

These bases and their ionization constants are as follows:

Letter.	Base.	<i>k</i> .
A	Diethylamine <sup>1</sup> . . . . .	1.26 × 10 <sup>-3</sup>
B	Methylamine <sup>1</sup> . . . . .	5.0 × 10 <sup>-4</sup>
C <sup>1</sup>	Trimethylamine <sup>1</sup> . . . . .	7.4 × 10 <sup>-5</sup>
D	Ammonia <sup>1</sup> . . . . .	2.3 × 10 <sup>-5</sup>
E	Hydrazine <sup>1</sup> . . . . .	2.7 × 10 <sup>-6</sup>
F	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SnOH <sup>1</sup> . . . . .	1.7 × 10 <sup>-7</sup>
G	<i>p</i> -Toluidine <sup>2</sup> . . . . .	1.6 × 10 <sup>-9</sup>
H	Aniline <sup>2</sup> . . . . .	4.9 × 10 <sup>-10</sup>
I	Alanine <sup>3</sup> . . . . .	3.8 × 10 <sup>-12</sup>
J	Glycocol <sup>3</sup> . . . . .	2.9 × 10 <sup>-12</sup>
K	Sarcosine <sup>3</sup> . . . . .	1.8 × 10 <sup>-12</sup>
L	Aspartic acid <sup>3</sup> . . . . .	1.3 × 10 <sup>-12</sup>
M	Betaine <sup>3</sup> . . . . .	7.6 × 10 <sup>-13</sup>

### Summary.

A diagram is presented which expresses the requirements of the concentration law regarding the equilibrium in solution between strong bases and acids of all strengths. A precisely similar diagram indicates the equilibrium in solution between strong acids and bases of all strengths. (The diagrams are not useful for solutions containing both strong bases and strong acids in which the acidity or alkalinity is high.)

These diagrams define with considerable accuracy the conditions of equilibrium at all hydrogen- and hydroxyl-ion concentrations, between all bases and all acids with the above-mentioned exceptions, and in all mixtures of such substances. They also define all isohydric solutions of such substances in which this quality is dependent upon equality in concentration of hydrogen- and hydroxyl-ions alone.

## THE HEATS OF SOLUTION OF THE THREE FORMS OF MILK-SUGAR.

BY C. S. HUDSON AND F. C. BROWN.

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Milk-sugar can be crystallized from solution in two forms, one of which is a monohydrate, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>·H<sub>2</sub>O, and the other an anhydrous modification, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, named *β*-anhydrous milk-sugar. When either of these crystalline milk-sugars is dissolved in water it changes partially to the other form until a condition of dynamic equilibrium is reached in which both forms are present in the solution. In distinction from the *β*-anhydride of milk-sugar there is an *α*-anhydride which is produced when hydrated milk-sugar is heated at 125° to constant weight. This *α* anhy-

<sup>1</sup> Bredig, *Z. physik. Chem.*, 13, 280 (1894).

<sup>2</sup> Nernst, *Theoretische Chemie*, 3rd Edition, p. 407.

<sup>3</sup> Winkelblech, *loc. cit.*

dride is markedly hygroscopic, it dissolves in water with an evolution of considerable heat, and its freshly prepared solutions are identical with those of hydrated milk-sugar; these facts indicate that the  $\alpha$ -anhydride is unstable in the presence of water and changes immediately to hydrated milk-sugar when dissolved. Measurements of the rate at which the equilibrium between the hydrate and the  $\beta$ -anhydride is approached and of the proportions of the two forms that are finally present in the solution have already been published.<sup>1</sup> The present research is a study of the heats of solution of these three forms of milk-sugar under the guiding hypothesis that when any one of them is dissolved in water there occurs the incomplete or balanced reaction in solution between the hydrate and the  $\beta$ -anhydride. These heats of solution are not simple quantities, because the dissolving of any form of the sugar is usually complicated by the presence of a second heat effect due to the change to the stable mixture of hydrate and  $\beta$ -anhydride. In order to distinguish the component parts of these complex heat effects the following nomenclature is adopted:

The *initial heat of solution* is the heat that is produced when any form of the sugar is dissolved under such conditions that the subsequent change to the stable mixture of hydrate and  $\beta$ -anhydride is greatly retarded.

