ment, upon conductivity data and may therefore be subject to some error.

Since this work was done an article has appeared by Lewis and Brighton[1] in which they express the hope that in the near future they will be able to calculate the activity of the lead ion in a solution saturated with lead chloride. On the assumption that the activity of the lead ion in a saturated solution of lead chloride is 0.562% of the total concentration, the potential of the lead electrode is readily calculated by the equation

$$E = E^\circ - \frac{RT}{2F} \ln C$$

in which

$E = 0.5187$
E° = normal electrode potential
C = concentration in mols of the ion in question.

The equation then assumes the form

$$0.5187 = E^\circ - \frac{RT}{2F} \ln (0.0388 \times 0.562) \text{ or } E^\circ = 0.4696.$$

This is the value of the normal electrode of lead against the 0.1 *N* calomel electrode at 25°.

Summary.

A lead standard cell has been prepared which has been found to possess a constant voltage which is reproducible to within a few hundredths of a millivolt. It has been found that the voltage shows a gradual decrease over an extended range of time a property frequently found in other cells.

A determination of the potential of the lead electrode against the tenth normal calomel electrode has been made and found to be 0.4696 at 25°. This value may be subject to a change when the activity of the lead ion in the solution in question becomes more accurately known.

Columbus, Ohio.

[Contribution from the Wolcott Gibbs Memorial Laboratory of Harvard University.]

THE TRANSITION TEMPERATURES OF STRONTIUM CHLORIDE AND STRONTIUM BROMIDE AS FIXED POINTS IN THERMOMETRY.

By Theodore W. Richards and Victor Yngve.

Received October 29, 1917.

Introduction.

Some years ago one of us[2] pointed out that the transition temperatures of hydrated salts, since they are invariant points, serve excellently as

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[1] This Journal, **39**, 1906 (1917).

[2] T. W. Richards, *Am. J. Sci.*, [4] **6**, 201 (1898).

fixed points in thermometry. The accuracy of this method of fixing temperatures has since been confirmed and its usefulness extended. The transition temperatures which have been the subject of careful investigation at Harvard are given below.

Transition system.	Transition temperature.
$Na_2SO_4.10H_2O$ to Na_2SO_4 + solution[1]	32.383°
$NaBr.2H_2O$ to $NaBr$ + solution[2]	50.674°
$MnCl_2.4H_2O$ to $MnCl_2.2H_2O$ + solution[3]	58.089°
$Na_2CrO_4.10H_2O$ to $Na_2CrO_4.6H_2O$ + solution[4]	19.525°
$Na_2CrO_4.10H_2O$ to $Na_2CrO_4.4H_2O$ + solution[4]	19.987°
$Na_2CO_3.10H_2O$ to $Na_2CO_3.7H_2O$ + solution[5]	32.017°

The present investigation adds to these the transition temperature (61.341°) of strontium chloride hexahydrate into the dihydrate, as well as a similar but merely preliminary result (88.62°) concerning strontium bromide.

In a preliminary manner the transition of strontium chloride hexahydrate had already been tested.[6] The transition temperature, about 61°, was found to be easily maintained, and appeared to possess the required degree of constancy. Tammann[7] had studied the effect of pressure upon the temperature of transition of strontium chloride hexahydrate; but an exact determination of this temperature seemed to be lacking. No reference has been found to a direct determination of the transition temperature of strontium bromide. Lescoeur[8] found that the dissociation tension of the hexahydrate of strontium bromide was less than that of a saturated solution of the salt at 20° and 40°, but that at 100° they were approximately equal. He concluded that a transition to a lower hydrate occurred at about this temperature—but strictly speaking no evidence was afforded as to where, between 40° and 100°, the transition actually occurred.

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[1] Richards and Churchill, *Proc. Am. Acad.*, **34**, 277 (1899); Richards and Wells, *Ibid.*, **38**, 431 (1903); Dickinson and Mueller, THIS JOURNAL, **29**, 1381 (1907), give 32.384° as the temperature of the transition.

[2] Richards and Wells, *Proc. Am. Acad.*, **41**, 435 (1906).

[3] Richards and Wrede, *Ibid.*, **43**, 343 (1907).

