

(about 64.5), derived from the more trustworthy experiments with potassium chloride. This seems to indicate that the migration number of the  $\text{SO}_4$  ion, derived from potassium sulphate, is too low, and the number found with copper sulphate is not, therefore, to be discarded. Consequently it will be assumed that the mean of the three numbers in the above table is the most probable value of this quantity. This is 70, which is also the value adopted by Kohlrausch in 1898.

Although in the case of a dibasic acid the calculation of the equivalent conductivity or migration number of the H ion can lead to no final results, nevertheless, it will be interesting to compare the number obtained with sulphuric acid with that obtained from other sources. At  $18^\circ$  the transport number of sulphuric acid, according to the above formula, is  $0.1788 - 0.0022 = 0.1766$ . Combining this with 70, the migration number just given for the  $\text{SO}_4$  ion, we obtain 396 for  $V_\infty$  of  $\text{H}_2\text{SO}_4$  at  $18^\circ$  and 326 as the migration number of the H ion at the same temperature. Noyes and Sammet have derived the value 330 for the latter quantity from transference experiments with hydrochloric acid. In 1898 Kohlrausch considered the most probable value to be 318.

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CLEVELAND, May, 1904.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 3].

## THE HYDRATION OF MILK-SUGAR IN SOLUTION.<sup>1</sup>

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Received July 8, 1904.

### CONTENTS.

1. The Anhydrous and Hydrated Forms of Milk-sugar. 2. The Multitrotation of Milk-sugar. 3. Theory of the Maximum Rate of Solution. 4. Experiments on the Rate of Solution of Milk-sugar Hydrate. 5. The Equilibrium between the Hydrate and Anhydride. 6. The Maximum Rate of Precipitation of Milk-sugar Hydrate. 7. Comparison of the Velocity-constants Derived from the Rate of Change of Rotation and from the Maximum Rate of Solution. 8. The Absolute Velocity of Hydration and Dehydration. 9. The Maximum Rate of Solution in Relation to the Equilibrium of Dissolved Substances in General. 10. Summary.

### I. THE ANHYDROUS AND HYDRATED FORMS OF MILK-SUGAR.

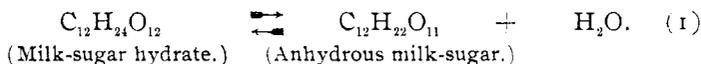
In a recent publication<sup>2</sup> I have shown the existence in aqueous

<sup>1</sup> Read at the Providence meeting of the American Chemical Society.

<sup>2</sup> *Ztschr. phys. Chem.*, 44, 487-494 (1903).

solutions of milk-sugar of an incomplete hydration reaction which establishes its equilibrium slowly and is the cause of the gradual change of optical rotatory power of freshly prepared milk-sugar solutions, or of the "multirotation" of this substance. The present investigation is a continuation of this study.

As was shown in the previous investigation, the reaction which takes place in milk-sugar solutions is represented by the equation



As further conclusive evidence that the reaction does not consist in a depolymerization of the sugar, the following fact may be cited: In dilute solution this hydration reaction can have no effect upon the osmotic pressure of the solution, and it is, therefore, to be expected that dilute solutions of equivalent concentration of either form of milk-sugar, or of a mixture of the two forms, will give identical values for those properties directly dependent upon osmotic pressure. That freshly prepared dilute solutions of hydrated and anhydrous milk-sugar, respectively, do give equal freezing-point depressions, corresponding with the formula  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , has been shown by Schmoeger<sup>1</sup> and by Tanret.<sup>2</sup> Also the freezing-point measurements of Loomis<sup>3</sup> upon dilute milk-sugar solutions that had reached equilibrium, gave in all cases 342 for the molecular weight, although from the experiments given in the present article the milk-sugar in a dilute solution which has reached equilibrium at 0° consists of about 45 per cent. hydrate and 5 per cent. anhydride.

The substance on the left of the reaction-equation is the milk-sugar of commerce, a hard, sparingly soluble, crystalline sugar, which can be obtained pure without difficulty by recrystallization at room temperature from aqueous solution. If the crystallization be carried on above about 95° the substance on the right, anhydrous milk-sugar,<sup>4</sup> separates out.

<sup>1</sup> *Ber. d. chem. Ges.*, **25**, 1455 (1892).

<sup>2</sup> *Bull. Soc. Chim.* (3), **15**, 358 (1896).

<sup>3</sup> *Ztschr. phys. Chem.*, **37**, 412 (1901).

<sup>4</sup> In the article cited above, I used the name "milk-sugar lactone" for this substance, but as its lactonic character is not fully established, the designation "anhydrous milk-sugar" seems preferable. For brevity it will be called simply "the anhydride" throughout this article. The hydrate is called by Tanret  $\alpha$ -lactose, the anhydride  $\gamma$ -lactose. The  $\beta$ -lactose of Tanret's classification, which is given the composition  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \frac{1}{2}\text{H}_2\text{O}$ , is a mixture of  $\alpha$ - and  $\gamma$ -lactoses.