The *final heat of solution* is the total heat that is produced when any form of the sugar dissolves to give a solution in which the stable mixture is present.

The *heat of passage* of one form to the other is the heat that is produced when a given quantity of the one form changes in solution to an equivalent quantity of the other form.

To illustrate these definitions by an example, when hydrated milk-sugar dissolves in cold water quickly no appreciable amount of the  $\beta$ -anhydrous form is produced and the heat which is absorbed during the dissolving is the initial heat of solution of the hydrate. On the other hand, if the hydrated sugar dissolves in alkaline water its partial change to the  $\beta$ -anhydrous form is instantaneous and the heat absorbed in dissolving is in this case the final heat of solution, which is obviously the sum of the initial heat of solution of the hydrate and the heat of passage of that portion of the hydrate which subsequently changes to the  $\beta$ -anhydride.

*The Method of Measuring the Heats of Solution.*—The calorimeter that was used is similar to one that has been described by A. A. Noyes.<sup>2</sup> The inner can is of brass, silver-plated and polished, and of a liter capacity. It rests upon three corks in a polished tin vessel and this in turn is supported by corks within the outermost vessel which is double-walled and water-jacketed. A close covering of thick felt completely surrounds the

<sup>1</sup> THIS JOURNAL, 26, 1065-1082 (1904).

<sup>2</sup> Z. physik. Chem., 43, 513-38 (1903).

calorimeter. The temperatures were read from a certified Beckmann thermometer graduated to hundredths of a degree. The contents of the inner can were stirred by a silver-plated brass propeller driven by an electric motor. In most of the experiments on the heats of solution the finely powdered sugar was loosely packed in a silver-plated brass tube of 50 cc. capacity which was suspended from the cover of the inner can. An aluminum disk was cemented water-tight in the lower end of this tube with paraffin and could be punched out at the proper time with a glass rod inserted through the calorimeter coverings. This arrangement allowed a sudden and controllable mixing of the dry sugar with the water while the calorimeter remained closed.

*The Initial Heat of Solution of Hydrated Milk-Sugar.*—Pure hydrated milk-sugar was prepared by recrystallizing once a very good quality of commercial milk-sugar crystals, and it was dried to constant weight at 100°. This hydrate does not lose its water of crystallization at this temperature even under prolonged heating. The determination of its initial heat of solution was carried out at 20° by the method that has just been described and the resulting data are given in the following table. In order to make certain that all the sugar dissolved, the stirrer was stopped and the calorimeter opened immediately after several of the measurements, but in no case could any undissolved sugar be seen.

TABLE I.—INITIAL HEAT OF SOLUTION OF HYDRATED MILK-SUGAR AT 20°.

Mass of water. Grams.	Mass of sugar.	Total water equivalent. <sup>1</sup>	Temperature change.	Heat of solution.	Time to dissolve. Minutes. <sup>2</sup>
999	31.26	1038	—0.361	—12.0	4
984	26.13	1022	—0.304	—12.0	2
999	26.10	1037	—0.302	—12.0	3
991	26.23	1029	—0.306	—12.0	2
996	26.08	1034	—0.302	—12.0	1
993	25.87	1031	—0.296	—11.8	2
987	25.87	1025	—0.302	—12.0	2
998	11.23	1031	—0.128	—11.8	1
1003	29.60	1042	—0.343	—12.1	2
1000	37.07	1041	—0.400	—11.8	4
				-----	
Average				—12.0	

The average of these ten determinations is —12.0 gram calories per gram for the initial heat of solution of hydrated milk-sugar at 20°. This value is somewhat larger than those which others have found, Berthelot<sup>3</sup>

<sup>1</sup> The water equivalent of the inner calorimeter and its attachments, including the immersed portion of the thermometer was calculated to be 29.9 grams. The specific heat of milk-sugar is 0.30, Magie, *Physical Review*, 16, 381 (1903).

