Le Chatelier[1] has stated that the curve representing the melting points of mixtures of sodium sulfate with increasing proportions of barium sulfate consists of three parts, the first corresponding with the formation of isomorphous crystals containing the two constituents in varying proportions, the second to the formation of a double sulfate and the third to the recrystallization of the added sulfate itself. An experiment in which we dissolved barium sulfate in sodium sulfate to about a 10 per cent. solution yielded crystals which, after washing, were examined spectroscopically and found to be practically free from sodium. This does not harmonize with the Le Chatelier observations and a new thermal analysis of the system $BaSO_4$-Na_2SO_4 appears to be desirable.

Crystallographic Study by A. A. Klein.

The material examined was received from Professor H. C. Cooper and labeled (*a*) barium sulfate, recrystallized from $BaCl_2$, and (*b*) barium sulfate, recrystallized from Na_2SO_4. It consisted of some isolated crystals mounted on two slides in Canada balsam, and of fragments and loose crystals.

Under the microscope the crystals are long, tabular and colorless, with frequent indications of parallel growth. They show parallel extinction, which, with the characteristic outline, establishes the crystallization as orthorhombic. Excellent cleavage was observed parallel to the long direction of the crystals. The indices of refraction were determined by the Schroeder van der Kolk method and were found to be very close to that of monobromonaphthalene (n = 1.648), inasmuch as a red tint is observed on the side toward the darkened portion of the field, whereas a blue color is noted on the opposit side. This is an exceedingly close approximation to the values of the indices of refraction given by Groth[2] for the D line of the spectrum, $\alpha = 1.6369$, $\beta = 1.6381$, $\gamma = 1.6491$. In convergent light a distinct positive, biaxial interference figure is frequently observed.

The above observations agree fully with those given by Groth for natural barium sulfate, namely, the mineral barite.

SYRACUSE UNIVERSITY,
SYRACUSE, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE TRANSITION TEMPERATURES OF SODIUM CHROMATE AS CONVENIENT FIXED POINTS IN THERMOMETRY.

BY THEODORE WILLIAM RICHARDS AND GEORGE LESLIE KELLEY.

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Introduction.

In previous papers[3] from this laboratory it has been shown that the

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[1] *Compt. rend.*, 123, 746 (1896).

[2] Groth's "Chemische Krystallographie," 1908, II, 388-389.

[3] T. W. Richards, *Am. J. Sci.*, [4] 6, 201 (1898); Richards and Churchill, Proc.

transition temperature of a crystallized salt is in some cases so easily observed and so constantly maintained as to form a convenient fixed point of reference for the scale of temperature. The cases of sodium sulfate (32.383°) and bromide (50.674°) and manganese chloride (58.089°) have been studied in detail and found to be very satisfactory in these respects.

Among other substances suggested for this purpose, sodium chromate is especially inviting because two of its transition temperatures are near 20°, a temperature at which it is frequently desirable to verify thermometers.

The outcome of the work on this salt described in the present paper was entirely satisfactory, and gives promise of great practical usefulness to those who are interested in exact thermometric measurement. Nevertheless, the problem was not so simple as it had at first appeared. The wealth of variety exhibited by the hydrates proved at first to be an embarrassment of riches, and led to some preliminary confusion, which has been happily reduced to order. Moreover, the salt is somewhat less easy to purify than the sulfate, and when it is impure, a given percentage of impurity causes a larger error in the transition temperature than in the case of the sulfate. This is largely because the transition is from the decahydrate to tetra- or hexahydrate, instead of to anhydrous salt, so that the amount of solution formed to dissolve the impurities is less, and therefore the concentration of the impurity in the solution is greater. Another difficulty arises from the fact that chromic acid is a weak acid, and hence its salts are easily capable of absorbing acid impurities. This was shown experimentally by passing pure carbon dioxide into the solution. Large volumes of the gas were absorbed, and the solution became perceptibly orange because of the formation of the dichromate. Boiling expels the gas but slowly, because the hydrolysis increases with rise of temperature. Indeed a boiling solution of the purest salt is so much hydrolyzed as to be red in color and to react strongly with phenolphthalein. Probably the passing of pure air, or boiling at low temperature for a long time in a partial vacuum, would be needed to displace all of the carbon dioxide, and even this might not serve. Of course the solution of the salt absorbs hydrochloric acid and other strong acid vapors yet more easily; and even the dry salt, which is unaffected by carbon dioxide, is attacked by stronger substances.