The anhydride here mentioned is not to be confused with a second anhydride obtained by heating the solid hydrate at 125° until it loses 5 per cent. water. This second anhydride has never been obtained by crystallization from solution. When it is dissolved in cold water heat is developed (while the other forms of milk-sugar absorb heat in dis-

The anhydrous sugar was obtained in large crystals by slowly evaporating at from  $95^\circ$  to  $100^\circ$  a solution of milk-sugar, best in a glass beaker; but in order to prevent decomposition of the sugar during the two days of heating that are necessary, care must be taken in the recrystallization of the hydrate used in preparing the solution, and pure water and well cleaned vessels must be employed. Traces of acid, and especially of alkali, cause rapid decomposition of the sugar.

From the fact that milk-sugar solutions deposit hydrate at room temperature and anhydride at  $95^\circ$ , it follows that between these two temperatures there is a transition-temperature for the two substances. Attempts to determine this temperature with accuracy have not met with success so far, but the experiments will be continued.

## II. THE MULTIROTATION OF MILK-SUGAR.

The rate of formation of anhydride at constant temperature in a dilute solution, containing, at the start,  $a$  mols hydrate and  $b$  mols anhydride per unit-volume, is

$$\frac{dx}{dt} = k_1(a-x) - k_2(b+x), \quad (2)$$

where  $x$  denotes the amount of anhydride which has been formed at the time  $t$ . The integral of this expression is

$$\frac{1}{t} \log \frac{Ka-b}{Ka-b-(1+K)x} = k_1 + k_2,$$

where  $K = \frac{k_1}{k_2}$  and  $x = 0$  when  $t = 0$ .

If  $R_H$  and  $R_A$  denote the molecular rotation of the hydrate and anhydride respectively, the initial rotation of the solution is  $r_0 = a R_H + b R_A$ , the final rotation is  $r_\infty = (a-x_\infty) R_H + (x_\infty + b) R_A$ , and the rotation at the time  $t$  is  $r = (a-x) R_H + (x + b) R_A$ .

solving), and the resulting solution has a specific rotatory power identical with that of freshly prepared solutions of the hydrate. This anhydride, therefore, when dissolved, passes almost instantly and quantitatively into hydrate, which then slowly forms the equilibrium given by (1). This initial hydration of an anhydride and the subsequent partial dehydration reminds one of the similar phenomena with the sugar glucose observed by Tollens: *Ber. d. chem. Ges.*, **26**, 1801 (1896). That this behavior of an anhydride has been pronounced "thermodynamically impossible" by several authors, Ostwald: *Ztschr. phys. Chem.*, **12**, 799 (1893), and Landolt: "Das optische Drehungsvermögen" (1898), p. 244, is obviously due to the misconception that the two anhydrides are identical. In the case of milk-sugar, the two anhydrides are different substances, and this is probably also true for the glucose anhydrides.

From these three relations it follows that

$$x = \frac{r-r_0}{R_A-R_H}, \text{ and } K = \frac{k_1}{k_2} = \frac{r_0-r_\infty-b(R_A-R_H)}{r_\infty-r_0-a(R_A-R_H)}.$$

When these values of  $x$  and  $K$  are substituted in the equation above, there results

$$\frac{1}{t} \log \frac{r_0-r_\infty}{r-r_\infty} = k_1 + k_2.$$

This formula holds for solutions containing, at the beginning, pure hydrate, pure anhydride, or a mixture of the two. At the time that it was first derived<sup>1</sup> experiments at three temperatures ( $10^\circ$ ,  $15^\circ$  and  $30^\circ$ ) were made which showed that the velocity-constant of the rate of change in rotation ( $k_1 + k_2$ ) is the same for solutions of hydrate and anhydride—a result which is predicted by the theory. Since then the same fact has been noticed by Roux.<sup>2</sup> In order to use the data as a control upon a direct measurement of  $k_2$ , which will be given further on, the rate of change in rotation at  $0^\circ$  has been determined. The solution formed from slowly recrystallized sugar and conductivity water was kept in the observation tube of the polariscope accurately at  $0^\circ$  by passing through the jacket of the tube a sodium sulphate solution, saturated at its cryohydrate temperature ( $-0^\circ.7$ ), as it was found that the water from a mixture of water and ice would not keep the temperature of the tube as low as  $0^\circ$ . The final rotation was obtained by adding to the solution a drop of ammonia which so greatly accelerated the rate of change of rotation that a constant value was obtained in half an hour.

#### MULTIROTATION AT $0^\circ$ OF A FRESHLY PREPARED HYDRATE SOLUTION.

Time (in hours).	Specific rotation calculated for $C_{12}H_{22}O_{11}$ .	$(k_1 + k_2)$ or $\frac{1}{t} \log_{10} \frac{r_0-r_\infty}{r-r_\infty}$ .
0	89.13	.....
1	86.87	0.0299
2	84.96	0.0284
3	82.79	0.0299
4	80.79	0.0306
5	79.14	0.0303
6	77.48	0.0299
7	75.84	0.0308
8	74.45	0.0307
9	73.02	0.0310
10	72.06	0.0303
11	70.71	0.0308
$\infty$	55.16	.....

