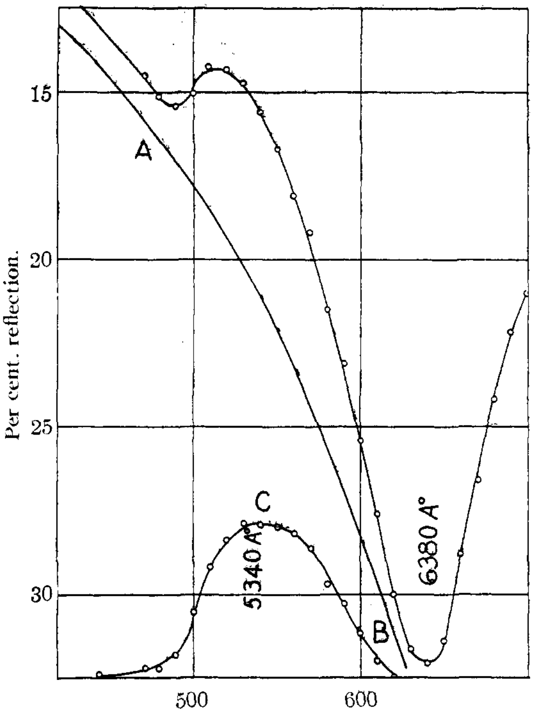

Fig. 1.—Reflection coefficient of the system KCl-$CuCl_2$ as a function of wave length (mμ).

most likely the trichlorocuproate ion since the potassium salt of this anion is known.[2] The trichlorocuproate ion does not exist in solid anhydrous cupric chloride for this substance does not show the absorption band under discussion.

Little can be said from these measurements regarding the mechanism of light absorption.

The fraction of light reflected depends on the state of subdivision of the substance and is not of any special significance. The dry powders used showed the reflections given in Fig. 2. It appears that at the reflection maximum (6400 Å.) the two salts ($CuCl_2$ and $KCuCl_3$) have about the same reflection coefficient and that no free, uncombined potassium chloride exists in the crystalline mass below mole fraction 0.5, indicating a complex KCl-$CuCl_2$ or K[$CuCl_3$].

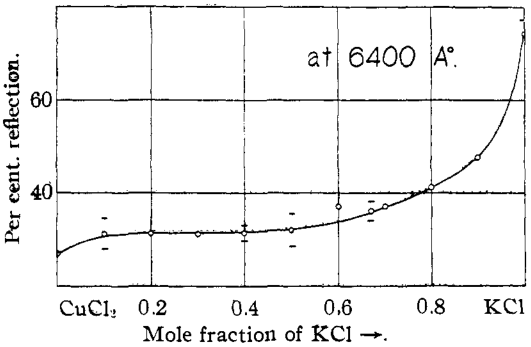

Fig. 2.—Reflection of light as a function of composition (system KCl-$CuCl_2$).

Summary

Solid anhydrous cupric chloride shows a maximum of reflection at 6404 Å. as do mixtures with dry potassium chloride. The mixtures have an absorption maximum at 5387 Å. which is ascribed to the trichlorocuproate ion.

MINNEAPOLIS, MINN. RECEIVED JANUARY 10, 1938

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[2] Gmelin-Kraut, "Handbuch der anorganischen Chemie," 7th Edition, V. I. C. Winter, Heidelberg, 1909, p. 1094.

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Transition Temperature of Sodium Sulfate Heptahydrate

BY E. ROGER WASHBURN AND W. JACK CLEM

T. W. Richards[1] suggested the use of transition temperatures of hydrated salts as fixed points in thermometry and in subsequent years he and his students[2] investigated many of these. Subsequent workers have verified these results[3] and added others.[4] The transition temperature of sodium sulfate decahydrate to anhydrous sodium sulfate and solution, 32.384°, is now considered to be one of the best established secondary standards of thermometry.

It would be of considerable advantage to have a secondary standard in the range near 25° but the nearest well established transition temperatures are those of sodium sulfate decahydrate (mentioned above) and of sodium chromate decahydrate to sodium chromate hexahydrate and solution[5] at 19.525°. This latter salt possesses the disadvantage of being difficult to obtain in

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[1] Richards and Churchill, *Z. physik. Chem.*, **26**, 690 (1898); Richards and Churchill, *Proc. Am. Acad. Arts Sci.*, **34**, 277 (1899).

[2] Richards and Yngve, THIS JOURNAL, **40**, 89 (1918).

[3] Dickinson and Mueller, *ibid.*, **29**, 1381 (1907).

[4] Wells and McAdam, *ibid.*, **29**, 721 (1907).