Theoretically the tendency of the solution to hydrolyze offers no ob-

Am. Acad. of Arts and Sciences, 34, 277 (1899); Richards and Wells, *Ibid.*, 38, 431 (1902); 41, 435 (1906); Richards and Wrede, 43, 343 (1907). These five papers are all to be found in full in the *Z. physik. Chem.*, the references being, respectively, 26, 690 (1898); 28, 313 (1899); 43, 465 (1903); 56, 348 (1906); 61, 313 (1908). The work on manganese chloride was finished by Dr. Wrede and one of us at the University of Berlin.

jection to the use of the salt as a means of fixing a definit point on the thermometer scale, because the Phase Rule, which determins the definitness of the points, does not consider the state in which the substance exists in any of the phases. The feeble nature of chromic acid is annoying and objectionable only for the practical reason that it makes the preparation and preservation of the pure salt more difficult. When the salt has once been prepared in the pure state, it must be carefully guarded in order to preserve its purity.

These difficulties, however, all disappear when the experimenter is forewarned against them; for easily effected precautions are capable of surmounting them all.

Preparation of Pure Sodium Chromate.

Several methods of further purification of sodium chromate were tried. Crystallization as the decahydrate is of no avail as a means of ridding the crystals of their most usual impurity, the sulfate, because this is isomorphous with the chromate. Indeed as will be shown the sulfate tends into the crystals, leaving the mother liquor somewhat purer than before the crystallization. The tetrahydrate is but little more satisfactory as a means of accomplishing the purification, ten successive crystallizations having failed to yield a pure salt. Moreover, inconvenience arises from the fact that it is stable under the solution only between 26° and 62.8°; and because its solubility has only a comparatively small temperature coefficient, the yields are small.

Attempts to prepare the salt by recrystallizing chromic anhydride were likewise abandoned as unprofitable. The best chromic anhydride obtainable was found to contain much sulfate, which was very slow to leave during the particularly wasteful process of its crystallization. In one case twelve successive crystallizations of a kilogram of chromic anhydride gave only a few grams of product which still contained traces of sulfur. These unsuccessful methods are recounted only to save other experimenters the trouble of attempting the same processes.

The sulfate can be quickly eliminated by relying upon the very different solubilities of silver chromate and sulfate. If a chromate is slowly precipitated by silver nitrate in dilute solution, using not quite enough of the precipitant to remove the chromate wholly from the solution, the precipitate contains very little sulfate. The chromate of silver is then thoroughly washed, and easily converted into sodium chromate by treatment with a solution of pure sodium chloride.

This method is, however, somewhat cumbrous and expensive. Therefore without further delay we may pass at once to another available method, the most satisfactory one of all, which depends upon the fact that sodium dichromate may be easily and quickly freed from sulfate by recrystallization. The dichromate is very soluble, and possesses a moderately great change of solubility with the temperature; 100 parts of water dissolve 162 parts of the dry salt at 100° and 109 parts at 15°.[1] Since, however, the salt crystallizes with two molecules of water, the actual loss on crystallization is less than would appear from a superficial inspection of these figures. The weight of the crystals separated from a saturated solution between these two temperatures from 162 grams of anhydrous salt dissolved in 100 grams of water is easily calculated from the equation

$$x + \frac{2H_2O}{Na_2Cr_2O_7}x + (162 - x)\frac{209}{109} = 262,$$

when $x = 87$ grams. Thus more than half of the salt is easily recovered from each crystallization, and if use is made of a wider range of temperature, permitted by the high saturated boiling point (139° with solubility 210 parts to 100 of water) a still larger yield may be obtained. Since the solubility diminishes but slightly below 15°, further cooling is not profitable. Thus the crystallization of this salt is convenient and efficient; and since sodium dichromate is not isomorphous with the corresponding salts either of potassium or of sulfuric acid (the most probable and insidious impurities) crystallization forms an admirable means of purification. The elimination of the sulfuric acid requires only three or four crystallizations if the crystals are separated centrifugally. A large excess of chromic acid causes unnecessary loss, because of the very great solubility of the trichromate,[1] but a small excess is convenient, because the elimination of the dark brownish tint of the trichromate from the mother liquor is a convenient guide as to the purity of the salt.

The crystallized, pure dichromate was treated with *somewhat less than the calculated amount* of pure sodium carbonate, and with the help of the excess of dichromate the carbon dioxide was easily removed by boiling the solution during an hour. From a neutral solution all the carbon dioxide cannot be expelled. The sodium carbonate for this purpose should be prepared by repeatedly crystallizing the purest soda of commerce in porcelain, or better in platinum dishes, until sulfates and chlorides are certainly absent.

The sodium chromate containing a small amount of sodium dichromate, prepared as described above, was neutralized with the help of phenolphthalein by means of a solution of pure sodium hydroxide, made from sodium by allowing this metal to stand in a platinum dish in a desiccator over a dilute solution of the hydroxide.

Some time was spent in determining the conditions under which phenolphthalein gives satisfactory results in the presence of pure sodium chromate. Schreinemakers[2] states that the chromate is neutral to phenolphthalein and recommends the use of this indicator in analyzing solutions of chro-

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[1] Stanley, *Chem. News*, 54, 194 (1886).