Average, 0.0302

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

<sup>2</sup> *Ann. chim. phys.* (7), 30, 422-432 (1903).

## MULTIROTATION AT 0° OF A FRESHLY PREPARED ANHYDRIDE SOLUTION.

Time (in hours).	Specific rotation calculated for $C_{12}H_{22}O_{11}$ .	$(k_1 + k_2)$ or $\frac{1}{t} \log_{10} \frac{r_0 - r_\infty}{r - r_\infty}$ .
0	39.6 <sup>1</sup>	.....
2	41.6	0.0298
3	42.6	0.0309
4	43.4	0.0306
5	44.2	0.0303
6	44.9	0.0300
7	45.7	0.0308
8	46.3	0.0305
9	46.9	0.0304
10	47.6	0.0312
$\infty$	55.2	.....

Average, 0.0305

These experiments again show that the velocity-constant of the change in rotation at constant temperature is the same for both hydrate and anhydride, and, together with the earlier ones, prove conclusively that the multirotaion of this sugar is due to a change in its state of hydration.

## III. THEORY OF THE MAXIMUM RATE OF SOLUTION.

On account of the slowness at room temperature of the hydration and dehydration of milk-sugar in solution, it is possible to measure a new kind of rate of solution, namely, the rate at which the concentration of the solution increases when it is kept continually saturated by vigorously shaking a large excess of solid with water. This rate will be here called the maximum rate of solution, since it cannot be further increased by increasing the contact between the solid and liquid phases. The concentration of the saturated solution first formed is called the "initial solubility"; it corresponds to the solubility of the hydrate when it alone is present in the solution. That this initial solubility is a definite concentration, independent of the amounts of the phases and capable of accurate measurements, is shown by the following experiments, where varying amounts of solid milk-sugar hydrate were rotated in the apparatus described by Noyes<sup>2</sup> at 0° for ten minutes with 50 grams of water under uniform conditions of fineness of the solid and rate of rotation. The concentrations are uniformly expressed as millimols  $C_{12}H_{22}O_{11}$  to 100 grams water. The analy-

<sup>1</sup> This value is not the specific rotation of the pure anhydride because the substance contained a small, but not definitely known, amount of hydrate.

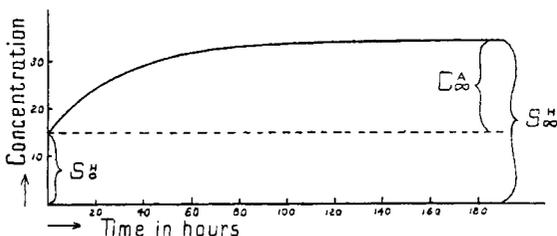
<sup>2</sup> *Ztschr. phys. Chem.*, 9, 606 (1893).

ses of these and the subsequent solutions were made by filtering the solution without evaporation during the filtering, weighing the resulting solution in the pipette, evaporating it to dryness and weighing the residue, which consists of a mixture of the two anhydrides and has the composition  $C_{12}H_{22}O_{11}$ . In filtering and weighing the solutions, a shortened pipette with a cock and a ground glass cap was used, and good results were obtained in the filtration by slipping a 2 cm. long piece of tightly fitting rubber tubing over the ground end of the pipette and stuffing some cotton into the end of this tubing.

Grams solid hydrate.	Concentration of solution.
3	12.09
5	14.27
10	14.70
30 <sup>0</sup>	14.78
30 <sup>1</sup>	14.80

From these experiments, the initial solubility of milk-sugar hydrate at  $0^\circ$  is 14.80 millimols per 100 grams water.

It was found, on long continued rotation of the large excess of hydrate with water at  $0^\circ$ , that the concentration of the solution slowly increases from 14.80, the initial solubility, at a constantly diminishing rate, to 34.82, at which it remains constant. This last limiting value may be designated the final solubility.



The obvious interpretation of this increase in solubility is that the initial solubility, 14.80, is the concentration of hydrate in solution, and that the total increase in solubility,  $34.82 - 14.80$ , is the concentration of anhydride that is in equilibrium in solution with the 14.80 millimols of hydrate. These relations are illustrated graphically by the accompanying illustration.

According to this interpretation the rate of increase in the solu-

<sup>1</sup> Rotated for fifteen minutes instead of ten minutes.

bility  $S_H$  of the solid hydrate is the same as the rate of formation of anhydride, which is

$$\frac{dS_H}{dt} = \frac{dC_A}{dt} = k_1 S_0^H - k_2 C_A, \quad (3)$$

where  $S_0^H$  denotes the concentration of hydrate in solution, which is constant and equal to the initial solubility of the solid hydrate,  $C_A$  denotes the concentration of anhydride in solution at the time  $t$ , and  $k_1$  and  $k_2$  are the same quantities that occurred in equation (2)—the velocity-constants of the two opposing reactions.