<sup>2</sup> The sugar was assumed to be completely dissolved when the rate of change of the temperature reached the value that it had before the sugar was added.

<sup>3</sup> *Mécanique Chimique*, 1, 545.

gives  $-10.2$ , Brown and Pickering<sup>1</sup>  $-11.5$ , Magie<sup>2</sup>  $-11.5$ . These differences are probably principally due to the fact that hydrated milk-sugar has a large temperature coefficient of its heat of solution. Magie has found the molecular heat of hydrated milk-sugar to be 108 in the solid state and 165 in solution, therefore the heat absorbed by the solution of 1 gram must increase  $(165-108)/360 = 0.16$  calorie for each degree rise of temperature. According to this, the difference between the value here found for the heat of solution and that given by Brown and Pickering and by Magie can be explained by a difference of only  $3^\circ$  in the temperature of the experiments. As Brown and Pickering's measurement was made at  $16^\circ$ , and probably also Magie's, while the present ones were performed at  $20^\circ$ , it is evident that an excellent agreement has been obtained by the different observers. Solubility measurements on hydrated milk-sugar also show that the heat of solution increases with the temperature, for if the solubilities at  $15^\circ$  and  $25^\circ$  are used to calculate the heat of solution for this range by the well-known method of van't Hoff,  $-11.5$  calories is obtained,<sup>3</sup> but if those at  $0^\circ$  and  $15^\circ$  are employed  $-10.3$  is found. If the former value is considered to refer to  $20^\circ$  and the latter to  $7.5^\circ$  the change in the heat of solution per degree is 0.10 calorie which agrees with the coefficient that was found above from the molecular heats.

In the data given in Table 1 there is no indication that the heat of solution changes in value according as the sugar is dissolved in much water or in little. If such an effect were present the solutions would of necessity also show considerable heat of dilution; this fact was accordingly made use of as a direct test. Fifty cc. of a semi-normal solution of milk-sugar were put in the tube of the calorimeter and after constant temperature was attained the bottom of this tube was punched out and the solution allowed to mix with 800 cc. water, which was 9 grams of sugar passing from half to three hundredths molal concentration. In the two experiments rises of temperature of  $0.001^\circ$  and  $0.003^\circ$  were observed, and they are so small that the absence of any considerable heat of dilution can be considered established. It follows from this that the heat of solution of milk-sugar does not change with the concentration in dilute solution (e. g., below 0.3 molal) and changes only very slightly in concentrated solutions.

As has been mentioned, hydrated milk-sugar forms  $\beta$ -anhydrous milk-sugar slowly during many hours after its solution in cold water. In order to make certain that the data given in Table 1 refer to the *initial* heat of solution it must be shown that this chemical change in the solution did not proceed far enough during the time of the measurement to give

<sup>1</sup> *J. Chem. Soc.*, **71**, 783 (1897).

<sup>2</sup> *Phys. Rev.*, **16**, 381 (1903).

<sup>3</sup> See page 970 below.

any heat effect. Now in that experiment which required the longest time, four minutes, 3 per cent. of the dissolved hydrate changed to the  $\beta$ -anhydride, according to previous measurements of the rate of this change.<sup>1</sup> It will be shown later in this article that when the change proceeds to equilibrium the heat effect is small, certainly not greater than one calorie per gram of sugar transformed; therefore only three hundredths of a calorie at the most is the error that is due to the change of the hydrated sugar after dissolving, and it can be neglected.

*The Preparation of Pure  $\beta$ -Anhydrous Milk-Sugar.*—Three methods for preparing  $\beta$ -anhydrous milk-sugar have been published; in the first a solution of any form of milk-sugar is boiled to dryness,<sup>2</sup> in the second alcohol and ether are added to a hot solution to precipitate the anhydride,<sup>3</sup> while in the third the solution is allowed to crystallize slowly at 95° from supersaturation.<sup>4</sup> The first and second of these methods give an impure anhydride contaminated with varying amounts of hydrated milk-sugar, but by following the directions given below which are based upon the third method, it has been found possible to secure a good yield of the  $\beta$ -anhydride in large crystals which are colorless and free from hydrate.

