solution was warmed and barium chloride added till no further precipitation occurred. The mixture was then digested at a gentle heat for one-half hour, filtered and the precipitated barium phosphate washed free of chlorides with a very dilute solution of sodium hydroxide. The filtrate after being slightly acidified with hydrochloric acid was concentrated to 250 cc. ; 100 cc. of this solution were pipetted out, and after removing the barium with sulphuric acid, the aluminum was precipitated with ammonia and ignited to Al_2O_3.

	Found per cent.	Theory for $NH_4H_2PO_4.AlPO_4$ per cent.
Al	11.53	11.42
P	26.16	26.13
NH_4	7.79	7.61

A salt prepared under slightly different conditions of acidity and concentration of the precipitant gave substantially the same results.

Properties of the aluminum salt—A qualitative study of the action of water on this salt, showed that it was hydrolyzed in precisely the same way as was noted in the case of the iron salt. Its solubilities are the same as those for the iron salt, except toward alkalies ; in the latter it dissolves completely, behaving like aluminum phosphate. On ignition it gives off ammonia and water.

QUANTITATIVE LABORATORY,
    Feb. 1907.

PHASE RELATIONS OF THE SYSTEM : SODIUM CARBONATE AND WATER

By R. C. WELLS AND D. J. McADAM, JR.

The experiments described in this paper concern the phase relations of sodium carbonate between 25° and 45°, an interval which includes all the known transition points of the hydrates. Somewhat over a year ago, Dr. L. F. Witmer and one of us were determining the solubility of this salt for the purpose of ascertaining the number of hydrates. We had made certain of at least two quadruple points when the new edition of Landolt and Börnstein's tables brought to our attention the inaugural dissertations, dealing in part with this very subject, by Herman Epple, Heidelberg, 1899 and C. H. Ketner, Leiden, 1901. After securing Epple's dissertation, we were surprised to find that he described the lower hydrates as octa and dihydrates. Our own analyses had led us to decide that they were hepta and monohydrates, although in order to get those results we had to take special precautions to prevent enclosed mother liquor from crystallizing as decahydrate and thus giving too high a percentage of water. Ketner, however, settled the matter very conclusively by analyzing a ternary mixture (sodium carbonate, alcohol and water) according to the method of Schreinemacher, and could obtain no other hydrates than those with 10, 7, and 1 molecule of water.

The transition points stated by these and previous investigators were then as follows :

	$10\cdot7\ H_2O$	$7\cdot1\ H_2O$
Richards and Churchill [1]	——	35.2^{5}
Epple..	31.8	——
Ketner [2]	31.85 falling	35.1
	32.1 rising	——

As regards the solubilities, Ketner's values for the heptahydrate in water were nearly two per cent. higher than ours.   But his solubility curves represented the phase relations only qualitatively and were not drawn to scale. Epple's results are more accurate, but there is an irregularity in his curve in the neighborhood of $36°$ which seems to indicate a new hydrate.

In view of these various discrepancies, new determinations were begun by us in 1906 and continued until we felt sure of solubility to within 0.5 per cent. of the weight of solution and of the transition temperatures to $0.02°$.

In order to eliminate the most likely sources of error first, some care was taken to purify sodium carbonate by filtration and recrystallization in platinum.   Thus obtained it was free from calcium, silica and chloride.

Theoretically the system is composed of three components, water, sodium oxide and carbon dioxide., but practically it appears unnecessary to consider more than the two components, water and sodium carbonate. It is known that the partial pressure of carbon dioxide in the air, amounting to about 0.0004 atmospheres, suffices to produce a trace of sodium acid carbonate in any exposed solution of sodium carbonate.[3] The rapidity of the absorption depends chiefly upon the exposure of the solution.   In a small stoppered bottle, no weighable amount of acid carbonate can be formed.   Even during recrystallization in open dishes the absorption is so slow that the crystals are hardly contaminated, although the solution gains in carbon dioxide.   Our sodium carbonate which had simply been recrystallized was tested for acid carbonate by adding pure dilute barium chloride in excess, then phenol-phthalein and noting the amount of standard sodium hydroxide required to produce a color.   This test in one case showed 0.09% of acid carbonate.   The remainder of our sodium carbonate, about half of the whole, was freed completely from acid carbonate without the production of oxide by prolonged gentle heating in platinum.   No certain difference in the solubility of the two samples could be detected.   Moreover by the use of special water, sufficiently pure for conductivity purposes, an excess of the gaseous phase was rendered still less likely.