The integral of this expression is

$$\frac{1}{t} \log \frac{K S_0^H}{K S_0^H - C_A} = k_2, \quad (4)$$

where  $K = \frac{k_1}{k_2}$  and  $C_A = 0$  when  $t = 0$ .

When the final solubility ( $S_\infty^H$ ) is reached,  $\frac{dC_A}{dt} = 0$  and hence from (3)

$$K = \frac{k_1}{k_2} = \frac{C_A^\infty}{S_0^H} = \frac{S_\infty^H - S_0^H}{S_0^H}.$$

If  $S_H$  denotes the concentration of the saturated solution at the time  $t$ ,  $C_A = S_H - S_0^H$ . When these values of  $K$  and  $C_A$  are substituted in (4) there results

$$\frac{1}{t} \log \frac{S_\infty^H - S_0^H}{S_\infty^H - S_H} = k_2.$$

This is the expression of the law governing the maximum rate of solution of milk-sugar hydrate.

The analogous maximum rate of solution when the anhydride<sup>1</sup> is the solid phase is

$$\frac{1}{t} \log \frac{S_\infty^A - S_0^A}{S_\infty^A - S_A} = k_1.$$

#### IV. EXPERIMENTS ON THE RATE OF SOLUTION OF MILK-SUGAR HYDRATE.

In the following tables are given the data concerning the maximum rate of solution of milk-sugar hydrate at  $0^\circ$ ,  $15^\circ$  and  $25^\circ$ . The time is expressed in hours, and the concentration in millimols  $C_{12}H_{22}O_{11}$  per 100 grams water. The sugar used in these ex-

<sup>1</sup> The experiments upon the anhydride are not concluded, and all that can be said with certainty is that the initial solubility of this substance at  $0^\circ$  is quite large, near 125 millimols per 100 grams water.

periments was carefully recrystallized, and in some of the experiments very pure "conductivity" water was employed, but the rate in this water was the same as that obtained with the usual distilled water of the laboratory. The values of the final solubility were obtained by continued rotation for a week.

Temp- erature.	Time ( <i>t</i> ) (in hrs.)	Concentration of solution ( $S_H$ ).			$\log_{10} \frac{S_H - S_0^H}{S_H - S_H}$
		1st series.	2nd series.	Mean.	
0°	0	14.81	14.78	14.80	.....
	12	20.63	20.61	20.62	0.0124
	24	24.68	24.95	24.81	0.0125
	36	27.73	27.64	27.68	0.0124
	48	29.90	30.08	29.99	0.0129
	72	32.64	32.43	32.53	0.0131
	∞	34.72 <sup>1</sup>	34.92 <sup>2</sup>	34.82	.....
				Average, $k_2$ ,	0.0127
15°	0	...	...	(20.9) <sup>3</sup>	.....
	1	24.9	24.6	24.8	0.0632
	2	28.6	28.4	28.5	0.0615
	3	31.5	31.4	31.4	0.0656
	5	36.5	36.3	36.4	0.0651
	7	40.1	39.8	40.0	0.0675
	10	43.5	43.3	43.4	0.0660
	∞	50.1 <sup>2</sup>	49.2 <sup>1</sup>	49.7	.....
			Average, $k_2$ ,	0.0648	
25°	0	...	...	(25.3) <sup>3</sup>	.....
	0.5	32.6	32.8	32.7	0.188
	1.0	38.4	38.8	38.6	0.186
	1.5	43.3	43.1	43.2	0.184
	2.0	47.2	47.0	47.1	0.184
	3.0	52.7	52.5	52.6	0.182
	4.0	56.6	56.4	56.5	0.185
	∞	63.3 <sup>1</sup>	63.5 <sup>2</sup>	63.4	.....
			Average, $k_2$ ,	0.185	

These values of the velocity constant  $k_2$  for the three temperatures agree with the relation

$$\frac{d \log k_2}{dT} = \frac{A}{T^2}, \text{ where } T \text{ is the absolute temperature.}$$

The integrated form of this equation,  $\log k_2 = b - \frac{a}{T}$ , gives for

<sup>1</sup> From undersaturation.

<sup>2</sup> From supersaturation.

<sup>3</sup> Obtained by extrapolation.

the three values,  $\log_{10} k_2 = 12.016 - \frac{3800}{T}$ . The values of  $k_2$  obtained from this formula, are compared in the table below with the observed values.

Temperature.	$k_2$ observed.	$k_2$ calculated.
0	0.0127	0.0125
15	0.0648	0.0664
25	0.185	0.184

For an increase of temperature of  $10^\circ$  this rate is accelerated 2.8 fold.

The three tables above show the maximum rate of solution in pure water. On account of the fact that the rate of change of rotation of milk-sugar solutions is greatly accelerated by bases<sup>1</sup> it seemed highly probable that the rate of solution would also be accelerated, and this was found to be the case. For example, in a thousandth-normal ammonia solution the following maximum rate of solution was observed at  $0^\circ$  for the hydrate.

