The general work on nitration is being continued in this laboratory by Mr. C. E. Burke, under the direction of the senior author.

McMaster University, Toronto, Canada,
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FURTHER STUDIES ON THE FORMS OF MILK-SUGAR.

By C. S. Hudson.

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Contents.—(1) Introduction; (2) The Solubility Relations of Milk-Sugar; (3) The Maximum Rate of Solution of the β-Anhydride; (4) The Transition Temperature between Hydrated and β-Anhydrous Milk-Sugar; (5) The Solubility Curves of Milk-Sugar in Relation to the Transitions of Substances in General; (6) The Vapor-Pressures of Saturated Solutions of Hydrated Milk-Sugar; (7) The Aqueous Vapor-Pressure of Solid Hydrated Milk-Sugar in Contact with the β-Anhydride; (8) The Specific Rotations of the Forms of Milk-Sugar; (9) The Influence of Concentration on the Equilibrium between the Forms of Milk-Sugar; (10) Summary.

1. Introduction.

In a previous publication[1] the writer has called attention to the fact that hydrated milk-sugar crystallizes from aqueous solutions at room temperature but β-anhydrous milk-sugar from solutions above 95°. There must accordingly be a transition temperature within these limits between these forms of milk-sugar. The present investigation was undertaken in order to find the location of this transition temperature; in the course of the investigation it became apparent that the transition from the one form of milk-sugar to the other illustrates to a fulness that has not been experimentally realized before, the general conditions which cause transition temperatures. As the milk-sugar transition becomes thus of general theoretical interest the measurements on it were made very fully and extend to several related phenomena. All of these measurements, which are described below, agree quantitatively with the conclusion that was obtained from the former studies, namely that aqueous solutions of milk-sugar contain two substances in equilibrium and that the mutarotation of milk-sugar results from the slow establishment in cold solutions of the equilibrium of the balanced reaction

$$\underset{\text{(Hydrate.)}}{C_{12}H_{24}O_{12}} \rightleftarrows \underset{(\beta\text{-Anhydride.})}{H_2O + C_{12}H_{22}O_{11}}.$$

In this connection it should be stated that there is no direct evidence that the freshly dissolved hydrate exists in solution in the hydrated condition. It is quite possible that it exists largely as the α-anhydrous modification which is a view that would be similar to the conclusion that

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[1] This Journal, 26, 1067 (1904). Opportunity is here taken to correct an error on pages 1077 and 1081, where common logarithms were employed in calculating the absolute rates of hydration and dehydration. Natural logarithms should have been used and the correct values are 3.36, 17.3, and 51.1 per cent. sugar changed per hour instead of 1.46, 7.52, and 22.2 per cent. respectively.

Lowry,[1] and Armstrong[2] defend for the related sugar, glucose. If this is the case, then the change between the hydrate and the α-anhydride must be an instantaneous one so that the equilibrium between these two forms is always preserved during the further slow partial change to the β-anhydride which causes the mutarotation, because the mutarotation reaction for milk-sugar follows the laws of dynamics that hold for a simple unimolecular change. It seems quite likely however from the similarity of milk-sugar to glucose that the above reaction equation is only a portion of what occurs in milk-sugar solutions and that the full reaction should be written

$$\underset{(\alpha\text{-Anhydride.})}{C_{12}H_{22}O_{11} + H_2O} \rightleftarrows \underset{(\text{Hydrate.})}{C_{12}H_{24}O_{12}} \rightleftarrows \underset{(\beta\text{-Anhydride.})}{H_2O + C_{12}H_{22}O_{11}}.$$

The velocity of the first of these balanced reactions must be instantaneous compared with the rate of the second one. This view reconciles the two theories of the mutarotation of the sugars which have been much discussed in the last few years, the stereoisomer and the hydrate theories. According to the first, which has been developed largely from a study of the forms of glucose and their mutarotation, the α-anhydride changes slowly and partially by a balanced reaction to its stereoisomeric form, the β-anhydride, while according to the hydrate hypothesis, which has been developed largely from a study of the forms of milk-sugar and their mutarotation, the hydrate changes slowly and partially by a balanced reaction to the β-anhydride. If it is true that the hydrate and the α-anhydride establish their equilibrium instantaneously, a view which I expressed four years ago,[3] then there is no ground for argument between the stereoisomer and the hydrate hypotheses, for they then become identical views, the stereoisomeric forms changing from one to the other through the formation of their common hydrate which itself is always in equilibrium with the α-form, though not always with the β-form.

2. The Solubility Relations of Milk-sugar.

The Final Solubility of Hydrated Milk-sugar.—The determinations of these solubilities were made from undersaturation and from supersaturation by rotating in a thermostat a bottle containing water or supersaturated solution and an excess of once recrystallized, hydrated milk-sugar; the agreement between the values of the solubility so obtained is proof that equilibrium was reached and this proof is very necessary in the case of milk-sugar because its cold solutions saturate very slowly. The analyses of the solutions were made by filtering them without evaporation through a cotton plug into a pipette, weighing the resulting clear

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[1] *J. Chem. Soc.*, 83, 1314 (1903).

[2] *Ibid.*, 1305 (1903).

[3] *Loc. cit.*, p. 1066.

solution in the pipette, evaporating it to dryness, heating at 130° to constant weight, and weighing the crystalline residue, which consists of the α- and β-anhydrides mechanically mixed and has the composition $C_{12}H_{22}O_{11}$.