[2] *Z. physik. Chem.*, 55, 72 (1906).

mates for excess of either hydroxyl or chromate ion. In our experiments it appeared that the solubility of the indicator in very concentrated sodium chromate solutions is too small under ordinary conditions to permit of a visible reaction with the low concentration of ionized hydroxyl which must exist there. This is especially true when alcoholic phenolphthalein is dropped into a saturated solution of the chromate. In this case the indicator seems to be precipitated by the salt in such form as to dissolve only very slowly on subsequent dilution. This difficulty was avoided by diluting the indicator with pure water in the first place. On the other hand a dilute solution of the salt is easily shown to be appreciably hydrolyzed, the color of phenolphthalein being distinctly visible superposed on the yellow of the salt. Increasing temperature of course causes increasing hydrolysis; in boiling solutions of the purest very concentrated sodium chromate the hydrolysis is sufficiently great to cause a distinctly reddish tint.

As an outcome of these experiments the neutralization was conducted in concentrated solutions of sodium chromate at room temperature, the indicator in dilute solution being added to the separate test portions. To the main mass of chromate, sodium hydroxide was added until the phenolphthalein just began to show its color in the separate test; and then sodium dichromate until the color just disappeared. This solution may have contained a constant and very slight excess of dichromate, but this substance is easily removed by subsequent crystallization being heteromorphous as regards sodium chromate.

The neutral salt prepared in this way may be further purified by crystallizing either as the decahydrate, hexahydrate, or tetrahydrate. The first named phase, $Na_2CrO_4.10H_2O$, is to be preferred on account of economy of material.

To crystallize the salt with four molecules of water the temperature of the solution must be kept above 26°; but at 26° 100 parts of water dissolve 86 parts of sodium chromate whereas at 0° 100 parts of water dissolve only about 32 parts of sodium chromate in equilibrium with decahydrate; hence arises one reason for the greater economy in crystallizing the decahydrate at the lower temperatures. Moreover, a greater rate of purification from every common impurity except sodium sulfate is possible by this method than through the other hydrates. Six or seven crystallizations as the tetrahydrate give only the same degree of purity as three or four crystallizations as the decahydrate.

The decahydrates of sodium sulfate and chromate are isomorphous, as already stated; hence the sulfate must be previously removed by crystallizing the dichromate in the manner already described.

Crystallization of the pure chromate is best carried out at 5° in platinum vessels; and centrifugal drainage, as usual, greatly increases its efficiency as a means of purification. After three or sometimes four crystallizations the sodium chromate was found to give a transition temperature which could not be raised by further crystallization. This is, of course, the criterion to be used in deciding how long to continue the purifying operations. The difficulties attending the purification of this substance are no greater than those attending the purification of sodium sulfate, provided that isomorphous substances are absent. The mother liquors may be made to yield at least two more crops of crystals; their evaporation for this purpose is free from danger only when the platinum vessels employed are so constructed as to prevent the entrance of carbon dioxide. The yield of pure sodium chromate may be nearly 50 per cent. of the amount corresponding to the pure sodium dichromate employed. Pure sodium chromate must be preserved in a desiccator, containing a small amount of a solution of sodium hydroxide solution to absorb carbon dioxide. If the salt is to be kept for any length of time it should be placed in platinum, gold or quartz vessels. The tetrahydrate is the most convenient form in which to preserve the salt for long periods, as it is permanent under usual conditions.

The Hydrates of Sodium Chromate.

The decahydrate, $Na_2CrO_4.10H_2O$, isomorphous with common Glauber's salt, is so well known that description is unnecessary. It is easily obtained in large crystals by inoculating a cold supersaturated solution of the former salt with a crystal of the latter. In order to avoid the suspicion of contamination with sulfate, inoculation was carried out successively on several watch glasses, the first being touched with sulfate, the second with chromate taken from the opposit side of the first and so on, the bulk of the material being inoculated with pure chromate from the last watch glass. Whenever the temperature of the laboratory had risen above 20° this procedure was necessary, because at this temperature all of the chromate in the laboratory suffered change into the tetra- or hexahydrate, and so none remained wherewith to start the crystallization of a new specimen. Like sodium sulfate, the chromate has a wide range of metastability of supersaturation, and like it, the chromate is efflorescent in the dry air of the steam-heated[1] laboratory. In order to make sure of the composition of the salt, a specimen which had been dried as much as possible without visible efflorescence was analyzed. 0.8316 gram of the salt lost on dehydration 0.4358 gram of water, or 52.43 per cent. The theoretical percentage is 52.70, hence there can be no doubt as to the formula $Na_2CrO_4.10H_2O$.[2]

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[1] Kopp's ascribing deliquescence to the salt must have been due to his working in a very moist atmosphere.

[2] These analyses, as well as those of the hexa- and tetrahydrate given further on, were kindly made by J. B. Churchill under the direction of one of us.