[4] Richards and Kelley, *Ibid.*, **47**, 171 (1911).

[5] Richards and Fiske, THIS JOURNAL, **36**, 485 (1914).

[6] Richards and Churchill, *Proc. Am. Acad.*, **34**, 277 (1899). Jeannel proposed to use the transition temperature of sodium acetate trihydrate (about 58°) as a thermometric fixed point "for constructing or calibrating thermometers" (*Compt. rend.*, **62**, 834 (1866)). This fact was not known to us until 1914 (THIS JOURNAL, **36**, 486 (1914)) and seems not to have made any impression on others nor to have been ever put to use.

[7] Tammann, "Krystalliseren und Schmelzen," **1903**, p. 251. This notice refers to the earlier work of Kremers, Mulder, and v. Sahmen, who found the values 60°, 66°, and 62.2°, respectively.

[8] Lescoeur, *Ann. chim. phys.*, [6] **19**, 554 (1890).

The Hydrates of Strontium Chloride.

Andreae[1] concluded from vapor-pressure measurements on the hydrates of strontium chloride that the hexahydrate passes into the dihydrate, a conclusion which we have confirmed by analysis of the transition product. In order to prevent the solidification of the adhering liquid phase on cooling, or during filtration, this latter process was conducted in closed vessels suitably arranged so that the whole process could be conducted in a thermostat at about 62° in a current of air previously moistened so as to be in hygroscopic equilibrium with the mixture. When no more liquid drained from the solid hydrate, it was removed, analyzed, and found to contain 2.29 H_2O. The slight excess of 0.29 H_2O was doubtless due to incomplete draining.

Purification of Strontium Chloride.

Calcium and barium are the two impurities which are the most difficult to eliminate from salts of strontium, because of the chemical similarity of these elements and the frequent tendency of their salts to form isomorphous crystals. The effect of recrystallizing strontium chloride as a means of eliminating these impurities was tested as follows: About 1% of each of the chlorides of barium and calcium was added to 20 g. of the strontium salt, the mixture recrystallized as hexahydrate, and the resulting crystals centrifuged and washed twice in the centrifuge. After three such recrystallizations practically no trace of barium could be found in the solid phase, while distinct evidences of the presence of calcium were found. Evidently barium is very rapidly eliminated from the hexahydrate, but calcium is eliminated but slowly, as would be expected from the usual forms in which the several salts occur at room temperature. On the other hand, we found that calcium can be eliminated by recrystallizing the dihydrate above the transition temperature, a process which, although it eliminates calcium, concentrates barium into the crystals instead of eliminating it from them. These two contrasting phenomena open the way for the complete purification of the salt, merely by crystallizing first above and then below 61.34°.[2] Great care must be taken to maintain the proper temperature in each case and to inoculate the solution with the proper hydrate. This is particularly necessary in the case of the hexahydrate, for the dihydrate may easily be obtained at temperatures below 61° unless due precaution is taken.

This double process, which was used in preparing one sample of chloride, is perhaps the best method yet found for freeing strontium from its

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[1] *Z. physik. Chem.*, **7**, 248 (1891).

[2] In some cases the order of crystallization might profitably be reversed, since crystallization at lower temperatures attacks the vessels less seriously, and the smaller quantities of the final processes are easier to handle in platinum or quartz than the large initial quantities.

analogs, because it does not involve any change of the anion, with the consequent danger of the introduction of other impurities. Moreover, purification is more speedily and easily attained than with any other process.

The principle involved in this method may well be of use in many other cases, for it rarely happens that a given impurity is isomorphous with two differently hydrated forms of a given salt. Hence, usually, crystallizing as one hydrate will eliminate one set of impurities, and as another hydrate will eliminate another set. Often, doubtless, all the impurities will thus be eliminated either first or last, as in the case of strontium chloride.

The nitrate of strontium also may be used as a means of purification, at least from calcium, if similar precautions are taken. From the tetrahydrated nitrate the elimination of both barium and calcium by crystallization is slow and unsatisfactory, but from the anhydrous nitrate calcium may be eliminated in a satisfactory manner, the barium being concentrated in the crystals. Hence strontium may be purified by recrystallizing first as the anhydrous nitrate until calcium is eliminated, and then as hexahydrated chloride until barium is eliminated; but on the whole this process is not so satisfactory as that in which the chloride alone is used in two different stages of hydration.