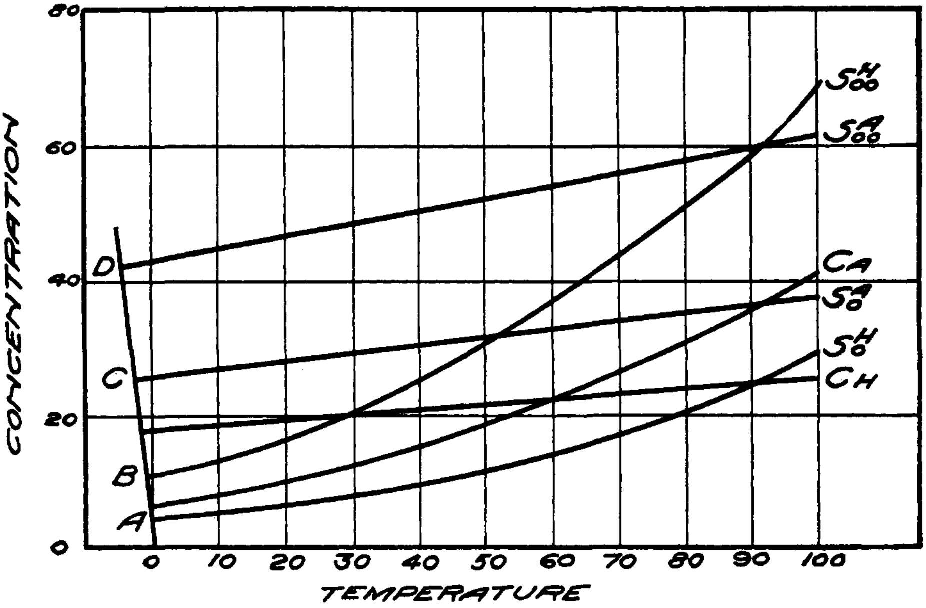

Fig. 1.—The solubility relations of milk-sugar.

Table I.—Final Solubility of Hydrated Milk-sugar.

Temperature.	Per cent. $C_{12}H_{22}O_{11}$ in solution.			Millimols $C_{12}H_{22}O_{11}$ in 100 grams water.
	From undersaturation.	From supersaturation.	Average.	
0	10.6	10.7	10.6	34.8
15	14.4	14.6	14.5	49.7
25	17.8	17.8	17.8	63.4
39	24.0	24.1	24.0	92.7
49	29.7	29.9	29.8	124.0
64	39.7	39.8	39.7	193.0
74	46.2	46.5	46.3	253.0
89	58.1	58.3	58.2	407.0

The data given in Table I are shown in Fig. 1 as the line S^H_∞.

The Final Solubility of β-Anhydrous Milk-sugar.—The solubility of this sugar is difficult to determine for two reasons: first, it is very soluble and its saturated solutions are viscous, and second, its saturated solutions are stable (*i. e.*, not supersaturated with respect to hydrate) only above 92°.

After repeated failures two solubilities which are substantially correct were obtained at 0° and 100°. The value at 100° was obtained in the same manner as has been described above for the hydrate; from undersaturation the value was 60.5 per cent., from supersaturation 61.9 per cent., average 61.2 per cent. In order to find the solubility at 0° the establishment of final saturation was hastened by the addition of ammonia to the water. About one hundred grams of selected β-anhydrous crystals, prepared by slow crystallization above 95°[1], were rapidly shaken with twenty cubic centimeters of a tenth-normal ammonia solution at 0°. In ammonia solutions of this strength the mutarotation and therefore the maximum rate of solution are instantaneous. Usually after fifteen or twenty minutes' rotation the solutions would begin to deposit hydrate because they were very highly supersaturated with respect to it, but in one experiment I was able to rotate a solution one and a quarter hours without crystallization occurring. Its content was then found to be 42.9 per cent. anhydrous sugar, which is certainly not far from the correct solubility at 0°. At another time at 25° in the same manner but with only fifteen minutes' stirring the value 41.3 per cent. was found, but this is low as the time was not sufficient to give saturation. It nevertheless indicates that saturation was reached in the experiment at 0°, for it shows that the value obtained after fifteen minutes' stirring at 25° is only slightly increased by continuing the stirring for one hour at 0°. The values which seem reliable are thus 42.9 per cent. at 0° and 61.2 per cent. at 100°. They are given in Fig. 1 and as the increase of solubility with temperaure is small, a straight line, S_{∞}^{A}, is drawn between them as the final solubility curve. The small increase of solubility agrees with the fact that the sugar shows small absorption of heat in dissolving, namely 2.7 cal.[2] per gram as found directly in a calorimeter, for if the final solubility data at 0° and 100° are used to calculate the heat of solution by the formula of van't Hoff, it is found to be —2.2 cal. per gram, in good agreement with the value shown by the calorimetric measurement at 20°.

The Initial Solubilities of the Two Forms of Milk-Sugar.—The initial solubility of the hydrate has already been determined at 0°, 15° and 25°, where it can be directly measured.[3] But to perform these measurements at higher temperatures is out of the question on account of the immediate formation of β-anhydride in the solutions. The following indirect method of finding these solubilities seems trustworthy. Since temperature and concentration have almost no influence on the equilibrium in solution,[4] the initial solubility of either form can be calculated from its final solubility by use of the equilibrium constant that has been determined at low temperatures, namely 1.5 parts of β-anhydride to 1 part of hydrate. By this method, using the preceding table of final solubilities of the hy-

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[1] This Journal, 30, 964 (1908).

[2] *Ibid.*, 30, 969 (1908).