Commercial crystallized milk-sugar is dissolved in hot water to form a saturated solution at 100°, which is then decanted into a copper beaker and rapidly boiled until its boiling-point rises to 104–105°. The copper beaker is then suspended in boiling water or steam for twenty-four hours. A crust forms over the solution soon after boiling ceases which hinders further evaporation and at the end of the twenty-four hours numerous well-formed crystals are found hanging to the sides of the beaker and the crust. The bottom of the beaker is covered with a compact mass of minute crystals which are rejected, as it is impossible to free them from the mother-liquor. It is well to roughen the surface of the copper beaker in order that the crystals may adhere better. To free the crystals from the solution, which is a thick syrup, an opening is cut through the crust, the beaker removed from the heater and as much as possible of the hot solution poured off; the crystals are then removed from the beaker, pressed between filter papers and immediately washed by decantation with glycerol heated to 140°, followed by hot 95 per cent. alcohol and then by ether.

In order to test the crystals that were prepared by this method for the presence of traces of the hydrate, a finally saturated solution of hydrated milk-sugar was prepared at 20°, filtered to free it of all suspended particles,

<sup>1</sup> THIS JOURNAL, 26, 1076 (1904).

<sup>2</sup> Erdman, *Ber.*, 13, 1915-31 (1880).

<sup>3</sup> Taurer, *Bull. soc. chim.* [3], 15, 354 (1896).

<sup>4</sup> Hudson, *Z. physik. Chem.*, 44, 488 (1903).

and cooled to  $0^{\circ}$ , at which temperature such a solution is known to be supersaturated with respect to the hydrate but greatly undersaturated with respect to the anhydride.<sup>1</sup> Several crystals of the anhydride that were prepared as described above were then placed in this solution. They dissolved completely without leaving a visible trace of insoluble matter, which would not have been the case if the crystals contained particles of the hydrate. This method of testing for the presence of the hydrate is quite delicate and the result shows conclusively that the  $\beta$ -anhydride is pure. This test for purity can be applied to a few other substances for which such a test has heretofore been lacking, for example to the  $\beta$ -anhydrous forms of glucose, galactose and the other mutarotating sugars.

The specific gravity of pure  $\beta$ -anhydrous milk-sugar at  $20^{\circ}$  is 1.59, of the hydrated form 1.54.

*The Initial Heat of Solution of  $\beta$ -Anhydrous Milk-Sugar.*—The initial heat of solution of this form of the sugar was measured in the same manner that has been described in the case of the hydrate. The sugar sample marked one was a year old, the other two were freshly prepared. The results are given in Table 2.

TABLE 2.—INITIAL HEAT OF SOLUTION OF  $\beta$ -ANHYDROUS MILK-SUGAR AT  $20^{\circ}$ .

Mass of water. Grams.	Mass of sugar.	Total water equivalent.	Temperature change.	Time to dissolve. Minutes.	Sample number.	Heat of solution
716	13.7	749	—0.039	2	1	—2.1
902	29.6	939	—0.063	2	1	—2.0
736	15.4	768	—0.051	2	2	—2.5
464	8.1	497	—0.038	1	3	—2.3
686	13.1	710	—0.051	3	3	—2.3

These experiments give —2.3 calories per gram as the heat of solution and since the chemical change that occurs in these solutions is the reverse of that in the solutions of the hydrate it proceeds too slowly to affect the measurements, and the value obtained is the initial heat of solution. The values for the heat of solution of this anhydride that have been found by previous observers are all larger than the above, undoubtedly because some hydrate was present in their samples; Brown and Pickering<sup>2</sup> found —5.4, Magie and Hudson<sup>3</sup> —3.6.

*A Precipitated Milk-Sugar Showing No Mutarotation.*—If a solution of any form of milk-sugar is kept for a day at room temperature or boiled and cooled, to allow the reversible chemical change that occurs in such

<sup>1</sup> THIS JOURNAL, 26, 1071-1074 (1904). The concentration of  $\beta$ -anhydride in a saturated solution of the hydrate at  $20^{\circ}$  is only about one-quarter the initial solubility of the anhydride at  $0^{\circ}$ .