[5] Richards and Kelley, *ibid.*, **33**, 847 (1911); Richards and Kelley, *Proc. Am. Acad. Arts Sci.*, **47**, 171 (1911).

the pure form. It is known that the transition temperature of the metastable sodium sulfate heptahydrate to anhydrous sodium sulfate and solution is in the desired range but no direct determination of this temperature previous to this study has been made. Further, the handbooks show great disagreement in the accepted value. The Landolt–Börnstein "Handbook"[6] gives the temperature of the quadruple point as 24.4° and the "International Critical Tables"[7] gives 28.2° as the transition temperature. Preliminary investigation in this Laboratory, with mercurial thermometers, indicated that the true value is probably between 23.4 and 23.6°.

Apparatus.—Hartley, Jones and Hutchinson[8] have shown that in about 90% of their trials they were able to crystallize spontaneously sodium sulfate heptahydrate if the solution were freed carefully from all traces of the decahydrate and then protected from contact with the atmosphere while cooling. Previous experience in this Laboratory had been that the heptahydrate crystallized in place of the decahydrate in open vessels during the hot summer days when the atmospheric temperature was higher than the sodium sulfate transition temperature. The calorimeter required, then, had to be so arranged that external air would be excluded and at the same time allow adequate stirring, in addition to the usual requirements of thermal insulation to prevent radiation effects.

The calorimeter used consisted of a hydrometer jar placed inside a tall metal can serving as an air jacket. This jar and jacket were then placed in an earthenware jar which served as an ice-bath or water-bath as the occasion arose. A cork, coated with "Vinylite A," was fitted with a thermometer and a stirrer consisting of two glass loops, one directly above the other, so that the thermometer was encircled by each of them. The stirrer, which acted vertically, passed through a specially constructed sleeve. The section of this glass sleeve which passed through the cork was of a diameter sufficiently great to prevent liquid being carried up the stirrer and wetting the sleeve. This wide section was about three inches (7.6 cm.) long. Sealed to the top of this was a glass tube of almost equal length which fitted the stirrer very closely. It was this arrangement which prevented undue contact between the atmosphere and the vapor in the calorimeter.

The temperature was measured by a Leeds and Northrup platinum resistance thermometer of the potential terminal type and a Mueller type bridge constructed by the same firm.

The Mueller bridge was calibrated by the manufacturer and suitable corrections were applied throughout the work.

The thermometer was calibrated at the ice point, the steam point, and the transition temperature of sodium sulfate decahydrate in this Laboratory and later was submitted to the National Bureau of Standards in order to confirm the method used in the calibration. The thermometer was calibrated in this way because, according to the specifications of the makers, it was not to be used above 100° and this precluded the use of the sulfur point as a standard temperature. The variation of the ice-point resistance with time is shown in Table I, which is taken from a typical set of data. The columns have the following significances: "Time" is the time in minutes from the initial reading; "Bridge resistance" is the average resistance, in ohms and with the proper bridge correction applied, of the readings with the current flowing through the various leads of the thermometer. This average reading eliminates the effect of lead resistances.

TABLE I

Time, min.	Bridge resistance, ohms	Time, min.	Bridge resistance, ohms
0	25.5485	19	25.5485
3	25.5485	26	25.5486
6	25.5484	41	25.5487
8	25.5484	Average	25.5485

Table II summarizes the results of the calibrations made at this Laboratory and at the Bureau of Standards. Our calibration at the steam point was made at 99 rather than 100° because the boiling point of water ranges around this value under our normal atmospheric pressures.

TABLE II

	Our calibrations, ohms	Bureau of Standards calibrations, ohms
The ice point	25.5485	25.547
The steam point (99°)	35.4518	
The steam point (100°)		35.552
Sodium sulfate point	28.8191	
δ value		1.45

Using the fundamental interval as the increase in resistance on heating from 0 to 99°, the corresponding δ_{99} value is 1.42.

Materials

Water.—Ordinary distilled water was redistilled through a block tin condenser from a boiler containing an alkaline solution of potassium permanganate. The distillate was collected hot and the first and last fractions were discarded.

Sodium Sulfate.—Both Mallinckrodt Analytical Reagent sodium sulfate (anhydrous) and Merck Reagent sodium sulfate (anhydrous) were used during the course of the investigation and no difference in purity could be detected from the temperature of the decahydrate transition point. The salt was recrystallized one or more times from the redistilled water described above. The purity of the salt, as indicated by the decahydrate transition temperature, did not change after the first recrystallization. A further check on the purity is offered by using the calibration values of the thermometer obtained by the National Bureau of Standards in calculating the transition temperature of sodium sulfate decahydrate observed in this Laboratory during the course of the independent calibration. If this is done, the value 32.386° is obtained for the transition point of the sodium sulfate decahydrate used.