[3] *Ibid.*, 26, 1074 (1904).

[4] *Ibid.*, 30, 969 (1908) for the effect of temperature; regarding that of concentration, see section 9 (p. 1781) of the present article.

drate, the following values for the initial solubility of the hydrate above 25° have been calculated, and are included in Table II with the directly measured values for the lower temperatures.

TABLE II.—INITIAL SOLUBILITY OF HYDRATED MILK-SUGAR.

Temperature.	Final solubility in millimols $C_{12}H_{22}O_{11}$ per 100 g. water.	Initial solubility in millimols $C_{12}H_{22}O_{11}$ per 100 g. water.	Per cent. sugar.	
			a.	*b.*
0	34.8	14.8	4.8	4.8
15	49.7	20.9	6.8	6.8
25	63.4	25.3	8.2	8.2
39	93.0	37.0	11.0	10.0
49	124.0	52.0	15.0	12.0
64	193.0	77.0	21.0	16.0
74	253.0	101.0	26.0	19.0
89	407.0	163.0	37.0	23.0

In the fourth column under "*a*" the solubility is expressed as parts sugar in 100 parts of a solution that contains only this sugar; in the fifth under "*b*" it is expressed as parts sugar of the hydrated form in 100 parts of a solution which contains both forms in equilibrium and is saturated with hydrate. This column furnishes the data that are drawn in the diagram of Fig. 1 as the line S_0^H. While no great accuracy can be claimed for this curve at the higher temperatures it is nevertheless closely enough determined to serve as a guiding line for theoretical considerations.

The initial solubility of the β-anhydride has been calculated in a similar manner from its final solubility at 0° and 100°.

TABLE III.—INITIAL SOLUBILITY OF β-ANHYDROUS MILK-SUGAR.

Temperature.	Final solubility in millimols per 100 g. water.	Initial solubility in millimols per 100 g. water.	Per cent. sugar.	
			a.	*b.*
0	220	132	31	26
100	461	277	49	37

The values of column 5 are drawn in the solubility diagram as the line S_0^A. The initial solubility at 0° has also been directly determined by rotating in a bottle at the rate of seventy revolutions per minute twenty grams of selected β-anhydride crystals, well powdered, with fifteen grams of water. After two, three and four hours' rotation the solution, which is undersaturated with respect to hydrate and therefore stable during this time, was found to contain 130, 133, 136 millimols per 100 g. water, giving by extrapolation 124 as the initial solubility. When a mechanical mixture containing an excess of hydrate and β-anhydride was rapidly stirred with water at 0° for an hour the solution was found to contain 138.9 millimols as the average of six such experiments, which showed a maximum variation of 2 millimols. These solutions were evidently saturated with both forms, so that if the initial solubility of the hydrate, 14.8, be subtracted from it the remainder, 124, is the initial solubility of the β-anhydride. It has been shown[1] that this solubility can also be calculated from the vapor pressure relations by the formula $S_0^A = P_h C_A / p$, where P_h is the aqueous vapor pressure of a mixture of solid hydrate and β-anhydride, C_A is the concentration of β-anhydride in the finally saturated solution of the hydrate, and p is the vapor pressure of the saturated solution of the hydrate. The values of these quantities at 0° are given in the reference, and from them S_0^A is found to be 143, approximately, as there is considerable uncertainty in the extrapolated value of P_h. These four independent determinations of the initial solubility of the β-anhydride at 0°, 132, 124, 124, and 143, agree very well and their agreement is a strong proof of the correctness of the view that solutions of milk-sugar contain the hydrate and the β-anhydride in slow reversible equilibrium. As has been mentioned in the introduction, however, they give no evidence regarding the instantaneously established equilibrium between the hydrate and the α-anhydride.

The Concentrations of Each Form in the Saturated Solutions of the Other Form.—These have been calculated for each form as the differences between the initial and final solubilities of the other form, and for temperatures between 0° and 100° are given in Table IV as per cent. of the form in question in a saturated solution of the other form.

The results are also drawn in Fig. 1 as the lines C_A and C_H.

TABLE IV.

	Concentrations	
Temperature.	C_A.	C_H.
0	5.8	17
15	7.7	..
25	9.6	..
39	14.0	..
49	18.0	..
64	24.0	..
74	27.0	..
89	35.0	..
100	....	24

The Ice Line and the Cryohydrate Temperatures of Milk-sugar.—The ice line for milk-sugar solutions—that is, the line of the solubility diagram (Fig. 1) which gives the freezing temperatures of milk-sugar solutions of various concentrations—is drawn from the recent freezing-point determinations of Loomis[2] and of Jones and Getman,[3] together with two values that I have found for concentrated solutions, using the Beckmann apparatus. The numerical values are given in the accompanying table,

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[1] *Physical Rev.*, **23**, 375 (1906).

[2] *Z. physik. Chem.*, **37**, 412 (1901).

[3] *Am. Chem. J.*, **32**, 326 (1904).

the concentrations being expressed as millimols anhydrous sugar per 100 grams water.

TABLE V.—FREEZING TEMPERATURES OF MILK-SUGAR SOLUTIONS.

