

of the circuit, we obtain for  $m$  the approximate value 0.005, showing that the mass of the carrier in metals is probably less than  $1/200$  that of the hydrogen atom.

### 5. Conclusions.

We believe that these experiments have set a limit for the mass of the carrier in metals considerably lower than any previous experimental work.<sup>1</sup> We see, moreover, no insuperable difficulties in carrying the sensitiveness of our method to a point where the electron, if it really is the carrier of electricity in metals, with a mass  $1/1800$  that of the hydrogen atom, should produce an appreciable effect. One of our main purposes in giving this brief description of our work on metallic conductors is the hope that we may be able to obtain funds for carrying this research to completion, a consummation which for many years has been the desire of one of the present authors.<sup>2</sup>

A tenfold increase in the accuracy of the observations would apparently be sufficient for the desired purpose, and it seems probable that this could be obtained if we could eliminate the accidental effects produced by uncontrollable variations in the earth's magnetic field and those produced by the small tipping of the disk which unavoidably occurs when the brake is applied. Probably the best way to accomplish this result will be to try to construct efficient screens for cutting out the earth's magnetic field from the apparatus. With the help of such a magnetic screen and some increase in the sensitiveness of the apparatus, which could be obtained by increasing the length of wire on the disk and its rim velocity, as well as obtaining a more sensitive galvanometer arrangement, it should be quite possible to solve the problem.

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## ON THE TRANSITION TEMPERATURES OF THE HYDRATES OF SODIUM CARBONATE AS FIXED POINTS IN THERMOMETRY.

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Recent investigations conducted in this laboratory, and confirmed elsewhere, have shown that the transition temperatures of hydrated crystalline salts provide excellent means for fixing definite points upon

<sup>1</sup> As far as we know, the only quantitative experiments reported in the literature are those of Nichols of which we have already spoken. Maxwell ["Treatise on Electricity and Magnetism," 3d edition (1892), Vol. II, et seq.] and Lodge ["Modern Views of Electricity" 3rd edition (1907), p. 89] have both attempted, without success, to obtain effects dependent on the mechanical momentum which might be associated with the passage of a current of electricity, but give no figures as to the sensitiveness of their methods.

<sup>2</sup> See Tolman, *Science*, 37, 192 (1913).

the thermometric scale.<sup>1</sup> The transition temperature of the decahydrate of sodium sulfate at  $32.383^{\circ}$  was first selected, for many reasons; and it has proved to be the most convenient of any as yet studied. Although sodium sulfate is thus to be preferred if only a single point near the ordinary temperature of the room is sought, obviously the knowledge of other points would be desirable. Accordingly, a number of other substances have been investigated with regard to their suitability for the purpose.

Among the salts suggested in the second Harvard paper (1899) was sodium carbonate. At that time little was known concerning the transition temperatures of the various hydrates of this salt; accordingly, a preliminary determination of one of the points was made, and it was shown that satisfactory constancy was attainable.<sup>3</sup> The intention was to study this and other points more carefully, but soon afterwards several investigations, especially those by Epple,<sup>4</sup> Ketner,<sup>5</sup> and Wells and McAdam,<sup>6</sup> largely covered the ground. These researches, especially the last, have shown clearly that the stable hydrates are the following: between  $-2.1^{\circ}$  and  $+32.0^{\circ}$ , the decahydrate; between  $32.0^{\circ}$  and  $35.4^{\circ}$ , the heptahydrate; and above  $35.4^{\circ}$ , the monohydrate. Wells and McAdam found also that the transition between the decahydrate and the monohydrate is  $32.96^{\circ}$ , and their diagram shows very clearly the situation.