The hexahydrate, $Na_2CrO_4.6H_2O$, has only a very small range of stability, as will be seen from an examination of the diagram on p. 854. The preparation of this hydrate was first described by Salkowski.[1] At temperatures below 19.53°, especially in contact with its solution, it tends to pass into the decahydrate modification and above 26°, into the tetrahydrate. Inasmuch as the temperatures within which it is stable are those most frequently found in the laboratory, it is the phase most frequently met with. When the decahydrate warms to 19.53° or the tetrahydrate cools to 26° particles of hexahydrate in the atmosphere induce the crystallization of this form so readily that it is often difficult to prevent the appearance of this phase. In two analyses, 1.4152 grams and 1.7786 grams of the salt lost respectively 0.5705 gram and 0.7122 gram of water on drying at 180° to constant weight. These results correspond to 40.3 and 39.4 per cent. of water respectively, and since the first sample was somewhat moist and the second was slightly effloresced, there can be no doubt that the substance was really $Na_2CrO_4.6H_2O$, a salt possessing theoretically 40.0 per cent. of water. The material gives a transition point at about 25.9° (hydrogen scale), being converted into tetrahydrate at that temperature.

The tetrahydrate, $Na_2CrO_4.4H_2O$, is stable in contact with its solution only at temperatures above 26° and below 62.8° ±. Even in the dry air of a steam-heated room it shows no evidence of efflorescence; therefore its aqueous vapor pressure must be very low. This hydrate is formed when a hot concentrated solution of sodium chromate is allowed to cool to a temperature above 26°, and the needle-shaped crystals melt at about 62.8°. Occasionally other crystals of a hydrate or anhydride separate from the solution above 62.8°. Because the hydration of the latter crystals at low temperatures is slow, enough water should be added to a very hot solution to keep the salt dissolved until the temperature 62.8° has been reached by the cooling material. Two analyses of the tetrahydrate showed 30.74 and 30.76 per cent. of water, sufficiently close to the theoretical value 30.72. On cooling a solution saturated at 63°, it frequently happens that no crystals appear, although upon adding a crystal of the tetrahydrate crystallization at once occurs.

In the accompanying figure the solubilities[2] of sodium chromate in contact with its various hydrates have been plotted for temperatures in the neighborhood of the room temperature. Evidently three transitions are possible within a small range. The decahydrate undergoes transition to the hexahydrate and solution at 19.53°, or into tetrahydrate and

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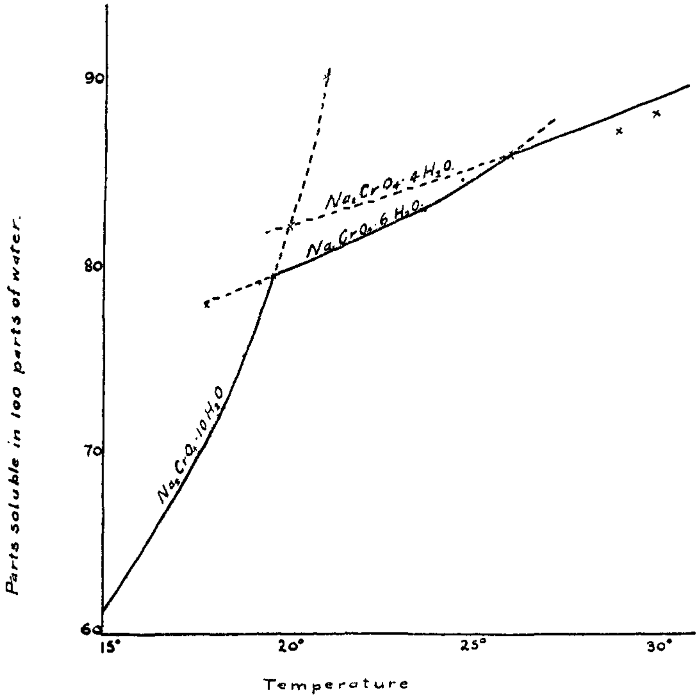
[1] Salkowski, *Ber.*, 34, 1947 (1901). The salt had been made and analyzed previously by Richards and Churchill, but no description had been published.

[2] Mylius and Funk, *Ber.*, 33, 3688 (1901); also Salkowski, *Ibid.*, 34, 1948 (1901). These are recorded in *Landolt-Börnstein Tabellen* (1905), page 557.

solution at 19.99°,[1] depending on which of these last-named hydrates is present. A similar transition from hexahydrate to tetrahydrate and solution occurs at 25.9° ±.

To bring about the transition at 19.99°, it is necessary to superheat the decahydrate past the lower transition point, 19.53°. Not many other instances of this sort have been carefully studied. Walker and Fyffe[2] have examined the solubility of $Ba(C_2H_3O_2)_2.3H_2O$ (which undergoes a transition into the monohydrate and solution at 24.7°) as far as 26.1°, 1.4° above its transition point; and the solubility of $\alpha Ni(IO_3)_2.2H_2O$ has been studied by Meusser[3] up to 50°, 13° above the temperature of its transition into the anhydride and solution.[4]



The addition of a foreign substance not isomorphous with the dekahydrate lowers the transition point as usual.[5] The addition of sodium chloride was found some time since by C. A. Bigelow and one of us to lower

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[1] This is probably the point found by J. L. R. Morgan as approximately 19.92, *Z. anorg. Chem.*, 55, 263 (1907).