<sup>2</sup> J. Chem. Soc., 71, 783 (1897).

<sup>3</sup> Princeton Univ. Bull., April, 1902.

solutions to reach equilibrium, and a mixture of strong alcohol and ether is then added, a crystalline precipitate is formed which does not show mutarotation when it is dissolved in water as do the other forms of milk-sugar. Tanret<sup>1</sup> who discovered this precipitate in 1896 regarded it until recently as a new form of milk-sugar, the stable modification to which the other forms revert in solution, ascribed to it the formula  $C_{12}H_{22}O_{11} \cdot \frac{1}{2}H_2O$ , and named it  $\beta$ -lactose. It is now generally accepted that this form is a mechanical mixture of hydrated and  $\beta$ -anhydrous milk-sugar in about the proportions in which they are present in solution in equilibrium. The view that this form of milk-sugar is such a mixture was expressed six years ago<sup>2</sup> and direct evidence was given to support it; but as the publication in which this evidence appeared had small circulation the data are presented again, using, however, the more accurate values of the heat of solution that are now at hand. If the alcoholic precipitate is a mixture of hydrated and  $\beta$ -anhydrous milk-sugar its initial heat of solution will be intermediate between those of its constituents. The exact value can be calculated from the fact that the two forms must be present in the mixture in the same proportion in which they occur in the stable solution or otherwise the precipitate would show mutarotation when dissolved. It has been shown from solubility measurements<sup>3</sup> that this proportion at room temperature is 1.5 parts  $\beta$ -anhydride to each part hydrate; the initial heat of solution of such a mixture is therefore calculated to be  $-[12.0 + (2.4)(1.5)] \div 2.5 = -6.2$  calories. Magie and Hudson<sup>1</sup> found by experiment the value  $-6.5$  calories for Tanret's alcoholic precipitate. The agreement of these values is clear evidence that this precipitate is a mechanical mixture of hydrated and  $\beta$ -anhydrous milk-sugar.

*The Heat of Passage in Solution between the Forms of Milk-Sugar.*—The establishment of equilibrium between the two forms of milk-sugar in solution proceeds so slowly at room temperature that no noticeable heat effect due to the transformation ordinarily occurs. Although the rate of production of heat in these solutions under usual conditions is thus too slow to admit of its measurement, the velocity of the chemical change can be enormously accelerated by suitable catalytic agents, especially an alkali, and the heat is then produced very quickly and can be measured.<sup>4</sup>

In the following experiments milk-sugar hydrate was dissolved quickly in water at 20° and immediately after its complete solution a small quantity, usually 0.5 cc. of tetranormal sodium hydroxide was added

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Princeton Univ. Bull.*, April, 1902.

<sup>3</sup> *THIS JOURNAL*, 26, 1074 (1904).

<sup>4</sup> This is the method that was used by Brown and Pickering (*loc. cit.*) in measuring several such heat effects in the carbohydrate group.

and the immediate rise in temperature measured. An equal quantity of the alkali was then again added and the accompanying rise in temperature again noted. The difference between the first rise and the second is taken to be due to the partial change of the hydrated milk-sugar to the  $\beta$ -anhydride. This conclusion is not strictly correct, and if theory were exactly adhered to the addition of the alkali that was made to the already alkaline solution should have been made to a neutral solution of milk-sugar which had reached equilibrium by long standing, but as several experiments showed that the two methods of addition of the alkali gave the same heating effect the more convenient one was subsequently followed. To make certain that the first addition of alkali caused a sufficiently rapid attainment of equilibrium, the change of rotation of several solutions was observed in the polariscope immediately after 0.5 cc. of alkali was added; the rotation was not quite constant at the end of one minute but did not change at all after two, proving that the catalysis was sufficiently rapid. As from five to twenty minutes elapsed in the experiments given below between the dissolving of the hydrate and the first addition of the alkali it is necessary to correct for the amount of hydrate that was transformed to  $\beta$ -anhydride during this interval; this quantity was calculated from the previous measurements of the velocity of the reaction at 20° and it is recorded in column five. The values in column four are calculated from the equilibrium constant of the reaction, 40 per cent. of the sugar in stable solutions being hydrate and 60 per cent.  $\beta$ -anhydride at 20°.