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(6) Landolt–Börnstein, "Physikalisch-chemische Tabellen," Vol. I, 1923, p. 675, also Vol. II, 1923, p. 1392.

(7) "International Critical Tables," Vol. IV, p. 236.

(8) Hartley, Jones and Hutchinson, *J. Chem. Soc.*, **93**, 825 (1908).

Procedure and Results

Anhydrous sodium sulfate was prepared by heating the decahydrate to about 40°. Most of the supernatant liquid was removed by decantation and the remaining salt was then combined with approximately an equal amount of sodium sulfate decahydrate and placed in the hydrometer jar which was to be used in the bath. This was placed in an air-bath and kept at a temperature of 40° or slightly higher for at least a day. The thermometer, cork and stirrer also were kept in the air-bath during this time. At the end of this heating period, the apparatus was assembled with ice in the earthenware jar. The salt suspension cooled rather rapidly to a temperature of 21–22° and then the temperature would rise rapidly, indicating the appearance of a new phase, usually the heptahydrate. When this happened, the ice-bath was replaced by a water-bath at a temperature of about 23° or the hydrometer jar was allowed to stand at room temperature. The suspension was stirred and readings were taken until, in many cases, a sharp rise in temperature indicated the appearance of sodium sulfate decahydrate.

Table III indicates the bridge readings made at various times during a single typical determination. The columns of numbers have the same significances as in Table I. A change of 0.1 ohm in resistance represents approximately 1° change in temperature. The greatest amount of supercooling in this determination is shown at time fifty-nine minutes and represents approximately 2.7° below the equilibrium temperature. Immediately after this the temperature began to rise sharply. Between times 72 and 76 the ice-bath was replaced by a water-bath at 23°.

TABLE III

Elapsed time, min.	Bridge resistance, ohms	Time, min.	Bridge resistance, ohms	Time, min.	Bridge resistance, ohms
0	29.104	67	27.91640	86	27.92115[a]
21	28.512	72	27.91690	87	27.92135[a]
38	28.070	Bath changed		88	27.92125[a]
59	27.646	76	27.92035	90	27.92145[a]
60	27.874	79	27.92110	93	27.92180[a]
62	27.915	81	27.92125[a]	95	27.92160[a]
64	27.91625	84	27.92125[a]	101	27.92170[a]

Average 27.92142 ± 0.00038

[a] Indicates values used in calculating the average.

Table IV condenses the data taken in all determinations made by the method described. The columns have the following significances: "Number of recrystallizations" indicates the number of times that the salt was recrystallized as sodium sulfate decahydrate before it was used. In this column, "Combined residues" indicates the salts obtained by evaporating the combined filtrates. "Surrounding temperature" indicates the temperature of the surrounding bath during the time of equilibrium; "Length of equilibrium" indicates the time in minutes that the equilibrium was maintained; "Bridge resistance" has the same significance as in Table I.

TABLE IV

Number of recrystallizations	Surrounding temp., °C.	Length of equil., min.	Bridge resistance, ohms
1	23	20	27.9214
Combined residues	26	33	27.9214
2	26	13	27.9212
4	23	81	27.9216
3	25	27	27.9216
Combined residues	25	31	27.9215

Average 27.9215 ± 0.0003

Conversion of the bridge resistance into temperature was accomplished by means of the equations proposed by Callendar[9] with the exception that a fundamental interval corresponding to 99° and the corresponding δ_{99} value was used. The platinum-scale temperature, *pt*, of the transition of sodium sulfate heptahydrate to anhydrous sodium sulfate and solution is calculated by substituting the proper values in the first Callendar equation

$$pt = 99\left[\frac{27.9215 - 25.5485}{35.4518 - 25.5485}\right] = 23.721^\circ$$

The deviation of the platinum-scale temperature from the temperature, *t*, by the air thermometer is calculated from the formula

$$D = t - pt = \delta_{99}\left[\frac{t}{99} - 1\right]\frac{t}{99}$$

As a first approximation, the value of *pt* may be substituted for *t*

$$D = 1.42\left[\frac{23.721}{99} - 1\right]\frac{23.721}{99} = -0.258^\circ$$

and

$$t = pt + D = 23.721 - 0.258^\circ = 23.463^\circ$$

This value is then substituted for *t* in the equation and the second approximation made

$$D = 1.42\left[\frac{23.463}{99} - 1\right]\frac{23.463}{99} = -0.256^\circ$$

and

$$t = pt + D = 23.721 - 0.256^\circ = 23.465^\circ$$

Another approximation does not change the value of *D* by an appreciable amount. The calculated value for the transition temperature of sodium sulfate heptahydrate to anhydrous sodium sulfate and solution is, then, 23.465°.