Concentration (millimols $C_{12}H_{22}O_{11}$ per 100 g. water)	Depression observed by			Molecular depression.
	Loomis.	Jones and Getman.	Hudson.	
1.00	0.0186	.....	.....	1.86
2.01	0.0372	.....	.....	1.85
5.06	0.0945	.....	.....	1.87
10.23	0.1907	.....	.....	1.86
20.89	0.3919	.....	.....	1.88
20.95	......	0.364	.....	1.74
31.85	......	.....	0.591	1.86
32.17	......	0.574	.....	1.78
43.91	......	0.792	.....	1.80
48.05	......	.....	0.911	1.89
56.2	....	1.030	.....	1.83

The determinations made by Jones and Getman are very different in value from what would be expected for higher concentrations from Loomis' values, and their numbers are not confirmed by the two determinations that I have made with great care. The way in which the molecular depressions of Jones and Getman change with the concentration is highly exceptional. I think no similar case has ever been found where the depression in dilute solution is less than 1.86 and increases gradually with the strength of the solution. The explanation which these authors give of their low molecular depressions is that the milk-sugar is polymerized in solution, but this explanation is not tenable for it involves the conclusion that since the depression approaches 1.86 with increasing concentration the assumed polymerization of the dissolved sugar is increased by dilution, a result that is contradicted by the mass-action law and all dissociation measurements. A combination of polymerization decreasing with the dilution, which is rational, with marked hydration would explain the results of Jones and Getman qualitatively, but this hypothesis is too complicated, and there is not only no additional evidence to support it but there is good evidence against it, for instance the agreement[1] between the observed values of the heats of solution of the two forms and the values calculated from theory on the assumption that milk-sugar is not polymerized in solution. I am led to the conclusions that the freezing-point determinations of Jones and Getman on milk-sugar are incorrect, and that milk-sugar does not polymerize in solution.

The intersections of the four solubility curves for the hydrated and β-anhydrous milk-sugar with the ice line represent four cryohydrate temperatures, that is, the freezing points of four saturated solutions. To

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[1] THIS JOURNAL, 30, 970 (1908), regarding the values for the hydrate. For those of the β-anhydride see p. 1769 of the present article.

realize the cryohydrate phenomena for the β-anhydrous sugar would be very difficult, owing to the strong supersaturation of the solution with respect to the hydrate that would be required, and the experiments have not been attempted. The cryohydrate temperature corresponding to final saturation of the hydrate is also too difficult of realization, but on the other hand the initial cryohydrate temperature of the hydrate can be directly determined with ease. In a large test tube equipped with a glass screw stirrer and immersed in a bath of melting ice, the test tube being isolated from the ice by an air space, shaved ice and powdered hydrated milk-sugar were mixed as thoroughly as was possible with continuous good stirring. In two experiments the constant reading of the Beckmann thermometer whose bulb was immersed in the cryohydrate mixture were —0.284° and —0.278°. From the table of freezing points of the previous page the temperature of freezing of an initially saturated solution of the hydrate, which has the concentration 14.8 according to the solubility measurements, is —0.277. This is in agreement with the directly determined temperature.

The final cryohydrate temperature of hydrated milk-sugar lies at —0.65, calculated from the solubility and freezing-point data. The initial and final cryohydrate temperatures of the β-anhydrous form are calculated in similar manner to be —2.3° and —4.1° respectively. These four cryohydrate temperatures are indicated on Fig. 1 as the points A, B, C, and D.

It is to be noted that a freshly prepared and initially saturated solution of the β-anhydrous form at 0° is a very concentrated solution, 40 per cent., about twice as strong as the highest concentrations that have as yet been used in freezing-point determinations of milk-sugar solutions. These strong solutions of the β-anhydride are completely stable for about five hours after their preparation, if they are kept at 0°, for it takes that much time for the slow hydration reaction to build enough hydrated sugar to saturate the solution with respect to it. They can therefore be worked with during five hours without the least danger of crystallization and are well suited for use in measuring the freezing points and osmotic pressures of concentrated solutions of milk-sugar. The commonly used hydrated form is so sparingly soluble that even with considerable supersaturation the freezing point determinations are not possible above 0.6 molal, but there is apparently no obstacle to working up as high as 1.2 molal, provided freshly prepared solutions of the β-anhydride are employed.

3. The Maximum Rate of Solution of β-Anhydrous Milk-sugar.

It may be inserted at this point that the data from which the initial solubility of the β-anhydride was directly obtained also give the maximum rate of solution of this sugar. The increase in solubility at 0°

with the time is shown in Table VI and the velocity coefficient of the maximum rate of solution is shown in column 3, calculated from the formula that was developed in the former article.[1]

TABLE VI.—MAXIMUM RATE OF SOLUTION OF β-ANHYDROUS MILK-SUGAR.

Time (t) hours.	Concentration (S_A).	$\frac{1}{t}\log\frac{S^A_\infty - S^A_0}{S^A_\infty - S_A}$,
0	124 (S^A_0)	......
2	130	0.0140
3	133	0.0143
4	136	0.0145
∞	220 (S^A_∞)	......
	Average,	0.0143

The velocity coefficient here obtained, 0.014, agrees with the value (0.017) that was previously calculated[1] from the rate of mutarotation of milk-sugar and the maximum rate of solution of the hydrate at 0°.

4. The Transition Temperature between Hydrated and β-Anhydrous Milk-sugar.

This temperature, whose existence is indicated by the fact that milk-sugar solutions deposit hydrate at room temperature but β-anhydride at 95°–100°, is shown by the foregoing solubility curves, Fig. 1, to lie at 92°–93°, because it must be the temperature at which the final solubilities of the two forms are equal.