TABLE 3.—HEAT OF PASSAGE IN SOLUTION OF HYDRATED MILK-SUGAR TO  $\beta$ -ANHYDRIDE AT 20°.

Water. Grams.	Total water equiv- alent.	Mass of hydrate			First rise.	Second rise.	Diff.	Heat of passage.
		originally dissolved.	finally changed.	Changed before catalysis.				
1002	1040	29.6	17.8	0.5	0.033	0.016	0.017	1.02
999	1038	31.3	18.8	0.6	0.028	0.012	0.016	0.91
999	1037	37.1	22.3	1.1	0.029	0.008	0.021	1.03
1000	1038	22.5	13.5	0.9	0.022	0.011	0.011	0.90
1004	1042	32.9	19.7	1.4	0.027	0.010	0.017	0.97

It appears from these measurements that the heat of passage is small, the average value being closely one calorie of heat developed for each gram of hydrate that changes in solution to  $\beta$ -anhydride. Brown and Pickering<sup>1</sup> give +0.19 as the heat developed when 1 gram of dissolved hydrate changes to the equilibrium mixture, but this is evidently a misprint and should read 0.25, which would give 0.4 calorie for the heat of passage, a value not greatly different from the one here found. It is exceptional that the formation of this anhydride should develop heat,

<sup>1</sup> *Loc. cit.*, p. 782.



because most dehydrations absorb it in large quantities. This absorption of heat does not agree with the conclusion that has been drawn from previous experiments on the initial and final solubilities of hydrated milk-sugar which appeared to show that the equilibrium of the hydration changes greatly with the temperature in a manner that would necessitate a strong heat absorption when the hydrate changes to anhydride.<sup>1</sup> In order to throw light on this disagreement between the solubility and the calorimetric measurements the following sensitive method was used to show whether there is a large change in the hydration equilibrium with temperature as the solubility measurements indicate, or whether this change is very small, as the small heat of passage here found leads one to infer. A solution of hydrated milk-sugar was prepared at 25°, kept at this temperature for twenty-four hours to establish equilibrium and then poured into a polariscope tube which was kept at 0° by a water jacket. The immediate rotation of the cooled solution was 26.2°, and it did not change perceptibly after a trace of sodium carbonate was added to the solution to establish instantaneously the equilibrium which holds at this lower temperature. That the presence of the carbonate did not mask any possible change in the polariscopic reading was shown by adding a trace to a milk-sugar solution which had stood at room temperature for a day and noticing that at this temperature no change in rotation was caused by the carbonate. It is quite evident that the change in the hydration equilibrium between 0° and 25° is too small to be shown by the polariscope. Several similar experiments to detect a slow thermal lag in the rotation gave nearly the same result as the one that has been described; the data are condensed into Table 4.

TABLE 4. THERMAL LAG OF MILK-SUGAR SOLUTIONS.<sup>2</sup>

Initial temperature.	Final temperature.	Time to cool.	Initial rotation.	Final rotation.
25	0	5 min.	26.2	26.2
25	0	5 "	17.4	17.4
60	20	5 "	26.6	26.3
60	20	8 "	27.3	26.8
60	25	10 "	17.1	16.8
100	0	8 sec.	23.3	22.5

When the temperature is greatly altered, as through 40° or more, a slight thermal lag in the rotation is noticeable and as the specific rotation

<sup>1</sup> THIS JOURNAL, 26, 1074 (1904).