Although the work of Wells and McAdam was very carefully done, it seems desirable to verify these points upon as many accurate instruments as possible, and also to determine how well fitted they may be for the standardizing of thermometers. If they are easily reproduced, the three transition temperatures would form an exceedingly useful means of

<sup>1</sup> T. W. Richards, *Am. J. Sci.*, [4] 6, 201 (1898); Richards and Churchill, *Proc. Am. Acad.*, 34, 277 (1899); Richards and Wells, *Ibid.*, 38, 435 (1906); *Ibid.*, 38, 431 (1902); Richards and Wrede, *Ibid.*, 43, 343 (1907); Richards and Kelley, *Ibid.*, 47, 171 (1911). Four of these papers are to be found in full in the *Z. physik. Chem.*, the references being respectively, 26, 690 (1898); 28, 313 (1899); 43, 465 (1903); 61, 313 (1908). The work on manganese chloride was finished by Dr. Wrede and one of us at the University of Berlin. The sixth paper appeared also in *THIS JOURNAL*, 33, 847 (1911). Jeannel (*Compt. rend.*, 62, 834 (1866)) suggested long ago the use of a transition point of hydrated sodium acetate for testing and standardizing thermometers, but no one seems ever to have followed up the suggestion or to have actually used it in this way. The fact that such a suggestion concerning any crystalline salt had been made before 1898 has been unknown to the present authors until now. We are indebted to Professor W. Lash Miller for his having called our attention to it.

<sup>2</sup> Dickinson and Mueller (*C. A.*, 2, 7 (1908)) found  $32.384^{\circ}$ , confirming as nearly as could be expected the value found in this laboratory.

<sup>3</sup> Through a typographical error the initial hydrate was stated to contain 10 H<sub>2</sub>O instead of 7 H<sub>2</sub>O (*Proc. Am. Acad.*, 34, 278 (1909)), but this error was eliminated when the paper was reprinted in the *Zeitschrift für physikalische Chemie*, two months later.

<sup>4</sup> Inaug. diss., Heidelberg, 1899.

<sup>5</sup> *Z. physik. Chem.*, 39, 645 (1902).

<sup>6</sup> *THIS JOURNAL*, 29, 721 (1907).

calibrating a Beckmann instrument, since they cover three and one-third degrees, with an intermediate point. The present paper is concerned with the redetermination of the lowest of the three points.

Purification of sodium carbonate is conveniently conducted by recrystallization. The purest "chemically pure" material of commerce was recrystallized ten times, the transition temperature of each successive group of crystals being taken; the purification was continued until no further change occurred in the transition temperature. The crystallization was conducted by cooling from about  $40^{\circ}$  to  $10^{\circ}$ ; and centrifugal draining helped to eliminate the mother liquor. During the last three crystallizations the substance came into contact only with silver or platinum.

Pure sodium carbonate is not easily kept without deterioration, because it, of course, attracts any trace of hydrochloric or sulfuric or even carbonic acid which may be in the air, either through leakage from stoppers of the laboratory reagent bottles or from the products of combustion of illuminating gas. If the best results are to be obtained from the salt, it must be protected with the utmost care, or better, used at once. We have often found that material even preserved over lime or potash for as short a time as twenty-four hours, may change several thousandths of a degree as to its transition temperature, unless the desiccator is well sealed. One of the samples (F), having been kept under a bell-jar not perfectly tight, had its transition point lowered as much as  $0.02^{\circ}$  in three weeks by impurities taken from the laboratory air. That the salt will keep perfectly pure, when properly guarded, is proved by the very constant results obtained from the purest samples, to be recounted in the following pages.