[2] Walker and Fyffe, *J. Chem. Soc.*, 83, 180 (1903).

[3] Meusser, *Ber.*, 34, 2440 (1901).

[4] See also Berthoud, "Sur l'impossibilité de surchauffer un solide," *J. chim. phys.*, 8, 337 (1910).

[5] Löwenherz, *Z. physik. Chem.*, 4, 349 (1889).

the transition temperature (19.53) about the expected amount. This result was not published at the time, but has since been confirmed by J. L. R. Morgan.[1]

A much more interesting effect is observed with isomorphous hydrates. For example, successive additions of sodium sulfate to the solution gave successive elevations of the transition temperature, even when the crystals contained no sodium sulfate.[2] These elevations were roughly proportional to the amount added. The experiments were not carried on with a view to determining the limits of this change, but an elevation of about 4° was found in some instances. The temperatures at first obtained were variable, but on vigorously stirring in an environment 0.5° warmer than the mixed hydrates, equilibrium was apparently reached after five minutes, and often remained undisturbed for fifteen minutes or longer. This raising of the transition point involves an interesting extension of the range of stability of the decahydrate.

So far as we can find this phenomenon of the raising of the transition temperature of hydrated crystals by the presence of isomorphous hydrated crystals is here described for the first time. It deserves and shall receive here in the near future more thorough investigation.

The relative composition of crystals and mother liquor seemed worthy of study. A solution of sodium chromate containing a considerable amount of sodium sulfate was cooled to 10° to crystallize. The crystals were drained in a centrifuge, washed with a little cold water, and again centrifuged. 7.05 grams of this solution contained 0.432 gram of sodium sulfate and 1.707 grams of the chromate, whereas 2.25 grams of the hydrated crystals contained 0.425 gram of the sulfate and 0.515 gram of the chromate. The solubility of the chromate at 10° is, roughly speaking, 50 parts in 100 of water and of the sulfate 9 parts in 100 of water. The distribution of the dissolved substances between their solution and mixed crystals is thus seen to be in the same sense as to their respective solubilities at the temperature of crystallization. The sulfate decidedly tends towards the crystals, the chromate towards the mother liquors.

As has been elsewhere pointed out, Salkowski was the first to observe that the curve of solubility of the hexahydrate cuts those of the deca- and tetrahydrates at about 19.5° and 26° respectively. Mylius and Funk[3] earlier observed that the transition from the decahydrate is accomplished through the intermediate tetrahydrate, which is stable between 20°

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[1] Morgan, *Z. anorg. Chem.*, 55, 263 (1907); 56, 168 (1907).

[2] This fact was first observed by Churchill and one of us over ten years ago, but has not been published until now. The value 19.6° (which made no pretensions to great accuracy) assigned at that time to the lowest transition temperature of sodium chromate was undoubtedly too high from this cause. *Proc. Am. Acad.*, 34, 277 (1899).

[3] *Abhandlung der Physik. Techn. Reichsanstalt*, 3, 449 (1900). This fact had also been observed but not published by Richards and Churchill before that time.

and 65°. Salkowski,[1] commenting upon their work in view of his later discovery of the hexahydrate, says that this statement must be extended to include the hexahydrate for its few degrees of stability. The statement of Salkowski must now be extended to include the fact that the transition from decahydrate to the anhydride may be through the hexa- and tetrahydrates, or in the absence of the hexahydrate, this transition may be through the tetrahydrate alone, as originally stated by Mylius and Funk.

We have confirmed the statement of Salkowski that the temperature of the transition from the hexahydrate to the tetrahydrate is in the neighborhood of 26°, but owing to lack of time we have been unable to determin this point with exactness.

The exact determination of the two lower transition points, for use in precise thermometry, will now be described.

The Apparatus.

The apparatus employed was like that employed in determining the transition temperature of sodium sulfate.[2] It was essentially similar to Beckmann's well-known freezing-point apparatus, consisting of two large test tubes, one within the other, immersed for nine-tenths of their length in a roomy, transparent water bath. The inner test tube, which contained the mixed hydrate, was 3.3 cm. wide and 16 cm. long (internal measurements) and had a capacity of 120 cc. The outer tube was large enough to allow a small air space between the two vessels at every point except the top, where the inner vessel was insulated from the outer one by a narrow rubber ring. This ring held the inner tube in place, preventing heat conductance through the glass to the material, and excluded the outer air from the space between the two tubes. Thus all the heat obtained by the melting material come to it from the outer bath through the confined air-jacket, which is an absolutely necessary provision, if accuracy is sought.