<sup>2</sup> A similar very slow change in the rotatory power at constant temperature following a change in temperature has been observed in the case of invert sugar (Palmer, *Z. physik. Chem.*, 22, 492-504 (1867)) and also with the magnetic rotation of methyl-acetylacetone (Perkin, *J. Chem. Soc.*, 61, 800-864 (1892)). In the first of these, the cause is obviously the same as with milk-sugar, though the effect is larger. The other case might well be studied further, as the method in which the magnetic rotation is employed is applicable to any slowly progressing reaction.

of the hydrate is greater than that of the  $\beta$ -anhydride, the direction of the lag indicates that at low temperatures there is slightly less hydration. This conclusion agrees in sign and approximate magnitude with the small positive heat of passage and shows that there is some error in the interpretation that has been placed upon the solubility measurements. It may be that the presence of the anhydride in solution affects the solubility of the hydrate except in very dilute solutions and that the contrary assumption has introduced the error in the conclusions from the solubility data. But the above experiments show conclusively that the equilibrium changes only very slightly with the temperature between  $0^\circ$  and  $100^\circ$ , there being slightly more hydration at the higher temperature.

The heat of passage of freshly prepared solutions of  $\alpha$ -anhydrous milk-sugar to the stable mixture of hydrate and  $\beta$ -anhydride has also been measured and the values are given in Table 5.

TABLE 5.—HEAT OF PASSAGE IN FRESH SOLUTIONS OF  $\alpha$ -ANHYDROUS MILK-SUGAR.

Water. Grams.	Total water equiv- alent.	Mass of anhydride			First rise.	Second rise.	Diff.	Heat of passage.
		originally dissolved.	changed to form.	changed before catalysis.				
600	629	21.4	12.8	1.0	0.034	0.017	0.017	0.91
542	571	16.9	10.1	1.4	0.037	0.021	0.016	1.05
584	612	16.3	9.8	1.2	0.034	0.017	0.017	1.21
542	573	11.6	7.0	0.3	0.033	0.020	0.013	1.11
515	541	12.2	7.3	0.2	0.027	0.015	0.012	0.90

The average of these determinations is 1.03 calorie per gram anhydrous sugar or 0.98 per gram hydrated sugar. This value is not noticeably different from that found for the solutions of the hydrate, one calorie, and serves as a further proof that the freshly prepared solutions of the hydrate and the  $\alpha$ -anhydride are identical.

The initial heat of solution of  $\alpha$ -anhydrous milk-sugar has been found by Jorissen and Van der Stadt<sup>1</sup> to be 7.3 calories per gram. This value includes the heat of passage to hydrate.

*The Final Heats of Solution.*—These are directly obtained from the initial heats of solution and the heat of passage. When 1 gram of the hydrate dissolves at  $20^\circ$  to form a stable solution containing the  $\beta$ -anhydride in the equilibrium proportion (1.5 parts anhydride per part hydrate) the final heat of solution is the initial heat of solution,  $-12.0$  calories, plus the heat of passage of 0.6 gram hydrate (0.6 calorie), which is  $-11.4$  calories. In like manner the final heat of solution of the  $\beta$ -anhydride is  $(-2.3-0.4) = -2.7$  calories per gram. From Jorissen and Van der Stadt's value of the initial heat of solution of the  $\alpha$ -anhydride,  $+7.3$  calories, its final heat of solution is  $(7.3 + 0.6) = 7.9$  calories per gram.

<sup>1</sup> *J. pr. Chem.*, [2], 51, 102-6 (1894).

*The Final Heat of Solution of Hydrated Milk-Sugar Calculated from Its Solubility.*—By the principles of the osmotic theory of solutions it is possible to calculate the heat of solution of milk-sugar from the change of its solubility with the temperature. The final solubilities of the hydrate are known at 15° and 25° and the final heat of solution is also known at 20°, so that a comparison of the conclusions of the two independent methods of measurement is possible. The values<sup>1</sup> for the solubility are 49.7 millimols per 100 grams water at 15° and 63.4 at 25°, and the molecular heat of solution ( $Q$ ) is, from the well-known formula of van't Hoff,  $\log. \text{nat. } 63.4/49.7 = Q/(1/288-1/298)$ , equal to  $-4130$  calories. Since the molecular weight of hydrated milk-sugar is 360, the final heat of solution per gram is  $-11.5$  calories. This calculated value agrees perfectly with that given by the calorimetric measurement,  $-11.4$ .