The transition phenomena for these two forms of milk-sugar are peculiar. In the first place the hydrate when in the solid state is so sluggish in its reactions that I have never been able to get it to really melt down to β-anhydride and saturated solution under any conditions. A slight indication of such melting was shown in an experiment where a mixture of powdered hydrate and β-anhydride was heated in a sealed tube at 100° overnight and then cooled at room temperature for a few hours. On opening the tube the sugar was found to be hard and in lumps showing that some melting and subsequent crystallization had probably occurred. When a similar powdered mixture was heated to 80° overnight and cooled no hardening took place and none would be expected, because this temperature is below the transition point. This sluggishness in the melting of the hydrate is again shown in the measurements of its aqueous vapor pressure that will be described later; in these experiments several weeks' heating were necessary to cause it to give its maximum pressure. Of course a direct thermometric determination of the transition temperature of this hydrate is not possible on account of the slowness of the melting.

I have attempted many times to detect this transition temperature by an observation of the volume changes in a dilatometer during the

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[1] THIS JOURNAL, 26, 1076 (1904).

melting.[1] These experiments have never given a clear result, the changes of volume that were observed being small and irregular, and could have been caused by unavoidable errors. After many of these failures to detect the transition in a dilatometer the densities of the two substances were measured and found to be 1.54 for the hydrate and 1.59 for the β-anhydride, and since the hydrate contains 5 per cent. of water these values of the densities show that the volume change on melting is too small to permit of accuracy in the dilatometric determinations, for if it is assumed that the hydrate passes to β-anhydride and water without change of volume the density of the β-anhydride is calculated to be 1.59, which is the same as the value that was found by experiment. Since milk-sugar is not an electrolyte the electromotive force method for finding transition temperatures is not applicable, and there remains thus only one method which might supplement the solubility determinations, namely the determination by the tensimeter. This has fortunately given an accurate measurement of the temperature, 94°, as will be described later on, and has thus confirmed the conclusion from the solubility curves, which give 92°–93°.

5. The Solubility Curves of Milk-sugar in Relation to the Transitions of Substances in General.

If one considers the diagram of the solubility curves of milk-sugar in Fig. 1, it will be noticed that they give a very simple explanation of the fact that below the transition temperature the hydrate is the stable form of milk-sugar but above it the β-anhydride. Consider by aid of the diagram a mixture of β-anhydride and water at 70°. The anhydride will dissolve to form a finally saturated solution, whose concentration is given by the line S^A_∞. Now the concentration of hydrate in such a solution is given by the line C_H, and it is seen to be greater than the initial solubility of the hydrate, line S^H_0; therefore hydrate will crystallize from the finally saturated solution of the β-anhydride; more hydrate will then form in solution from the dissolved β-anhydride to preserve the equilibrium ratio, and more solid β-anhydride will pass into solution to take the place of that which changes to hydrate. In the nature of the relations shown by the diagram there can be no stop to this dissolving of β-anhydride and precipitation of hydrate in the presence of an excess of water until all the β-anhydride is dissolved and the solution reduced in concentration to that of a finally saturated solution of the hydrate, line S^H_∞. Precisely similar reasoning shows that above the transition temperature hydrate must ultimately, by a process of dissolving and precipitating, change to β-anhydride and its saturated solution, the immediate cause of the change being the fact that at these higher tem-

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[1] For a description of the method see van't Hoff, *Vorlesungen über Bildung und Spaltung von Doppelsalzen.*

peratures the concentration of β-anhydride that is present in equilibrium with hydrate in the saturated solutions of the hydrate is greater than the initial solubility of the anhydride, or in other words that the curve C_A lies above S_0^A.

At the transition temperature, C_H becomes equal to S_0^H, and C_A to S_0^A; in other words a saturated solution at this temperature of either substance is also saturated with respect to the other, and both substances are stable at this temperature in the presence of this common saturated solution.[1]

There is also another question which comes up for consideration by aid of the relations shown in the figure. It has been proved from thermodynamic reasoning that if two substances exhibit the phenomenon of transition the one which is stable at a given temperature always has at this temperature the smaller solubility.[2] This law refers to the final solubilities and it may be seen that the curves S_∞^A and S_∞^H of Fig. 1 are in agreement with it, the final solubilities becoming equal at the transition temperature. On the other hand, the figure shows that there is no such equality at this temperature between the initial solubilities of the two forms, that of the β-anhydride being much the greater both above and below the transition temperature. It is therefore emphasized that while the final solubilities of the two forms of a substance are equal at the transition temperature, there is no such relation between the initial solubilities of the two forms.

6. The Vapor Pressures of Saturated Solutions of Hydrated Milk-sugar.

A knowledge of these pressures is useful in determining the transition temperature of the hydrate, which is necessarily that temperature at which the saturated solution of the hydrate has the same vapor pressure as a mixture of solid hydrate and β-anhydride. The measurements of the vapor pressures of the solutions were made with two Bremer-Frowein tensimeters, using mercury as the differential indicator. The tensimeters were thoroughly evacuated with a Töpler pump and were found to have no air correction. The pressures were measured from undersaturation by raising the temperature slowly and from supersaturation by lowering it slowly, and the agreement of the two values is proof that final equilibrium was reached. One bulb of the tensimeter contained ten cc. of boiled distilled water and the other four grams of moistened hydrate. The reading of the tensimeter thus gave the difference between the vapor pressure of pure water and that of the saturated solution of the hydrate. The numerical results are given in the following table in centimeters of mercury at 0°.

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[1] These solubility relations that must hold at the transition temperatures of all substances were clearly described by van't Hoff ten years ago. See his *Vorlesungen über Theoretische und Physikalische Chemie*, Vol. I, pp. 217–221.