[1] Pr. Am. Acad., 34, 278.

[2] Z. physik Chem., 39, 645.
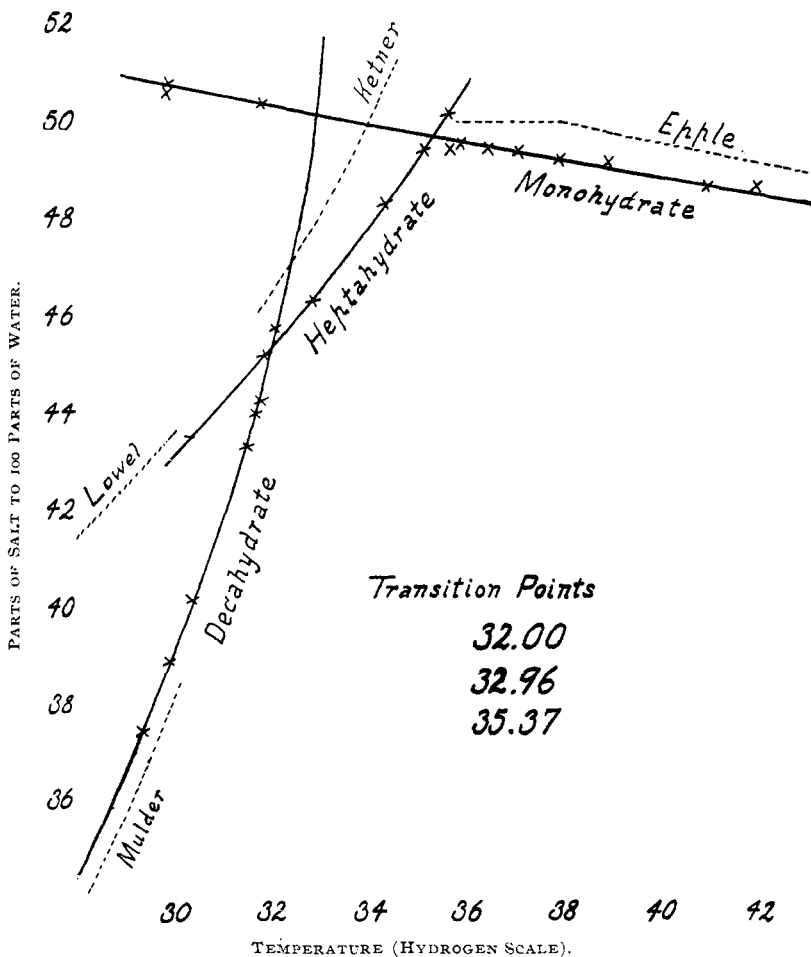
[3] Küster and Grüters, Ber., 36, 749 (1903).

Since the solubility of sodium carbonate varies greatly with the temperature, a thermostat was required which would remain constant to a hundredth of a degree. The thermostat used was heated electrically and regulated by an auxiliary current working through a relay which made and broke the heating circuit. The sensitiveness of the regulation was increased by the use of a rapidly rotating stirrer. The vessels containing the salt were agitated beneath the water of the thermostat.

Titration with normal hydrochloric acid was chosen as the simplest method of estimating the carbonate. A standard shade of methyl orange was made by saturating water with pure carbon dioxide, and used as the end point in all cases. It was found that all loss by effervescence could be prevented either by holding the flask into which acid was being run considerably inclined, or better, by placing a funnel in the mouth of the flask while the acid was being run in.