Time (in hours).	Concentration.	$\frac{1}{t} \log_{10} \frac{S_{\infty}^H - S_0^H}{S_{\infty}^H - S^H}$ .
0	14.80	.....
3	18.59	0.0308
6	21.65	0.0308
10	24.71	0.0302
14	26.91	0.0294
19	28.78	0.0281
$\infty$	34.56	.....
		Average, 0.030

By the use of thousandth-normal ammonia the rate is increased 2.4 fold.

This catalyzing effect of foreign substances upon the rate of attainment of equilibrium can be used in obtaining supersaturated solutions whose realization would otherwise be out of question<sup>2</sup> on account of the fact that the reaction is so slow that the solution would have to be kept supersaturated with respect to the stable solid phase for many hours, sometimes even days, before the desired final solubility of the unstable solid phase would be reached; thus, in case the anhydride is rotated with water at  $0^\circ$ , the concentration of the immediately resulting solution is about 125 and would slowly increase during a week to several fold this amount.

<sup>1</sup> Urech: *Ber. d. chem. Ges.*, **15**, 2130-2133 (1882), Cf. especially; Trey: *Ztschr. phys. Chem.*, **46**, 620-719 (1903).

<sup>2</sup> Cf. Meusser: *Ber. d. chem. Ges.*, **34**, 2436 (1901).

if it were not for the fact that as soon as the concentration of the hydrate produced by the reaction becomes greater than its initial solubility (14.80), the solution becomes supersaturated with respect to the solid hydrate and, on further stirring, this soon precipitates out. By the use of tenth-normal ammonium hydroxide solution, instead of water, the hydration reaction can be so greatly accelerated that the final solubility of the anhydride can be obtained in a few minutes, before crystallization of the hydrate has begun. In all such cases of slow maximum rate of solution of an unstable substance the use of a catalyzer may be of service, because when the maximum rate is highly accelerated it is necessary to preserve the supersaturation with respect to the stable form for only a few minutes in order to reach final saturation with respect to the unstable form. If the slowness of attainment of saturation is caused by a hydration reaction, bases, and in less measure, acids, will probably be efficient catalyzers.

#### V. THE EQUILIBRIUM BETWEEN THE HYDRATE AND ANHYDRIDE.

It has been shown in Section 3 that  $K = \frac{S_{\infty}^H - S_0^H}{S_0^H} = \frac{C_A}{S_0^H}$

The values of  $K$  for  $0^{\circ}$ ,  $15^{\circ}$  and  $25^{\circ}$ , calculated from the initial and final solubilities of the hydrate, are the following:

Temperature.	Initial solubility $S_0^H$ .	Final solubility $S_{\infty}^H$ .	Equilibrium ratio $K$ .
$0^{\circ}$	14.80	34.82	1.35
$15^{\circ}$	20.9	49.7	1.44
$25^{\circ}$	25.3	63.4	1.51

It will be seen from the values of  $K$  that the degree of hydration greatly decreases with rise of temperature.

#### VI. THE MAXIMUM RATE OF PRECIPITATION OF MILK-SUGAR HYDRATE.

Let the supersaturated solution contain  $C_H$  hydrate and  $C_A$  anhydride in equilibrium,  $C_H$  being necessarily greater than the initial solubility of the hydrate,  $S_0^H$ . When a large excess of solid hydrate is mixed with this solution at a low temperature, the immediate result is the precipitation of some hydrate until the concentration of hydrate in the solution decreases from  $C_H$  to  $S_0^H$ . This precipitation disturbs the existing equilibrium between hydrate and anhydride, and as a consequence hydrate begins to be formed slowly in solution from anhydride. It is obvious that

after the initial precipitation has occurred, the subsequent rate of precipitation cannot be greater than the rate at which hydrate is produced in solution from anhydride. This subsequent rate of precipitation can be deduced by the same considerations that were presented in discussing the maximum rate of solution. It is assumed that the surface of the solid is so large, the stirring is so thorough and the temperature is so low that the velocity of the physical process of crystallization of the dissolved hydrate as solid hydrate is incomparably greater than the velocity of the chemical process which produces hydrate in solution from anhydride. Under these conditions, after the initial precipitation has occurred, the velocity of the subsequent precipitation reaches a maximum and is the same as the velocity with which hydrate is formed or anhydride destroyed in solution; namely, as before:

$$\frac{dS_H}{dt} = \frac{dC_A}{dt} = k_1 S_O^H - k_2 C_A.$$

The integral of this expression is

$$\frac{1}{t} \log \frac{C_0 - (1 + K) S_O^H}{C_A - K S_O^H} = k_2,$$

where  $C_0$  denotes the initial concentration of a solution saturated with respect to hydrate, but containing an excess of anhydride over

that corresponding to equilibrium, and  $K = \frac{k_1}{k_2}$ . Now  $K = \frac{S_\infty^H - S_0^H}{S_0^H}$ , and  $C_A = C_t - S_0^H$ , where  $C_t$  denotes the concentration of the solution at the time  $t$ . When these values of  $K$  and