[2] van't Hoff, *Vorlesungen über Theoretische und Physikalische Chemie*, Vol. II, p. 127.

TABLE VII.—VAPOR PRESSURE OF SATURATED SOLUTIONS OF HYDRATED MILK-SUGAR.

	Depression of the vapor pressure.					
	Tensimeter 1.		Tensimeter 2.			
Temperature.	Undersat.	Supersat.	Undersat.	Supersat.	Mean.	Vapor pressure.
50	....	0.24	0.21	....	0.22	8.98
60	0.51	0.49	0.53	....	0.51	14.38
70	1.08	1.08	1.11	1.04	1.08	22.25
80	2.35	2.37	2.37	2.22	2.33	33.21
90	4.88	4.90	4.89	4.76	4.86	47.73
100	9.53	....	9.75	....	9.64	66.40

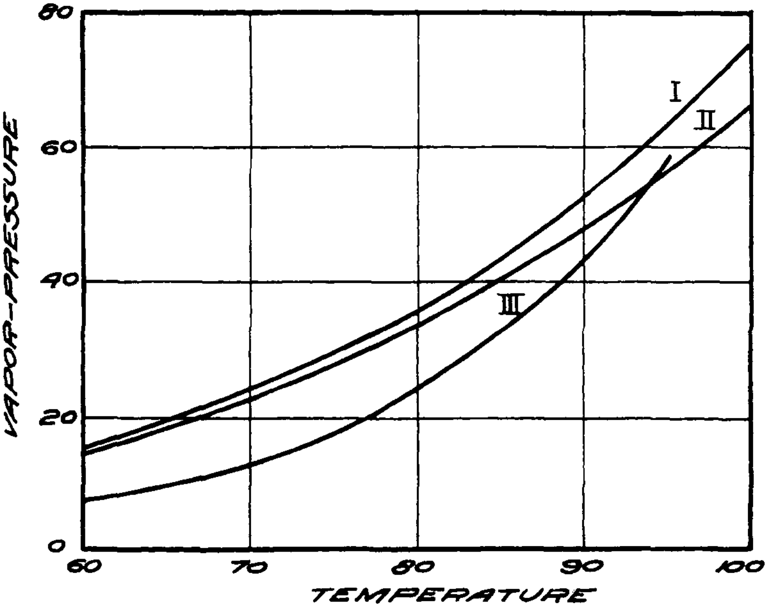

Fig. 2.—The vapor pressure relations of milk-sugar.

The vapor pressures of the saturated solutions as given in column 7 have been calculated from the vapor pressures of water by subtracting the depressions of column 6 and are drawn in Fig. 2 as the line II, I being the vapor pressure of pure water.

7. The Aqueous Vapor Pressure of Solid Hydrated Milk-sugar in Contact with the β-Anhydride.

These pressures have been determined with three tensimeters marked 1, 2, and 3 in Table VIII below, using phosphorus pentoxide or water or a saturated solution of hydrated milk-sugar in one of the small bulbs and a well pulverized mixture of hydrate and β-anhydride in the other, mercury being used as the pressure indicator. The disengagement of water vapor from this solid mixture takes place very slowly, even at temperatures near 100°, and below 60° the rate becomes so slow that the measurements could not be made. The tensimeters were heated continuously for several weeks in a thermostat and constant pressures were finally obtained both from undersaturation and supersaturation, which differed for the same tensimeter by not more than 2 per cent. The averages of these values are given in the following table in cm. mercury at 0°, and they are also drawn in Fig. 2 as the line III.

TABLE VIII.—AQUEOUS VAPOR PRESSURE OF SOLID HYDRATED MILK-SUGAR IN CONTACT WITH THE β-ANHYDRIDE.

	Vapor pressure				
Temperature.	1.	2.	3.	Average.	By formula.
60	6.80	7.74	....	7.3	(7.3)
70	12.5	12.3	....	12.4	13.7
80	24.5	24.5	24.9	24.6	24.7
90	....	43.1	43.5	43.3	(43.3)

In the last column are given the pressures as calculated from the formula of the usual type, $\log. P = 10.2176 - 3115/T$, whose two constants have been determined from the values of P and T (absolute) at 60° and 90°, common logarithms being employed.

The Transition Temperatures as Indicated by the Vapor Pressure Relations.—If the vapor pressure of the hydrate be calculated at 95° from the formula in the previous paragraph it is found to be 56.6 cm. mercury. If the vapor pressure curve of the hydrate be continued to this value at 95° it is found to cross the curve of the vapor pressure of the saturated solution of the hydrate at very nearly 94°. This is then the transition temperature as shown by the vapor pressure relations. The solubility measurements gave 92-3° as this temperature; the agreement of these independent determinations is satisfactory and the transition temperature may therefore be taken as 93°.