The inner large test-tube containing the sodium chromate was closed at the top by a rubber stopper, carefully freed from loosely adhering matter which might contaminate the materials. It was pierced by two holes, through which short glass tubes were passed. One of these tubes was of the same length as the thickness of the stopper, and served to hold the stirrer; while the other reached 0.7 cm. above the stopper and below to within 1 cm. of the sodium chromate, and served to admit and support the thermometer. To the upper end of the latter tube a short length of stout rubber tubing was attached, the object of which was to hold the thermometer in place at any desired level. A water jacket

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[1] *Loc. cit.*

[2] Richards and Wells, *Z. physik. Chem.*, 43, 465 (1903); *Proc Am. Acad.*, 38, 43 (1902).

around the thermometer is necessary only where the temperature of the room is several degrees distant from 20°, because a correction for the protruding column can be applied with sufficient accuracy when the temperature difference is small.

The stirrer was made of a piece of platinum wire 15 cm. in length, at one end bent into the shape of a ring, at the other end sealed into a glass tube which served as a handle.

The thermometers were three in number. The first, an excellent Beckmann thermometer, the scale of which was divided into hundredths of a degree, was used for the preliminary experiments, where the constancy of the transition temperature of successive fractions was the main issue. Two Baudin thermometers, 15200 and 15276, standardized with the greatest care at the Bureau Internationale des Poids et Mesures, were used in the final determination of the points on the hydrogen scale. These thermometers have been previously described;[1] their scales are divided into tenths of a degree, and readings within 0.001° were made by means of a Geneva cathetometer, observing the marks not only in the usual way, but also through the glass behind the mercury. The freezing points were taken both before and not long after the transition temperatures, and during the intervening time the instruments were carefully protected from large temperature changes.

The Temperature of the Transition from $Na_2CrO_4.10H_2O$ to $Na_2CrO_4.6H_2O$.

When moist crystals of the decahydrate are melted without the addition of the solid hexahydrate, the temperatures obtained are variable and generally low. This is undoubtedly due to the fact that the water of crystallization, together with the water adhering to the crystals, is enough to dissolve the sodium chromate completely, thus preventing the formation of solid hexahydrate.

In order to avoid this difficulty, it was found best to heat about one-fifth of the moist hexahydrate in a quartz or platinum vessel to 60°, thus driving off perhaps a third of the water of crystallization. The cooled product yielded solid $Na_2CrO_4.4H_2O$ and its solution. This was added to the remainder of the $Na_2CrO_4.10H_2O$, after which the whole mass was warmed to 28° C in the test tube in which the determination was to be made. The proportion of $Na_2CrO_4.4H_2O$ to $Na_2CrO_4.10H_2O$ should be such that at this temperature the whole is in solution. The solution was then cooled by dipping the test tube into a beaker containing water at twenty degrees. When the temperature of the solution had fallen to 25°, a crystal of $Na_2CrO_4.6H_2O$ was added; it produced copious crystallization. On further cooling to 18° or slightly lower a crystal of decahydrate was added, and still more heat was taken from the mixture,

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[1] Richards and Wells, *Proc. Am. Acad.*, 38, 43 (1902); *Z. physik. Chem.*, 43, 465 (1902).

with stirring, until the mixture of the two solid phases and solution of sodium chromate was plastic.

The temperature of the water bath was kept one or two tenths of a degree higher than the equilibrium point (19.5°) and the room temperature also was kept not far away. This latter condition was not very essential, because with one of our thermometers the stem exposure was 6.5° and with the other only 0.5°.

In a preliminary set of readings, corrected in the usual way for calibration, for internal and external pressure, for error in the fundamental interval, for the corrected ice point, for the exposed column, and to the hydrogen scale, the following values were found:

Preliminary determination by thermometer 15200	19.518°
Preliminary determination by thermometer 15276	19.525°
	19.522°

The Beckmann thermometer in this mixture indicated 0.580°. Upon crystallizing the material once more, and separating the mother liquor by centrifugal action, the crystals still gave exactly the same transition point, 0.580°, the atmospheric pressure having remained essentially constant. Therefore it was clear that the material was as pure as it could be obtained by crystallization, and the final estimation was made.

The individual readings were corrected for stem exposure, and all averaged to give the observed value used in calculating the temperature referred to the hydrogen scale. The ice points, which are the most uncertain part of this determination, were taken as the averages of four separate fairly concordant sets of readings, two of which were made some time before the determinations, and two immediately afterwards. As the thermometers are old and well-seasoned, this procedure seemed likely to furnish the best results.