We supposed at first that one of the most important questions would be the material of the vessels in which the solution was agitated. It seemed quite likely that the glass, used by previous investigators, would dissolve considerably in the long periods required to obtain complete saturation. The matter was tested in several ways. In the first place a considerable number of determinations were made in platinum, using a platinum bottle, contents 50 cc. The results were not perceptibly different from those of determinations made in glass. However in one case, two portions of the same sample of sodium carbonate were agitated in glass and platinum respectively at 41° for four successive days. The solubility in platinum was found to be 48.56 and that in glass 48.51 parts of salt to 100 parts of water. This is a surprisingly small difference, but it was confirmed by several other parallel determinations. In the experiment mentioned the glass test tube lost 2.2 mg. This would show that the contamination by silica during one day's agitation in glass would not affect the solubility. This is partly due to the fact that sodium carbonate is such a soluble salt, but it may be possible that the attack of glass is not so rapid in a saturated solution as in a dilute solution. It should be noticed in this connection that any impurity in the sodium carbonate solution would make the solubility result too high if the salt is determined as chloride gravimetrically, but too low in our method of determination where impurity, if present, would be weighed in the solution. The percentage error in the first way would be considerably higher than in the second way, however. This may be one reason for the fact that our solubilities are not so high as those of Epple. We assured ourselves of the original purity of our salt, used a fresh portion each day for determinations in glass and estimated the salt content in several cases in both ways. The results were consistently satisfactory in every case.

In obtaining the different hydrates and working in metastable regions,

we profited much by the observations of Younge and Burke upon the hydrates of sodium thiosulphate.[1] The weighing pipette[2] was hung in a tall cylinder in the thermostat with its little filter of cotton wool attached so as to be at the same temperature as the solution. In the case of the monohydrate, the cotton wool had to be quite tightly packed or a considerable amount of the solid ran through and this invariably gave high

Transition Points
32.00
32.96
35.37

PARTS OF SALT TO 100 PARTS OF WATER.

TEMPERATURE (HYDROGEN SCALE).

results. Any experiment where there was a visible excess of solid was rejected. This may also account in part for the high results of Epple. The rubber stoppers used to close the tubes had been very thoroughly cleaned by boiling in caustic soda solution. At the end of an experiment the tubes were brought just far enough out of the water to allow

[1] This Journal. 28, 315.
[2] Ostwald-Luther, p.132.

the stoppers to be wiped.   All but the monohydrate settled quickly ; but this acquired that property only after very long agitation.   Since all the solutions were filtered, no special time was given for settling.   After drawing enough of the solution into the weighing pipette by suction applied through a rubber tube, the pipette was thoroughly cleaned on the outside, the filter removed, the pipette weighed and the contents then washed into a flask and titrated.

Equilibrium was approached both by dissolving and precipitating salt. The time required to attain equilibrium in either way was much shorter the greater the surface of the solid phase present.

The hydrochloric acid used was very carefully standardized against the purest sodium carbonate in the same fashion as the salt was determined. Three samples of sodium carbonate were used, one of which had been many times recrystallized in platinum, and all heated to constant weight at 350° in a pure environment.

First sample, 1cc. HCl = 0.0523	gm. sodium carbonate
Purer salt,	0.05319
Purest salt,	0.05316
Average chosen	0.05318

It is hardly necessary to say that the burettes were calibrated and that the acid was always measured at very nearly the same temperature.

A table is given with the solubilities found.   The results are also plotted in a diagram, together with a part of the work of other investigators which falls in this region.   Loewel described two heptahydrates,[1] but our salt is evidently the less soluble variety.   Several attempts were made to prepare the more soluble variety, but without success, nor could its transition point, which should be at about 25°, be found.

The three other transition points were obtained in the thermometric way, using a tenth-degree thermometer which could be estimated to hundredths.   The precautions outlined in previous papers.[2] were followed here, except that the thermometer was not enclosed in a jacket.   A jacket was deemed unnecessary because an accuracy of a hundredth of a degree was all that was sought for, and the stem temperature could be sufficiently well determined.   Moreover the thermometer was standardized in the same kind of an apparatus at almost precisely the same temperature, 32.38° so that all constant errors would be eliminated.