This more complicated process was used first in our work, the better one having not been perfected. The solution of over a kg. of commercially pure nitrate was heated to boiling, acidified, and hydrogen peroxide added to oxidize iron which might be present. Strontium hydroxide, from oxide prepared by igniting the pure nitrate, was now added until the solution was alkaline, the solution was filtered through a washed filter paper and the nitrate was recrystallized hot four times in porcelain. After each crystallization it was drained centrifugally and washed twice with pure warm water, for if cold water is used in washing the tetrahydrate is formed and calcium retained. The resulting salt will be referred to as Sample E. The extreme mother liquor from the last sample was concentrated and tested spectroscopically for calcium, but no evidence of calcium was found. Suitable trials showed that 0.005 mg. of calcium could be detected under similar conditions. Hence the crystallized samples of nitrate were probably very free from this impurity, since it tends toward the solution.

The nitrate was now converted into the carbonate by treatment with the distillate from a mixture of pure ammonium carbonate and hydroxide in water. The strontium carbonate was separated from the supernatant ammonium nitrate by filtration through a hardened, washed filter paper in a large Gooch crucible, and was washed with several liters of water, and dissolved in pure hydrochloric acid.

The strontium chloride thus prepared after seven crystallizations (two in porcelain and five in quartz) yielded Sample *e*. The transition temperature of this sample did not differ from that of the previous crop of crystals. Sample *f* was obtained by recrystallizing *e* in quartz. Sample D was obtained by recrystallizing six times in porcelain the mother liquors from the preparation of Sample *e*. Sample E was made by further recrystallizing D in porcelain; of these, Sample *f* was, of course, the purest.

The very convenient first-mentioned method was now used in the preparation of a new series of samples of strontium chloride.

The purest strontium chloride of commerce was recrystallized twice, in porcelain, as the dihydrate above 62°. The extreme mother liquor from the last crystallization showed, when concentrated, no traces of calcium when examined spectroscopically. The crystallized chloride was then recrystallized twice, in porcelain, as the hexahydrate. This yielded Sample L. Sample M was obtained by recrystallizing L in porcelain, and the identity of its transition temperature with that of L showed that the barium had been eliminated even from L. As will be seen, both temperatures agreed essentially with those of the purest salt *f* prepared from the nitrate. Thus strontium chloride is really very easy to purify.

The Transition Temperature of Strontium Chloride, $SrCl_2.6H_2O$ to $SrCl_2.2H_2O$.

The apparatus used in the determination of the transition temperatures was essentially identical with that used by Richards and Wrede.[1] A tall beaker 37 cm. in height and 14 cm. in diameter was used as the external bath. A large tube, closed at one end, 35 cm. long and 3 cm. in diameter, was supported within the bath to serve as an air jacket. Inside this tube was placed a smaller one, of a practically insoluble glass, 2 cm. in diameter and 30 cm. long. This inner tube was fitted with a stirrer—a stout platinum wire bent into a ring and sealed to a glass rod.

In addition to the stirrer and the standard thermometer, the inner tube also contained an auxiliary thermometer for determining the temperature of the emergent thread, since the larger tube was not wholly below the water in the bath. There was usually a small correction on this account. In order to remove all doubt as to the value of this correction, in some of the determinations a small heating coil of resistance wire was placed in the upper part of the tube and enough electrical energy was passed through the wire to heat the air in the tube to the temperature of the bulb of the thermometer. The correction determined in this manner was 0.003 of a degree, while that computed from the reading of the auxiliary thermometer was 0.004 of a degree. The first value was used in correcting all the readings.

The thermometer used was Baudin thermometer 15275, standardized

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[1] *Proc. Am. Acad. Sci.*, **43**, 344 (1907).

with great care at the Bureau des Poids et Mesures, and previously described.[1] It was read by means of an accurate cathetometer from both sides in order to eliminate errors which might be due to irregularities in the glass or a possible deviation of the thermometer from a truly vertical position. The ice points were taken immediately after reading the transition temperatures, and all the precautions mentioned by Guillaume[2] were observed.