The water of crystallization in the various phases of the salt was determined by titrating weighed amounts of the roughly pulverized crystals (dried in air until just to the point of efflorescing) by means of half normal hydrochloric acid, methyl orange being used as the indicator. The substance employed in the final determinations showed an average molecular weight of 281, the theoretical molecular weight of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  being approximately 286. After these crystals had been entirely transformed at  $32.02^{\circ}$  into the other phase in equilibrium at that temperature, the crystals constituting this new phase were separated from the supernatant mother liquor, pressed on warm filter paper in a warm room at about this temperature and analyzed as before. The resulting crystals, when freshly prepared, were found to have a molecular weight averaging 234, leaving no doubt that the phase in question was the heptahydrate, which has a theoretical molecular weight of 238. Pursuing the same quest further, we heated the substance for some time above  $40^{\circ}$ , when a new phase appeared which was found, after separation of the mother liquor, to have the molecular weight of 124—thus being without question the mono-

hydrate, which has this theoretical value. All of these phases, on standing, in a desiccator over a large excess of concentrated sulfuric acid for three or four weeks, give a substance having a molecular weight below 107, showing that under these conditions the water is practically all removed ( $\text{Na}_2\text{CO}_3 = 106$ ). These conclusions, except the last, all correspond with the statements of Wells and McAdam.

The successive products of the first five recrystallizations, made from distilled water in porcelain dishes, were all prepared before April 15, 1911, portions of each having been saved for the study of their transition temperatures. After an intermission of a week, two more crystallizations in porcelain were made, and then all of the seven samples were carefully compared as to their transition points.

The preliminary determination of the constancy of the transition temperature was made by means of a sensitive Beckmann thermometer in an apparatus essentially like the Beckmann freezing-point apparatus, as indicated in previous papers. The large test-tube containing the salt was surrounded by an air jacket, and this latter was immersed in a water bath, kept about  $0.3^\circ$  higher than the temperature to be observed by means of a suitable electric coil. The transition point showed a slight and steadily decreasing rise with increasing purity, until sample *E* was reached. Two subsequent recrystallizations made no further change in this value—apparently this was the purest salt which could be obtained by recrystallization in porcelain. In the meantime the crystallization was being carried further, from the purest water, in platinum; with this product another constant point  $0.001^\circ$  or  $0.002^\circ$  higher than the preceding, was soon reached. This seemed to be the maximum, and therefore the true transition point of the really pure substance.

After the ninth product (sample *I*) had had its transition point re-determined several times over a period of several weeks, it was recrystallized once more; and because the corrected reading of the Beckmann thermometer at the transition point of this material gave almost exactly the same value as the preceding, the final determination of the transition temperature was made as soon as possible.

Before the final readings are presented, a tabulated statement of the preceding results may be given; it is of interest as indicating the exact measure of the impurity eliminated in each of the successive steps. One may note that the Beckmann readings needed correction for the pressure ( $0.002^\circ$  per centimeter of barometer) and for the temperature of the emergent column ( $0.001^\circ$  per degree Centigrade). The comparison of the observed values in the second column and the corrected values in the sixth is not without interest, because it shows how erroneous may be the reading of a sensitive mercury thermometer not thus corrected. The true temperature given in the last column was obtained by adding the quantity

31.628 to each of the readings of the Beckmann thermometer; this quantity was found in the final experiments to be recorded further on.

Date. 1911.	Material of dish.	Observed.	Bar.	Cor. pres.	t° of emergent column.	Emergent column cor- rected to 25°.	True tem- perature.
Apr. 25	Porcelain	A = 0.309	764.0	0.308	27	0.306	31.934
Apr. 27	"	B = 0.352	771.0	0.350	28	0.347	31.975
Apr. 28	"	C = 0.370	760.0	0.370	28	0.367	31.995
Apr. 29	"	D = 0.380	765.0	0.379	24	0.380	32.008
Apr. 15	"	E = 0.382	760.0	0.382	19	0.388	32.016
Apr. 24	"	G = 0.382	758.0	0.382	19	0.388	32.016
Apr. 24	Platinum	H = 0.388	763.0	0.387	23	0.389	32.017
Apr. 25	"	I = 0.389	764.0	0.388	23	0.390	} 32.018
		0.395	758.0	0.395	30	0.390	
May 12	"	0.392	757.0	0.393	28	0.390	
May 13	"	J = 0.394	757.0	0.395	30	0.390	} 32.017
May 13	"	0.393	761.0	0.393	29	0.389	
May 15	"	K = 0.389	761.0	0.389	25	0.389	