Thermometer 15200:

Reading in salt (cor.)	19.804°	In ice	+0.201°
Correction, calibration	—0.026		+0.002
Correction, internal pressure	+0.027		+0.009
	19.805°		+0.212°
Corrected reading in ice	—0.212		
	19.593°		
Correction, fundamental interval	+0.014		
	19.607°		
Correction to hydrogen scale	—0.084		
	19.523°		

Thermometer 15276:

Reading in salt (cor.)	19.750°	In ice	0.143°
Correction, calibration	—0.025		—0.001
Correction, internal pressure	+0.039		+0.012
	19.764°		+0.154°
Corrected reading in ice	—0.154		
	19.610°		
Correction, fundamental interval	+0.001		
	19.611°		
Correction to hydrogen scale	—0.084		
	19.527°		
Total average of two final readings	19.525 ± 0.002°		

The average of the two preliminary readings was 19.522° ± 0.004°, a result as near as could be expected to the final value, considering the range of error of each. The value 19.525°, the result of the final determination above, may be accepted for the present as the most probable figure.

The Temperature of the Transition from $Na_2CrO_4.10H_2O$ to $Na_2CrO_4.4H_2O$.

This mixture of hydrates is somewhat more difficult to prepare than the mixture of deca- and hexahydrates. From a study of the diagram on page 854 it appears that the tetrahydrate is metastable with respect to the hexahydrate between the temperatures 19.53° and 25.9° ±. The difficulty is to exclude the hexahydrate during the cooling of the tetrahydrate and solution from 26° to 19.99°, the transition point of the deca- to the tetrahydrate. Even after the decahydrate has appeared and has in part relieved the supersaturation, care must be taken to exclude the intermediate hydrate. At 19.99° both decahydrate and tetrahydrate are metastable with respect to the hexahydrate. If to a mixture of the two former a crystal of the latter be added, a depression and irregularity in the temperature occurs, and the temperature gradually falls to that of the lower transition point.[1]

The mixture of hydrates is prepared (within the test-tube in which the transition temperature is to be determined) by a method closely resembling

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[1] Gernez's supposed disintegration of $Na_2CrO_4.4H_2O$ in the presence of 10 H_2O salt [*Compt. rend.*, 149, 77 (1910)] would not affect this point, as Gernez reasonably supposes this disintegration is due simply to the formation of the decahydrate from included water within the salt, and not to the formation of a hydrate with less than 4 H_2O.

that described for preparing the mixture of decahydrate and hexahydrate. To the decahydrate is added such a quantity of tetrahydrate that nearly all the solid will be in solution at 28°. By heating the mixture to this temperature, one may feel certain that none of the hexahydrate is present. The tube is then closed by a clean stopper through which the handle of a stirrer passes. The stopper serves to protect the contents from accidental inoculation by hexahydrate. When the solution has been cooled to about 19°, it is inoculated with some freshly prepared decahydrate, which must be free from hexahydrate. Further gradual subtraction of heat, with constant stirring, gives a mixture of the desired plastic consistency.

The material used in the preliminary determination of this transition point was the same as that used in the preliminary determination of the equilibrium temperature of the mixed deca- and hexahydrates. With the Beckmann thermometer the new point was 1.039°. On the Baudin thermometers all individual readings were corrected for stem exposure and averaged as before.

Preliminary reading by thermometer, 15200	19.984°
Preliminary reading by thermometer, 15276	19.990°
Average,	19.987°

The material used in the final observations was the same as that used for the previous final work, after conversion into a mixture of deca- and tetrahydrate. With the Beckmann thermometer it gave the transition point 1.039, the same as that given by the salt used in the preliminary tests just recorded.

Final Determination I.

Thermometer 15200:

Reading in salt (cor.)	20.269°	In ice	0.201°
Correction, calibration	—0.028		+0.002
Correction, internal pressure	+0.027		+0.009
	20.268°		0.212°
Corrected reading in ice	—0.212		
	20.056°		
Correction, fundamental interval	+0.014		
	20.070°		
Correction to hydrogen scale	—0.085		
	19.985°		

Final Determination II.

Thermometer 15276:			
Reading in salt (cor.)	20,209°	In ice	0.143°
Correction, calibration	—0.022		—0.001
Correction, internal pressure	+0.039		+0.012
	20.226°		0.154°
Corrected reading, in ice	—0.154		
	20.072°		
Correction, fundamental interval	+0.001		
	20.073°		
Correction to hydrogen scale	—0.085		
	19.988°		
Total average of two final readings	19.987° ± 0.002		

It is interesting to note that the difference between the two transition temperatures is given as almost exactly the same quantity by the final readings of the two thermometers.

Difference by thermometer 15200 = 0.462°
Difference by thermometer 15276 = 0.461°

This, of course, gives a means of calibrating the Beckmann thermometer, which gave 0.459° for the interval—evidently the marks were a trifle too far apart on the latter instrument.

The close parallelism of the results with the two Baudin thermometers seems to indicate that the most probable cause of error in such work is not due to mistakes in observing either of the transition temperatures, but rather to the difficulty of determining the ice point. There can be no question that either of the sodium chromate equilibrium temperatures is a far better means of fixing the scale of a thermometer to be used near room temperature than is the freezing point of water.