$C_A$  are substituted in the expression above, there results

$$\frac{1}{t} \log \frac{C_0 - S_\infty^H}{C_t - S_\infty^H} = k_2.$$

The following experiment was made to test this rate of precipitation. A saturated solution of hydrate in warm water was prepared, cooled at  $0^\circ$  and rotated with as large an excess of solid hydrate as could be conveniently used. After about twenty minutes the solution was analyzed and its concentration taken as  $C_0$ , the time of the removal of the following portions being measured from the moment of this first removal. The concentration fell as follows:

Time (in hours).	Concentration.	$\frac{1}{t} \log_{10} \frac{C_0 - S_{\infty}^H}{C_t - S_{\infty}^H} = k_2.$
0	64.62 (C <sub>0</sub> )	.....
12	57.01	0.0107
24	51.37	0.0106
36	47.61	0.0105
48	44.65	0.0100
∞	34.82	.....
Average,		0.0105

The value of  $k_2$  is sufficiently constant and agrees fairly well with the value of  $k_2$  obtained from the maximum rate of solution (0.013). Probably the small difference between the two values is due to the fact that the rate of the physical precipitation was not great enough to keep the concentration of hydrate in solution from somewhat exceeding the value  $S_{\infty}^H$ .

VII. COMPARISON OF THE VELOCITY-CONSTANTS DERIVED FROM THE RATE OF CHANGE OF ROTATION AND FROM THE MAXIMUM RATE OF SOLUTION.

The values of  $K = \frac{k_1}{k_2}$  being known from the initial and final

solubilities, and the value of  $k_2$  being known from the maximum rate of solution, the values of  $k_1$  and of  $(k_1 + k_2)$  can be at once found. In the following table are given the values of  $(k_1 + k_2)$  obtained in the one case in this way from the preceding solubility experiments and in the other case from polarimetric observations of the rate of multirotation. The polarimetric data for 0° are given in Section II of this article; while for 15° and 25° the values are taken from my earlier article,<sup>1</sup> with the unit of time changed from the minute to the hour.

Temperature.	Solubility experiments.				Multirotation observations. $k_1 + k_2.$
	$k_2.$	$\frac{k_1}{k_2} = K.$	$k_1.$	$k_1 + k_2.$	
0°	0.0127	1.35	0.0172	0.0299	0.0304
15°	0.0648	1.44	0.0933	0.158	0.178
25°	0.185	1.51	0.279	0.464	0.475

The agreement in the values of  $(k_1 + k_2)$ , obtained by the two independent methods, is satisfactory.

<sup>1</sup> *Ztschr. phys. Chem.*, **44**, 490.

## VIII. THE ABSOLUTE VELOCITY OF HYDRATION AND DEHYDRATION.

In a milk-sugar solution which has reached equilibrium the actual velocities of the two opposed and balancing reactions of hydration and dehydration can be readily calculated.<sup>1</sup> Thus, in the final saturated solution of the hydrate, the rate of formation of hydrate is

$$\frac{\partial C_H}{\partial t} = k_2 C_\infty^A,$$

where  $C_\infty^A$  is the concentration of anhydride corresponding to the final solubility of the solid hydrate. For the three temperatures,  $0^\circ$ ,  $15^\circ$  and  $25^\circ$ , the values of these quantities for the saturated solutions are the following:

Temperature.	$C_\infty^A$	$k_2$	$\frac{\partial C_H}{\partial t}$	Per cent. sugar undergoing change in one hour.
$0^\circ$	20.02	0.0127	0.254	1.46
15	28.8	0.0648	1.87	7.52
25	38.1	0.185	7.05	22.2

The calculation of the values given in the last column may be explained by an example. In equilibrium with 100 grams water at  $0^\circ$  are 20.02 millimols anhydride and 14.80 millimols hydrate (see Section V). In one hour in this solution are formed  $(20.02 \times 0.0127) = 0.254$  millimols hydrate, and of necessity the same amount of anhydride is also formed during the same time. The sugar which undergoes change in one hour is thus 0.508 millimols, which is 1.46 per cent. of 34.82, the total sugar in the solution.

## IX. THE MAXIMUM RATE OF SOLUTION IN RELATION TO THE EQUILIBRIUM OF DISSOLVED SUBSTANCES IN GENERAL.

The method of studying the equilibrium of dissolved substances which has been presented in this article, is applicable to any kind of reaction which proceeds slowly in solution, and is independent of special analytical or physical methods for determining separately the concentrations of the different substances involved; for it is only the change of the total amount of substance in solution that has to be measured. The study of slowly progressing hydration reactions and isomeric transformations are two special applications of the method.

<sup>1</sup> Cf. Nernst: "Theoretische Chemie," 4th edition, p. 573.

