties. The first of these was the impossibility of completing the action with the quantity of acid required for the first change. If a

* "Deut. Chem. Ges. Ber.," ix, 42-44.

larger quantity of acid were used, the first changes were so rapid as to evade measurement; moreover, the oxalic acid formed, by crystallizing in the acid liquid, made accurate observation impossible. By adding the acid in small successive portions, we nevertheless succeeded in obtaining an outline of the reaction, of which the curve drawn below is an accurate general expression.



Dubrunfaut, who has also examined this action,* asserts that the rotatory power first rises to $\frac{1}{10}$ of the original amount, then falls gradually to zero, again rises to $\frac{1}{4}$ of the original rotation, and once more falls to zero: the highest rotation corresponding to galactose, the first point of inactivity to mucic acid; the second rise probably to dextro-tartaric acid; and the second fall to the formation of oxalic acid. Our experiments show the formation of a lævo-rotatory substance, perhaps lævo-tartaric acid. The general form of the curve constitutes it an interesting and novel addition to chemical curves.

V. *Note on Solubility.*—The mutual relations of water and lactin in solution undergo a change upon which the change of rotation most probably depends. Water shaken with a large quantity of very finely powdered lactin at a temperature of 17° C., takes up a quantity of lactin corresponding to a solubility of 1 part lactin in 10.64 parts water. With four hours' contact, the solubility increases to 1 part lactin in 7.49 parts water. The permanent solubility got by the analysis of the mother-liquor of lactin crystallized over oil of vitriol is 1 part lactin in 3.23 parts water. In the solution of the lactin a fall of temperature of $0^{\circ}.45$ C. was observed. Pohl† also found a depression of temperature ($0^{\circ}.88$ C.); while Dubrunfaut alleges that heat is evolved.

Conclusions.

- I. The initial specific rotation of lactin is $92^{\circ}.63$.
- II. The permanent specific rotation of lactin is $59^{\circ}.17$.

* "Compt. rend.," xlii, 228.

† "Journ. Pr. Chem.," lxxxii, 154.

III. The change of rotation of a solution of lactin can be expressed by a mathematical equation.

IV. When the specific rotation $64^{\circ}8$ is reached, the law of change must be expressed by a different equation.

V. The initial solubility of lactin is 1 part lactin in 10.64 parts water.

VI. The permanent solubility is 1 part lactin in 3.23 parts water.

IV. "On the Microrheometer." By J. B. HANNAY, F.R.S.E., F.C.S., lately Assistant Lecturer on Chemistry in the Owens College, Manchester. Communicated by H. E. ROSCOE, LL.D., F.R.S., Professor of Chemistry in the Owens College, Manchester. Received December 11, 1878.

(Abstract.)

In this paper the author reviews the work done by chemists and physicists in determining the relation between the chemical composition of a liquid and its rate of flow through a capillary tube. Poiseuille* ascertained, in a very accurate manner, all the physical laws relating to the rate of flow, as regulated by temperature, pressure, and dimensions of the tube; but on examining saline solutions he could make nothing of the numbers presented, because he used percentage solutions instead of solutions proportional to the equivalent of the body dissolved. Graham,† noticing that Poiseuille had discovered a hydrate of alcohol by running various mixtures of alcohol and water through the tube, examined mixtures of the various acids with water, and found that the hydration proceeded by distinct steps of multiple proportions. Several others, notably Guerout,‡ have since worked on the same subject, but as they have only worked on organic liquids, and have done all the rates at the same temperature, the results throw no light on the phenomena. Thus water runs about five times as quickly at 100° as at 0° ; and in a series of alcohols, such as Guerout experimented upon, the differences between their boiling points were very great, so that, their vapour tensions or molecular mobilities being quite incomparable while at the same temperature, the experiments do not admit of any real interpretation. The author reserves the organic part of the investigation, which requires the determination of vapour tensions, till a future paper, and in the present deals with saline solutions.

The phenomenon of the flow of liquids through capillary tubes has

* "Ann. de Chim. et de Physique," [3], t. vii, 50.

† "Phil. Trans.," 1861, p. 373.

‡ "Comptes rendus," lxxix, p. 1201; lxxxi, p. 1025.