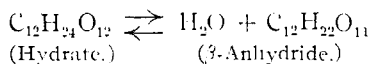
### Summary.

1. Each of the three forms of milk-sugar shows two heats of solution according as the rate of the balanced reaction that occurs in milk-sugar solutions proceeds very slowly or very rapidly. In the former case the initial heat of solution is observed, in the latter the final heat of solution, which is the sum of the initial heat of solution and the heat generated by the rapidly progressing reaction, called the heat of passage.

2. The following data on these heat effects at 20° have been determined with a calorimeter.

	Hydrated milk-sugar.	$\alpha$ -Anhydride.	$\beta$ -Anhydride.
Initial heat of solution.....	$-12.0$ cal. gram	$+7.3^2$	$-2.3$
Final heat of solution.....	$-11.4$	$+7.0$	$-2.7$
Heat of passage to $\beta$ -anhydride	$+1.0$	$+1.0$	..

3. The equality of the heat of passage of the hydrate and the  $\alpha$ -anhydride is further evidence supporting the accepted view that the  $\alpha$ -anhydride passes instantly to hydrate when dissolved, which then slowly builds  $\beta$ -anhydride according to the balanced reaction



4. Evidence from two independent sources shows that the initial heat of solution of the hydrate increases about 0.1 calorie per degree rise in temperature.

5. The dilution of strong milk-sugar solutions (0.5 molal) causes a very slight development of heat, which cannot be due to any change in the equilibrium of the balanced reaction with concentration because the heat development at room temperature on dilution is instantaneous while any change of the balanced reaction at this temperature would be very slow.

<sup>1</sup> THIS JOURNAL, 26, 1072 (1904).

<sup>2</sup> From the work of Jorissen and Van der Stadt, *loc. cit.*

The heat of solution is independent of the concentration when this is less than about 0.3 molal.

6. Pure  $\beta$ -anhydrous milk-sugar has been prepared by an improved method of slow crystallization, and a delicate test shows that it is free from hydrate. Its specific gravity at 20° is 1.59, that of the hydrate being 1.54.

7. The present data on the heats of solution confirm quantitatively the view that the crystalline substance which alcohol and ether precipitate from cold stable milk-sugar solutions is not a pure substance as was first supposed but is a mechanical mixture of the hydrate and the  $\beta$ -anhydride. It does not show mutarotation when redissolved in water because the two substances are present in it in the same proportions approximately in which they occur in stable solutions.

8. When the temperature of a stable solution of milk-sugar is suddenly changed a slight thermal lag is observed in its rotatory power, which indicates that the hydration is slightly increased with rise of temperature between 0° and 100°. The direction and magnitude of this lag agree with the conclusions drawn from the observed value of the heat of passage.

9. The final heat of solution of hydrated milk-sugar is calculated from the solubilities at 15° and 25° to be -11.5, agreeing with the calorimetric measurement at 20°, which gives -11.4.

UNIVERSITY OF ILLINOIS,  
URBANA, ILL.

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## A NEW INSTRUMENT FOR REDUCING GAS VOLUMES TO STANDARD CONDITIONS.

BY GRANT T. DAVIS.

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The necessity for making a considerable number of accurate measurements of gas volumes has led to the working out of the following device for their reduction to standard volume. Since all that is necessary for the physical reduction of a gas to standard volume, is to subject it to a definite pressure, a water column of variable length was first tried, but this was discarded in favor of a column of known length with a fixed scale. The length of the column of mercury ( $L_m$ ) necessary to compress a gas to standard volume at temperature "t" is found by the formula,  $V = \frac{v(p-p')}{760(1+at)}$ , the conditions being such that  $v=V$ ; then  $p=760(1+at) + p'$  and  $L_m = p - 760$ . The length for the water column was taken as  $L_m \times 13.59$ , and correction was made for the expansion of water with rise in temperature.

The apparatus for use with gases which can be collected over water consists of a piece of iron pipe about two meters long, fitted with a T near the top and an elbow at the lower end. The elbow is closed by a rubber