Calculation of the Heat of Vaporization of Water from Solid Hydrated Milk-sugar.—When water vapor evaporates from milk-sugar hydrate leaving β-anhydride behind, more heat is absorbed than is the case when it evaporates from pure water. The heat of vaporization from the hydrate can be calculated from the vapor pressures of Table VIII. Using the values of the pressures there given at 60° and 90° in the formula, $\log. nat. P'/P = (Q/1.98)/(1/T' - 1/T)$ it is found that Q, the molecular heat of vaporization, is —14203 cal., or the heat of vaporization per gram of water vapor is $-(14203 \div 18) = -789$ cal. On the other hand, from the values of the heats of solution of the hydrated and β-anhydrous milk-sugar given in a former article[1] the heat of vaporization of the water can also be calculated. Imagine 360/18 grams of hydrated milk-sugar to dissolve in water to form a dilute solution, to precipitate as 342/18 grams of β-anhydrous sugar while $18/18 = 1$ gram of water evaporates

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[1] THIS JOURNAL, 30, 970 (1908).

from the solution; the final result is the vaporization of one gram of water from solid hydrated milk-sugar to leave the β-anhydride behind and the heat change at 20° is $-(584 + (12)(360/18) - (1)(360/18) - 2.3(342/18) = -760$ calories, where -584 is the heat of vaporization of water from the dilute solution or from water at 20°, -12 is the heat of solution of hydrated milk-sugar per gram, 1 the heat of passage in solution from the hydrate to the β-anhydride, and 2.3 the heat of precipitation of the latter. This value agrees fairly well, considering the large number of experimentally measured constants involved, with the value (-789) calculated from the vapor pressures at the higher temperatures.

8. The Specific Rotations of the Forms of Milk-sugar.

The specific optical rotation of freshly prepared solutions of milk-sugar changes with the time and finally reaches a constant value, which has been found by Schmoeger to be 52.5° in dilute solution at 20° for sodium light per gram $C_{12}H_{24}O_{12}$, or 55.3° per gram $C_{12}H_{22}O_{11}$. In the present investigation measurements have been made of the specific rotations that are to be found immediately after the dissolution of the hydrate and the β-anhydride, that is, the specific rotations of these two forms of the sugar, the value 55.3° to which these initial specific rotations finally change being the specific rotation of the equilibrium mixture of the two forms.

Table IX.—Specific Rotations of the Forms of Milk-sugar.

Hydrated milk-sugar. Temperature 25°.							β-Anhydrous milk-sugar. Temperature 25°						
No.	r_5.	r_{10}.	r_{20}.	r_∞.	r_0.	r_0/r_∞.	No.	r_5.	r_{10}.	r_{20}.	r_∞.	r_0.	r_0/r_∞.
1	29.6	28.8	27.5	19.7	30.3	1.54	1	24.8	25.8	27.7	37.8	23.8	0.63
2	26.8	26.3	24.8	17.8	27.4	1.54	2	9.3	9.8	10.5	14.0	8.9	0.64
3	29.6	28.9	27.2	19.8	30.4	1.54	3	16.7	17.5	18.7	24.0	16.0	0.64
4	28.2	27.7	26.7	18.8	28.7	1.53	4	13.2	13.9	14.9	19.7	12.6	0.64
5	22.1	21.6	20.5	14.3	22.6	1.58	5	15.6	16.2	17.3	23.3	15.0	0.64
					Average,	1.55						Average,	0.64
Temperature 15°.							Temperature 15°.						
6	21.8	21.6	21.1	14.2	22.0	1.55	6	14.3	14.5	15.0	21.9	14.1	0.64
7	25.3	25.0	24.2	16.5	25.6	1.55	7	15.7	15.9	16.3	23.9	15.5	0.65
8	20.3	20.0	19.4	13.2	20.6	1.56	8	12.0	12.2	12.7	18.3	11.8	0.64
9	20.1	19.7	19.3	13.0	20.4	1.57	9	16.4	16.7	17.4	25.2	16.1	0.64
10	20.6	20.4	19.8	13.3	20.8	1.57	10	17.5	17.9	18.5	26.7	17.1	0.64
					Average,	1.56						Average,	0.64

The determinations of the initial rotations were made at 15° and 25° by dissolving the pure substances in water and reading the rotation by the polariscope at short intervals after the dissolution; by extrapolation the initial value could then be found with accuracy. The experimental data are collected in Table IX. The numbers are the observed rotations of the solutions rather than the specific rotations, and the index beside the r at the top of the column shows the time of the reading in minutes after the beginning of the dissolution of the sugar, which usually lasted two minutes. The column under r gives the readings after a pinch of sodium carbonate had been added to the solution to hasten the change to the final rotation. By direct test it was ascertained that the sodium carbonate in the quantity used, or in a much larger quantity, has no influence on the value of the final rotation. The hydrated sugar was recrystallized once and the β-anhydrous sugar was very carefully selected under a reading glass from a supply of the crystals of this substance that had been prepared by slow crystallization in the manner described in the former article. The length of the polariscope tube was 40 cm. Its temperature was kept constant by a jacket through which water flowed continually.

In the last columns the ratios r_0/r_∞ of the separate experiments are given and it can be seen that there is no perceptible change in the value of this ratio with the ten degrees change of temperature for either form of the milk-sugar. Therefore if 55.3° is taken from Schmoeger's work as the specific rotation of the stable solutions at 20°, the initial specific rotation of hydrated milk-sugar is $(55.3) \times (1.55) = 86.0°$, and of β-anhydrous milk-sugar $(55.3) \times (0.64) = 35.4°$. As the freshly prepared solutions of α-anhydrous milk sugar are identical with those of the hydrate, the specific rotation of this α-anhydride is also 86°. These values refer to sodium light and 20°, and the sugar is considered to be anhydrous, with the formula $C_{12}H_{22}O_{11}$.

The equilibrium constant of the hydration reaction in solution is $\frac{86.0-55.3}{55.3-35.4} = 1.54$ and it does not change perceptibly with the temperature between 15° and 25°. This constancy over a range of temperature agrees with the conclusion[1] from the small heat of passage between the hydrate and the β-anhydride that the equilibrium between the two substances in solution is only slightly affected by large changes of temperature. The value 1.54 is not very different from that which is given by independent solubility measurements, 1.48.