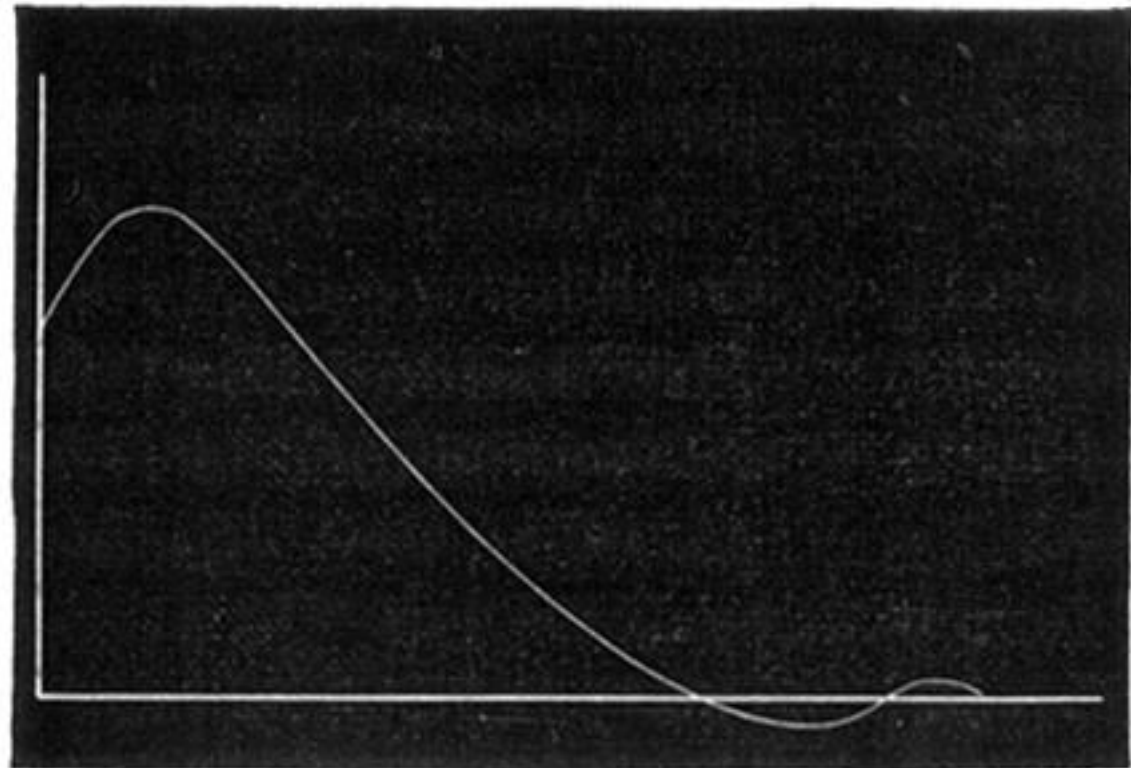
Table I.—Results of Experiments on Lactin.

Nature of Solution	Aqueous.			Containing 1 gramme Sod. Chlor. in 60 cc.			Containing 1 gramme Pot. Chlor. in 60 cc.			Aqueous.			Containing 5 grammes Pot. Chlor. in 60 cc.			Containing 5 grammes Sod. Chlor. in 60 cc.			10 grammes Pot. Chlor.	10 grammes Sod. Chlor.
Average Temperature	10°3	10°6	11°0	12°2	10°1	12°8	12°2	10°5	12°1	11°3	10°1	12°9	11°4	12°1	11°8	10°2	11°7	12°9	11°9	11°5
$\alpha = 2$	12·017	12·975	12·750	14·285	13·687	13·833	14·070	14·147	14·923	13·624	13·523	14·190	17·033	15·460	16·012	13·730	14·633	15·317	16·483	14·083
3	12·567	12·587	12·279	13·723	13·293	13·157	13·487	13·712	14·292	13·010	13·077	13·600	16·435	14·847	15·503	13·350	14·035	14·717	15·987	13·650
4	12·217	12·087	11·883	13·187	12·847	12·583	13·060	13·202	13·833	12·042	12·640	13·040	15·880	14·312	14·954	12·877	13·500	14·085	15·480	13·263
5	11·900	11·650	11·467	12·840	12·490	12·078	12·567	12·831	13·367	12·100	12·243	12·547	15·433	13·887	14·505	12·557	13·193	13·690	15·053	12·853
6	11·450	11·369	11·119	12·362	12·155	11·797	12·250	12·445	13·000	11·790	11·673	12·147	15·017	13·380	14·037	12·197	12·793	13·293	14·650	12·607
7	11·167	11·109	10·883	12·050	11·817	11·330	11·935	12·143	12·675	11·490	11·617	11·843	14·633	13·073	13·747	11·900	12·525	12·900	14·290	
8	10·933		10·616	11·817	11·530	11·070	11·540	11·850	12·377	11·193	11·340	11·567	14·270	12·737	13·333	11·667	12·253	12·650	13·943	12·063
9		10·339																		
10	10·540		10·223	11·927	11·110	10·683	11·133	11·405	11·810	10·763	10·933	11·147	13·768	12·220	12·607	11·172	11·833	12·223	13·320	11·600
11		10·023																		
12	10·210		9·833	11·067	10·713	10·447	10·787	11·057	11·563	10·390	10·547	10·733	13·273	11·820	12·453	10·785	11·463	11·852		11·210
13		9·683																		
14	9·350		9·517	10·825	10·392	10·213	10·347	10·727	11·117	10·190	10·257	10·583	13·000	11·477	12·167	10·313	11·140	11·560	12·533	10·873
Permanent Rotation.....	8·583	8·562	8·604	10·143	9·283	9·625	9·770	9·620	10·340	9·280	9·133	9·893	11·783	10·667	11·083	9·332	10·140	10·780	10·923	9·567
Extremes of Temperature	9°3 to 11°3	9°7 to 11°3	10°4 to 11°8	12°5 to 13°2	9°4 to 10°6	11°3 to 13°8	11°5 to 12°5	9°8 to 12°3	11°5 to 14°5	11°3 to 11°6	9°5 to 11°3	12°3 to 13°3	11°3 to 11°8	12°1 to 14°3	11°6 to 12°0	9°8 to 10°3	11°3 to 12°4	12°5 to 13°2	11°3 to 12°3	11°3 to 11°7
Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20

No. 21.

α_m	3	7	11	15	19	23	27	Permanent.
Rotation α	9·250	9·117	7·967	7·117	6·875	6·700	6·550	6·417

Rotation.



Hydric Nitrate.