Complete constancy having thus been obtained, the final temperature readings were made on very exact Baudin thermometers, 15200 and 15276, which have already been described in Harvard papers.<sup>1</sup> Every precaution was taken with the observation, which was made with a very accurate Geneva cathetometer; the thermometers were fixed in a perfectly vertical position, and many readings were made, both from the front and through the back of the stems. Thanks are due to Dr. A. W. Rowe and Dr. G. L. Kelley for their help in making additional readings of these crucial observations. The usual corrections for calibration, internal pressure, external pressure, the fundamental interval and the average ice point (likewise thus corrected) were applied, as well as further correction for the emergent column. This last was computed in the usual way, and is probably correct to within 0.001° or 0.002°. The final results are tabulated below.

After these determinations, the original Beckmann thermometer was again inserted into the mixture; it then indicated a temperature 0.001° lower than before—an almost negligible difference, perhaps due to impurities taken from the glass and the air during the several hours needed for the exact thermometric readings.

Thus, the transition from the decahydrate of sodium carbonate to the heptahydrate was found to take place at 32.017°. This value is near the reading (32.00°) found by Wells and McAdam, but decidedly higher than the result of Ketner (31.85°). The latter evidently had been less successful in purifying his substances; for impurities usually lower the transition temperature.

<sup>1</sup> *Proc. Am. Acad.*, 38, 434 (1902); *Z. physik. Chem.*, 43, 467 (1903).

## THE TRANSITION TEMPERATURE OF SODIUM CARBONATE: DEKAHYDRATE-HEPTAHYDRATE.

Designation of thermometer.	15276.	15200.
Observed reading.....	32.187	32.257
Cor. for calibration.....	+ 0.006	— 0.005
Cor. for interior pressure.....	+ 0.056	+ 0.038
Cor. for exterior pressure.....	+ 0.001	+ 0.001
Cor. for fundamental interval.....	+ 0.001	+ 0.022
Cor. for corrected ice point.....	— 0.154	— 0.212
Cor. for emergent thread <sup>1</sup> .....	+ 0.023	+ 0.020
	32.120	32.121
Cor. to hydrogen scale.....	— 0.104	— 0.104
	32.016	32.017
Final value.....	32.016	32.017

Although this point is quite sufficiently sharp to serve as a means of standardizing thermometers, it is probable that the other two points (namely, that involving the decahydrate and monohydrate, and that involving the heptahydrate and monohydrate) are even sharper and more easily maintained, since as a rule, other things being equal, an increased latent heat of transition means increased precision. With any given salt, the larger the number of molecules of water lost in transition, the larger will usually be the latent heat of the change. The transition from the decahydrate to the heptahydrate observed in the experiment just described involves a loss of only three molecules of water, whereas that from the heptahydrate to the monohydrate means a loss of twice, and that from the decahydrate to the monohydrate three times as much.

### Summary.

In this paper one of the transition temperatures of hydrated sodium carbonate, namely, that between the decahydrate and the heptahydrate, has been carefully determined with standard instruments, and found to be  $32.017^{\circ}$  on the hydrogen scale, a value not very much above that of Wells and McAdam, who found  $32.00^{\circ}$ . Incidentally, the hydrates stable at various temperatures have been analyzed and have been found to correspond to the statements of these investigators. It is shown, moreover, that all of the hydrates lose water easily at ordinary temperatures into air dried by concentrated sulfuric acid, leaving the salt essentially anhydrous, whereas some previous experimenters have thought that one molecule of water still remained under these circumstances.

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<sup>1</sup> Twenty-four degrees of thermometer 15276 and twenty-one degrees of thermometer 15200 were exposed to the room temperature of  $26.0^{\circ}$ .