9. The Influence of Concentration on the Equilibrium between the Forms of Milk-sugar.

The mutarotation of milk-sugar proceeds very slowly at room temperatures and as the difference between the specific rotatory powers of the hydrated and the β-anhydrous forms is quite large, the first being 86° the other 35°, even a slight change in the equilibrium that exists between the forms can be readily observed with a polariscope. This fact permits a delicate test of the influence of concentration on the equilibrium between the forms of milk-sugar in solution. The method that has been used is to

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[1] THIS JOURNAL, 30, 968 (1908).

allow a freshly prepared solution of the hydrate to remain at 25° for a day to establish equilibrium and then to dilute this solution and observe whether its specific rotation changes slowly from the value that it has immediately after dilution. Such a slow change could be due only to a displacement of the equilibrium between the forms of milk-sugar in solution, because it is wholly improbable that such slow after-effects could be due to changes in the true specific rotatory power of any pure substance. Conversely a change in equilibrium would surely produce a slow change of rotation, whose rate is moreover known, since it would be that of the mutarotation of milk-sugar for which accurate data have been obtained. In all, four experiments were made with the uniform result that not the slightest slow change of rotation, and consequently no change in equilibrium, could be observed when the stable solutions of milk-sugar were diluted.

Experiment 1.—A 0.15 molal solution (4.5%) of hydrated milk-sugar was kept at 25° for twenty hours, which is ample time for it to establish equilibrium, and then diluted with an equal volume of water. The rotation immediately after dilution was 4° 34′, an average of four readings; thirty minutes after dilution no change in the shading of the polariscope field could be seen, and three settings of the instrument gave 4° 36′. A milligram of sodium carbonate, which accelerates the reaction enormously, was added but it produced no change in rotation. After the alkali had acted fifteen minutes, a length of time in which it would have caused any mutarotation to proceed to completion, three settings of the polariscope gave 4° 35′. In this experiment, then, no slow after-effect resulting from dilution was found.

Experiment 2.—Another portion of the 0.15 molal solution was diluted to about 0.4 molal. The immediate rotation was 3° 9′, after half an hour it was 3° 8′, and fifteen minutes after the addition of sodium carbonate, the reading was still 3° 9′. No slow after-effect was observed.

Experiment 3.—A molal solution was prepared by dissolving hydrated milk-sugar in boiling water; it was then cooled slowly to 25° and kept at that temperature during twenty-four hours, in a test tube corked with cotton. Although the solution was strongly supersaturated no crystallization took place. A portion of it was then diluted to about 0.25 molal. Its immediate rotation was 18° 38′, and after the addition of sodium carbonate no change in the field of vision appeared, four settings of the polariscope giving 18° 39′. No after-effect in this case.

Experiment 4.—A portion of the same molal solution was diluted to about 0.20 molal. Its immediate rotation was 14° 15′; after the addition of sodium carbonate no change was noticed and new settings of the instrument gave 14° 15′. Even after the strong dilutions of the last two experiments not the slightest indication of a change of hydration on dilution was detected, although a change in the reading of 3′ would well have been noticeable if it had occurred. These experiments show that the equilibrium in solution between the forms of milk-sugar is not appreciably altered by these changes of concentration.

Summary.

Solubility determinations on hydrated and β-anhydrous milk-sugar show that the transition temperature between these two substances is 93°, and this value is confirmed by the vapor pressure measurements.

The solubility relations of milk-sugar are shown in figure one. They are the first experimentally realized example of such relations and are typical of the solubility relations of all substances which have transition temperatures. On account of the slowness with which milk-sugar forms its saturated solutions, in distinction from the behavior of most substances, these suggestive solubility relations can be experimentally followed.

The specific rotations of the three forms of milk-sugar have been measured at 15° and 25°, and the results show that the equilibrium in solution does not change with the temperature perceptibly in this interval. Other experiments show that the equilibrium does not change with the concentration, since there is no slow change in the rotatory power of milk-sugar solutions after dilution.

It is shown that the arguments which respectively support the rival hypotheses of hydration and stereoisomerization in explaining the mutarotation of the sugars may be summed up and the two hypotheses reconciled by the following reaction equation, in which the equilibrium of the first balanced reaction is established instantaneously while that of the second is formed slowly, giving rise to the slow change of rotation:

$$\alpha\text{-form} + H_2O \underset{\text{(fast)}}{\rightleftarrows} \text{Hydrated form} \underset{\text{(slow)}}{\rightleftarrows} H_2O + \beta\text{-form}.$$

The following natural constants have been measured: the initial and final solubilities of hydrated and β-anhydrous milk-sugar, 0°–100°, Tables I to IV; the freezing points of milk-sugar solutions, Table V; the maximum rate of solution of the β-anhydride, Table VI; the vapor pressures of saturated solutions of hydrated milk-sugar, Table VII; the aqueous vapor pressures of the solid hydrate in contact with the β-anhydride, Table VIII; the specific rotatory powers of the three forms of milk-sugar, Table IX *et sequitur*; the transition temperature of hydrated to β-anhydrous milk-sugar (93°). The heat of solution of the β-anhydride has been calculated from the solubility data, and shown to agree with the directly measured value. The heat of vaporization of water from hydrated milk sugar has been calculated from the vapor pressures of the hydrate and also from the heats of solution and transition of the two forms and the two values agree satisfactorily.

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