The standardization of the thermometer was accomplished by sodium sulphate, which was purified by four recrystallizations.   According to its transition point, the thermometer, after making a correction of 0.01° for

[1] Ann. chim. phys. (1851) 33, 382.
[2] Richards : Am. J. Sci. 6, 203 ; Richards and Wells : Pr. Am. Acad. 38, 431.

the projecting column was 0.05° too high at that point. It was correct
at 0.00°. The proper correction, whenever needed, was obtained by

TABLE OF SOLUBILITIES OF SODIUM CARBONATE.

	Corrected temperature (Hydrogen scale)		Parts of anhydrous salt to 100 parts of water
Na$_2$CO$_3$·10H$_2$O	27.84		34.20
	29.33		37.40
	29.85	38.87⎫ 38.91⎭	38.89
	30.35	40.18⎫ 40.05⎭	40.12
	31.45		43.25
	31.66		43.95
	31.72	44.10⎫ 44.32⎭	44.21
	32.06		45.64
Na$_2$CO$_3$·7H$_2$O	30.35		43.50
	31.82		45.16
	32.86		46.28
	34.37		48.22
	34.76		48.98
	35.15		49.23
	35.17		49.34
	35.62		50.08
Na$_2$CO$_3$.H$_2$O	29.86		50.53
	29.89		50.75
	31.80		50.31
	35.17		49.63
	35.37	49.89⎫ 49.46⎭	49.67
	35.66		49.37
	35.86		49.44
	36.45		49.36
	36.90	49.38⎫ 49.20⎭	49.29
	37.91	49.17⎫ 49.22⎪ 49.04⎬ 49.07⎪ 49.07⎭	49.11
	38.92		49.09
	41.94		48.51
	40.93	48.53⎫ 48.54⎪ 48.45⎪ 48.56⎭	48.52
	43.94		47.98

interpolation from these observations. This correction does not include
reduction to the hydrogen scale.

The transition temperatures of sodium carbonate were then found as follows :

	$10H_2O{-}7H_2O$	$10H_2O{-}1H_2O$	$7H_2O{-}1H_2O$
Uncorrected temperature...........	32.15	33.10	35.50
Correction, projecting column......	+ .02	+ .03	+ .04
Correction, error of thermometer....	— .05	— .05	— .05
Correction, hydrogen scale.........	— .12	— .12	— .12
Corrected Transition Point.........	32.00	32.96	35.37

In comparing these transition temperatures with those mentioned at the beginning of the paper, it is seen that the first is very near Ketner's value. Ketner's transition temperatures do not agree at all with his solubility determinations, however, and it looks as if his acid must have been incorrectly standardized. The phases were not stated by Richards and Churchill but they evidently, at 35.2°, had an equilibrium between the heptahydrate and monohydrate. The point 32.96 between the decahydrate and monohydrate is new. In order to obtain it, the solution was heated a considerable time above 36° in order to destroy all heptahydrates, then cooled and inoculated with decahydrate. The point, once obtained, was fully as constant as any of the other transition points.

In conclusion, it may be observed that the transition points and solubility determinations are now in good accord.

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ON SOME FERROCYANIDES OF CALCIUM, BARIUM AND MAGNESIUM

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When potassium ferrocyanide is added to solutions of calcium, barium and magnesium salts, containing free ammonia or ammonium salts, difficultly soluble precipitates are obtained. Concerning the composition of these precipitates some confusion seems to have arisen. The general idea has been that they were double ferrocyanides of potassium and the alkaline earth metals. Tests, however, showed that the product always contained ammonia; hence, it seemed of interest to ascertain whether the precipitate was a definite chemical compound or a mixture of ferrocyanides.

H. Baubigny, in an article on the separation of calcium, barium and strontium[1], suggests that, after the removal of the barium as barium chromate, and after getting rid of the excess of the chromate, the calcium be precipitated by means of potassium ferrocyanide in ammonium chloride solution. On the authority of Rose, he calls this precipitate a potassium calcium ferrocyanide. He also recommends the use of potassium ferrocyanide as a test for calcium.

[1] Chem. News., 72, 27.