The Temperature of the Transition from $Na_2CrO_4.6H_2O$ to $Na_2CrO_4.4H_2O$.

The material used in this determination was sodium chromate obtained from the mother liquors of previous preparations, purified by recrystallization as decahydrate until the temperature of transition from the decahydrate to the hexahydrate as shown by the Beckmann thermometer was 0.580. A supersaturated solution of this pure salt at 25° was inoculated with hexahydrate and further cooled with stirring to 18°, the decahydrate being scrupulously excluded. The plentiful crystals of hexahydrate were then centrifuged to remove the excess of mother liquor, and in order to make certain that none of the decahydrate was present, the crystals were allowed to stand in a bath at 25° for an hour. No change occurred in the appearance of the material. Just before taking the transition temperature a few crystals of the tetrahydrate were added.

Whether on account of the interference of other unknown hydrates, or of the comparatively small heat of this transition, or of the unavoidable haste in which the experiments had to be conducted, much less constant results were obtained in this case than in the preceding. It appeared that the equilibrium temperature of the hexa- and tetrahydrates was not far from 25.90° on the hydrogen scale; but this figure is subject to further revision.

This point is worthy of further investigation, for it is exceedingly convenient, taken together with the other points given by this same salt, as a means of calibrating a Beckmann thermometer. The interval between the decahydrate-tetrahydrate point (19.987°) and the higher transition temperature is almost 6°, the usual length of a Beckmann thermometer. By adding a degree to the scale, which could easily be done in future, the lowest transition temperature of sodium chromate could be brought within the scope of the instrument. To be able to verify a thermometer over its whole length, and at the same time to evaluate accurately the interval 0.462 on one part of the scale, all with the single purified salt, is indeed a highly desirable circumstance.

Of course the determination of all the three points as given in this paper must be looked upon as merely preliminary, because time permitted the study of these temperatures on only two thermometers. The average of the readings of many thermometers should ultimately be taken. Nevertheless we believe that the averages given in this paper are sufficiently exact to be a great boon to those desiring to verify thermometers about the temperature of the room.

It is a pleasure to acknowledge the usefulness of a grant made many years ago by the Rumford Fund of the American Academy of Arts and Sciences for this purpose. Much of the material used in the investigation was purchased with its aid.

Summary.

1. The great advantage of sodium chromate as a means of verifying thermometers at three fixed temperatures in the neighborhood of 20° is emphasized.

2. A method for the easy preparation of pure sodium chromate has been elaborated.

3. The existence of three hydrates of sodium chromate, namely, the deca-, hexa- and tetrahydrates has been confirmed.

4. The accurate estimation of the point of conversion of each of these hydrates into each of the other two has been shown to be easily feasible.

5. The addition of heteromorphous substances lowers the transition points as usual.

6. The addition of sodium sulfate (which gives an isomorphous decahydrate) raises the temperature of the decahydrate-hexahydrate equilib-

rium. This is perhaps the first observation of this type of phenomenon.

7. The temperature of the decahydrate-hexahydrate transition is found to be approximately 19.525°, on the international hydrogen scale.
8. The temperature of the decahydrate-tetrahydrate transition is found to be approximately 19.987 on this scale.
9. The temperature of the hexahydrate-tetrahydrate transition is found to be approximately 25.90°, on this scale.
10. All these points, especially the last, are to receive further investigation at Harvard in the near future.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]
INVESTIGATIONS ON LIGHT AND HEAT PUBLISHED WITH AID FROM THE RUMFORD FUND.

A METHOD FOR DETERMINING HEAT OF EVAPORATION AS APPLIED TO WATER.

BY THEODORE W. RICHARDS AND J. HOWARD MATHEWS.

Received April 8, 1911.

Among usual calorimetric measurements none has been in the past less satisfactory than the measurement of heat of vaporization. The methods employed have been almost as untrustworthy as they have been numerous. The results for water are indeed not very divergent, but in most other cases there is little or no concordance. In the case of ethyl formate, for example, the variation in the values given by different experimenters is over 10 per cent.; in the case of ethyl acetate, the extreme difference is over 13 per cent. These cases have been selected because they concern substances carefully investigated by many observers; less carefully studied cases might have been selected which show even greater discrepancies. Evidently most of the results are in error: but which are the correct ones? The newest values are by no means necessarily the best, for wide discrepancies have appeared in the most recent work. Part of the errors were undoubtedly due to impurity in the materials, and some to faults in the methods.

Desiring really to know the heats of evaporation of a few liquids, we felt hopeless concerning our ability to select among these discordant figures. New research was evidently needed, involving great care in purification of material, and careful choice of the best details of experimentation. The present paper contains an account of the evolution of a satisfactory method.

A brief account of previous methods may well precede the description of our own experimental work, as this was based partly on the successes and partly on the failures of others.

The methods used for measurements of heats of evaporation are of two classes. In one the energy used in the process of vaporization is