The crystals of strontium chloride hexahydrate were placed in the inner 2 cm. tube, and this was warmed for a few minutes in a beaker of water kept a few degrees above the temperature of transition. When the mixture assumed a plastic condition the tube was dried and put in place, and the temperature readings were taken. The ice points, even when taken with all known precautions, are the most uncertain part of this work.

SAMPLE L, DETERMINATION I, MARCH 15, 1915.

Thermometer 15275:		
Barometer reduced	749.0 mm.	749.0 mm.
24 mm. inverting mixt	3.1	...
58 mm. water	...	4.3
	752.1 mm.	753.3 mm.
Reading in salt	61.464°	In ice +0.052
Correction calibration	—0.013	0.000
Correction exterior press.	+0.001	+0.001
Correction interior press.	+0.044	+0.013
Corrected reading in ice	—0.066	+0.066°
Correction for fundamental interval	—0.001	
Correction to hydrogen scale	—0.088	
Final corrected result	61.341°	

Eleven such final corrected results, from six different samples of salt, were thus obtained, and are given below. The "probable errors" computed according to the theory of least squares are appended.

TABLE II.

Transition Temperatures of Strontium Chloride.

Date 1915.	Sample.	Temperature.	Date 1915.	Sample.	Temperature.
Feb. 26	*e*	61.331°	Mar. 23	E	61.342°
Mar. 1	*e*	61.334	Mar. 15	L	61.341
Mar. 2	*f*	61.337	Mar. 16	L	61.340
Mar. 8	D	61.333	Mar. 19	M	61.344
Mar. 9	D	61.333	Mar. 24	M	61.338
Mar. 17	D	61.335			

Total mean, 61.337° ± 0.001°

Mean of last five, 61.341° ± 0.0007°

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[1] Richards and Wells, *Proc. Am. Acad. Sci.*, **38**, 43 (1902).

[2] Guillaume, "Traité pratique de la Thermometrie de Precision," 1889.

The determinations are seemingly divided into two groups, the first six and the last five. Of these groups, as usual, the later seems to be the more trustworthy. The technique was then more familiar and the ice points more convincing than at first. Moreover, the salt used in the last five trials was probably purer than the earlier samples, except Sample *f*, which gave a reading almost as high as the later ones.

Accordingly, 61.341°, or, roughly, 61.34°, is the most probable value of the temperature transition of the hexahydrate of strontium chloride into the dihydrate under atmospheric pressure, in terms of the international hydrogen scale.

The Hydrates and Transition Temperature of Strontium Bromide.

The hexahydrate of strontium bromide is well known, but the composition of the next lower hydrate does not seem to have been determined. Experiments conducted in the same manner as those described above with strontium chloride gave fairly convincing but not absolutely final evidence that this is a dihydrate, analogous to the corresponding chloride. The bromide used was prepared according to a method used in an early determination of the atomic weight of strontium.[1] Its acid solution had remained for some time in the glass vessel, but it was recrystallized five times afterwards, and the last two crops of crystals gave the same transition temperature. This determination was made in the same apparatus which served for the foregoing work with the chloride, and as a result the temperature of the transition was found to be 88.62°. Although not final, this value seems to be more trustworthy than most of those heretofore published, concerning data of this kind, except those quoted on the first page. We are glad to express our indebtedness to the Carnegie Institution of Washington for some of the apparatus and material used in this research.

Summary.

Two methods for preparing pure strontium chloride are described.

The existence of strontium chloride dihydrate has been confirmed.

The temperature of the transition of the hexahydrate of strontium chloride into the dihydrate has been found to be approximately 61.341° on the international hydrogen scale.

Evidence has been found which points to the existence of strontium bromide dihydrate.

The temperature of the transition of strontium bromide hexahydrate into the lower hydrate has been found to be approximately 88.62° on the international hydrogen scale.

CAMBRIDGE, MASS.

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[1] Richards, *Proc. Am. Acad. Sci.*, 30, 369 (1894).