It is true that thus far but few reactions of this character have been discovered; for unfortunately, in the usual method of determining solubilities, no attention is given to the detection of a possible maximum rate of solution, and the frequently observed sluggishness of solutions in reaching final saturation has always been looked upon as an unpleasant experimental difficulty, whereas if the slowness is caused by the occurrence of a chemical reaction it can be turned to valuable service. From indications found in the literature it appears that cobalt and nickel iodates and anhydrous manganous and thorium sulphates possess slow maximum rates of solution. It is highly probable that all the multirotating sugars have such a rate. Probably the chromium salts are to be included, because the change of color of the solutions from violet to green proceeds slowly at room temperature.

Several substances were studied to determine whether they show a measurable maximum rate of solution even at  $0^{\circ}$ ; namely, iodine in water, in alcohol and in ether; barium nitrate, potassium sulphate and sodium chloride in water. The results of these experiments show that these substances can be made to form their final saturated solutions at  $0^{\circ}$  from undersaturation in less than fifteen minutes, if a large excess of solid is used, and thorough mixing of the solid and liquid phases is provided for. In the case of the iodine solutions the concentration was estimated by the color, the solutions which resulted from fifteen minutes rotation not differing perceptibly from solutions which were rotated for several hours. The data concerning the three salts are given in the following tables, where the time elapsing between the mixing of the salt with the water and the removal of a portion of the solution for analysis is given in the first column, and the concentration of the corresponding solution in grams anhydrous salt in 100 grams water is given in the other columns.

Time after mixing.	Potassium sulphate. Concentration.		Barium nitrate. Concentration.	
	I.	II.	I.	II.
10 minutes	....	7.31	....	4.90
20 minutes	7.32	....	4.91	....
24 hours	7.36	7.40	4.89	4.91
48 hours	7.36	7.32	....	....
From supersaturation	7.34		4.90	

In the case of sodium chloride the concentration was found to be 35.7 grams per 100 grams water fifteen minutes after mix

ng, while its solubility at  $0^{\circ}$ , as ordinarily determined, is, according to the work of six different investigators,<sup>1</sup> 35.5-35.7.

It is evident from these results that if iodine and these salts form compounds with the solvents, the reactions proceed with high velocity even at  $0^{\circ}$ .

It has been known for generations that arsenious oxide forms its saturated solution slowly, even in the presence of large quantities of the solid. This fact has led to the hypothesis that the slowness of the rate of solution is caused by a slowly progressing hydration. If this were the explanation of the slowness of attainment of saturation, arsenious oxide would unquestionably show a low maximum rate of solution independent of the contact between solid and solution, similar to that observed with milk-sugar. A number of experiments have shown conclusively, however, that such a measurable maximum rate of solution does not exist. In these experiments about 80 grams of recrystallized arsenious oxide, 50 grams of water or of supersaturated solution and a handful of glass beads were vigorously shaken by hand in a bottle immersed in a thermostat at  $25^{\circ}$ . The bottle and the glass beads were previously treated several days with strong chromic acid in order to prevent their giving up alkali to the solution, and thereby accelerating the rate of solution. After fifteen minutes shaking the concentrations of the solutions obtained from undersaturation in three experiments were 20.6, 20.6 and 20.5 grams  $\text{As}_2\text{O}_3$  per liter solution. Likewise from supersaturation the values 20.6, 20.5 and 20.7 were obtained after shaking for fifteen minutes. The concentration of the supersaturated solutions at the start was 50. The solubility of  $\text{As}_2\text{O}_3$  at  $25^{\circ}$  is, therefore, 20.6 grams  $\text{As}_2\text{O}_3$  per liter of solution, which agrees with the value (20.4) obtained by Bruner and Tolloczko<sup>2</sup> after eighteen hours stirring. In other experiments that I have made where the relative amount of solid oxide was small, or where the mixing of the solid and liquid was not aided by the presence of heavy foreign bodies, such as glass beads or garnets, several hours were necessary for the attainment of saturation, and the rate varied with the relative amount of solid present; but, as is shown by the experiments here given, the necessary precautions for a thorough contact between the two phases are taken, the saturated solution can be obtained

<sup>1</sup> Comey: "Dictionary of Solubilities," p. 376.

<sup>2</sup> *Ztschr. anorg. Chem.*, **37**, 456 (1904).

both from supersaturation and from undersaturation in less than fifteen minutes. The slowness with which arsenious oxide usually dissolves is, therefore, not due to a slow chemical reaction. It seems likely that under ordinary conditions the oxide is only slowly wetted by the water on account of a film of air which persistently adheres to the surface of the oxide and prevents the intimate contact of the solid and liquid phases which is necessary for the process of solution.

#### X. SUMMARY.

The results of this investigation may be summarized as follows.

Anhydrous milk-sugar was obtained in large crystals by evaporating a solution of the hydrate above  $95^{\circ}$ , while at room temperature the hydrate itself separated. This shows that there is a transition-temperature somewhere between these two points.

Measurements were made of the change in rotatory power at  $0^{\circ}$  of freshly prepared solutions of both the hydrated and anhydrous milk-sugar; in each case the rate was accurately expressed by the logarithmic formula applicable to incomplete reactions of the first order, and, as the theory requires, the constants of the formula were found to be identical in the two cases. These results are further proof that the multirotation of this sugar is due to change in its state of hydration in solution.