Using the observed resistance at the transition point and the calibrations furnished by the Bureau of Standards in a similar calculation gives the value 23.468° for the transition point.

Mueller[10] has shown that the probable variation of a dial contact is less than ±0.0002 ohm, and

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[9] Callendar, *Trans. Roy. Soc.*, **A178**, 161 (1887); Callendar and Griffiths, *ibid.*, **A182**, 119 (1891).

[10] E. F. Mueller, Scientific Papers of the Bureau of Standards, No. 288 (Oct. 23, 1916).

for the bridge used in this investigation this would be a total variation of not to exceed ±0.0004 ohm. Each of the measurements used in calibrating the bridge was within this limit and no single measurement of the transition temperature differs from the average by more than this amount. As 0.0004 ohm represents approximately 0.004°, it appears that the transition temperature of sodium sulfate heptahydrate to anhydrous sodium sulfate and solution is 23.465 ± 0.004°.

In his work on the sodium sulfate decahydrate temperature, Richards[1] reported that lowering the outside temperature by two or three degrees lowers the temperature of the salt by about 0.01°. Dickinson and Mueller[3] found no changes exceeding 0.001° were observed by raising or lowering the outside temperature by as much as 10° if a large tube is used and if many crystals are formed by sudden cooling. In the case of the sodium sulfate heptahydrate transition point, the data show that the external temperature probably can vary by at least 3° from the equilibrium temperature without changing the temperature of the salt, but an ice-bath surrounding the tube does lower the temperature, probably by several hundredths of a degree. From experience it would seem that the sodium sulfate heptahydrate transition temperature probably is influenced slightly more by external conditions than is the transition temperature of the decahydrate.

Summary

A method has been described for preparing sodium sulfate heptahydrate and for maintaining the sodium sulfate heptahydrate transition temperature. This temperature has been determined to be 23.465 ± 0.004°. Because the salt is purified easily and the transition temperature is near the most used part of the thermometer scale, this point is proposed as a useful secondary standard in calibrating thermometers along with the sodium sulfate decahydrate transition point.

Lincoln, Nebraska Received October 11, 1937

[Contribution from the Biochemical Research Foundation of the Franklin Institute]

An Ultracentrifugal Study of Gelatin

By Edward B. Sanigar, Laura E. Krejci and Elmer O. Kraemer

Introduction

Krishnamurti and Svedberg[1] some years ago carried out an ultracentrifugal investigation of a photographic gelatin at 20°. In the range of *p*H 4.6–6.0 they found the sedimentation velocity to be high and difficult to reproduce, and to increase rapidly with aging of the solution, the increase being greater the nearer the *p*H was to the isoelectric point. At *p*H's 4.0 and 7.5, the sedimentation velocity was low, corresponding approximately to that of a protein like egg albumin, and was independent of time. According to the evidence provided by the light scattering capacity of gelatin, as given by Kraemer and Dexter[2] and by Krishnamurti,[3] it appears that the molecular aggregation associated with gelation does not occur at these *p*H's even at 20°. On the other hand, the results given by Kraemer[4] on the viscosities of dilute gelatin solutions with these *p*H's at temperatures below 30° reveal quite definitely the fact that aggregation and gelation do occur under these conditions. It seemed desirable, therefore, to extend the ultracentrifugal study to higher temperatures where the effects of gelation would be more definitely repressed. From previous work[2,4,5] it appeared that a temperature definitely above 30° would be desirable.

Experimental Procedure

Four commercial gelatins were investigated: Coignet Gold Label Gelatin (ossein) (Gelatin A), Grayslake Gelatin (pigskin) (Gelatin B), Eastman De-ashed Gelatin (calfskin, first extraction) (Gelatin C), Atlantic Super-X Gelatin (calfskin, first extraction) (Gelatin D). Each gelatin was studied at two different concentrations, *i. e.*, 2 g. and 0.4 g. of anhydrous gelatin per 100 cc., respectively.

For the preparation of the more concentrated solution, 5 g. of air-dry gelatin (moisture content *ca.* 20%) was allowed to swell for about an hour in 25 cc. of water containing 0.5 g. of phenol, and solution was completed at 37.4°

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(1) Krishnamurti and Svedberg, This Journal, **52**, 2897 (1930).

(2) Kraemer and Dexter, *J. Phys. Chem.*, **31**, 764 (1927).

(3) Krishnamurti, *Proc. Roy. Soc.* (London), **A129**, 490 (1930).

(4) Kraemer, "Colloid Symposium Monograph," Vol. IV, 1926, p. 102.

(5) Kraemer and Fanselow, *J. Phys. Chem.*, **32**, 894 (1928).