It was found when a large excess of milk-sugar hydrate agitated with water there is formed within a few minutes a solution whose concentration (called the initial solubility) is independent of the quantity of solid substance used, but that, owing to gradual dehydration of the dissolved hydrate, this concentration slowly increases up to a constant limiting value (called the final solubility), at which the solution contains that quantity of anhydrous sugar which is in equilibrium with the constant quantity of hydrate corresponding to the initial solubility, which the solution always contains. Therefore, whenever a substance exhibits this phenomenon of a rate of solution independent of the contact between the solid and liquid phases (here designated therefore a maximum rate of solution), and shows an initial and final solubility, it is possible to derive the velocity and equilibrium of the chemical change that is taking place in the solution even in cases where the substances involved cannot be separately determined by any chemical or physical method.

Measurements of this maximum rate of solution were made with milk-sugar hydrate at  $0^\circ$ ,  $15^\circ$  and  $25^\circ$ , and found to correspond to the requirements of the Mass-action Law. The change in the rate of hydration for these two intervals of temperature is accurately expressed by the usual equation,  $\frac{d \log k}{dT} = \frac{A}{T^2}$ , and the increase in rate for a rise in temperature of  $10^\circ$  is 2.8 fold. The reaction is greatly accelerated by bases, as was previously observed by Urech and by Trey, for the constant was found to be 2.4 fold greater in a 0.001 normal ammonium hydroxide solution than in pure water.

The rate of precipitation of the solid hydrate from a solution saturated with it, but containing an excess of the anhydrous sugar over that corresponding to equilibrium, was also measured, and the velocity-constant was found to agree fairly well with that derived from the rate of solution experiments.

The equilibrium ratio ( $K$ ) of anhydrous to hydrated milk-sugar has been calculated from the initial solubility ( $S_0^H$ ) and final solubility ( $S_x^H$ ) of the solid hydrate by the expression  $K = (S_x^H - S_0^H)/S_0^H$  and was found to have the value 1.35 at  $0^\circ$ , 1.44 at  $15^\circ$  and 1.51 at  $25^\circ$ , showing that the degree of hydration of the sugar in solution decreases greatly with rising temperature. The initial solubilities at these three temperatures are 14.8, 20.9 and 25.3 millimols per 100 grams water, and the corresponding final solubilities are 34.82, 49.7 and 63.4.

The separate velocity-constants ( $k_1$  and  $k_2$ ) of the two opposing reactions of hydration and dehydration can be derived from these solubility experiments, while from the experiments on the multi-rotation their sum ( $k_1 + k_2$ ) is obtained. It has been shown that the two methods give concordant values.

A calculation from the velocity-constant of the amount of sugar that undergoes hydration and dehydration in one hour in the equilibrium mixture showed this to be 1.5 per cent. at  $0^\circ$  and 22.2 per cent. at  $25^\circ$  of the total quantity present.

The general applicability of the principle of the maximum rate of solution to the study of hydration and other chemical changes in solution has been discussed. A few cases from the literature are cited in which the phenomenon probably exists, and experiments upon the rate of solution at  $0^\circ$  of barium nitrate, potassium

sulphate, sodium chloride and iodine in water, and of iodine in alcohol and in ether, and at 25° of arsenious oxide in water are described. Not one of these substances gives evidence of any slow chemical change accompanying the process of solution. Even in the case of the arsenious oxide, in regard to which a contrary opinion has long prevailed, this has been clearly demonstrated by the dependence of the rate of solution on the surface of contact between the solid and solution and by obtaining in fifteen minutes, with very thorough mixing, a value of the solubility, 20.6 grams  $As_2O_3$  per liter, substantially identical with that obtained by Bruner and Tolloczko after eighteen hours stirring.

BOSTON, MASS., July, 1904.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 81.]

### THE ATOMIC WEIGHT OF TUNGSTEN.

BY EDGAR F. SMITH AND FRANZ F. EXNER.

Received July 26, 1904.

THE atomic weight of tungsten having received attention at various times, during recent years, in this laboratory, we were induced to institute a new series of experiments in this direction inasmuch as we had, after much labor, obtained pure tungstic acid<sup>1</sup> from which were prepared large quantities of pure hexachloride and also pure metal. Roscoe has stated that when tungsten hexachloride is directly decomposed with water and the resulting acid ignited to oxide, the latter will contain chlorine which cannot be expelled by heat. We had hoped to pursue this method, but as it had the condemnation of so high an authority the hexachloride was introduced into freshly distilled ammonia water, contained in a weighed platinum dish, with the expectation of eventually getting ammonium tungstate and chloride which would leave the trioxide upon ignition. Experience showed that the quantity of the resulting ammonium chloride was so great that even with the most careful ignition there was much danger of expelling mechanically appreciable amounts of the oxide. Nor was it forgotten that it is very doubtful whether from such a mixture the chlorine could be completely removed by heat.

<sup>1</sup> *Proc. Am. Phil. Soc.*, 43, 123.