Finally,

$$Ca = HCO_3 + CO_3 + H_2CO_3 \tag{11}$$

if there is no excess or deficiency of CO_2. The six equations give

$$\frac{H^4(2H + k_1)^2}{H^2 + k_1H + k_1k_2} = \frac{k_1k_2k_w^2}{k_3}. \tag{12}$$

The solution of (12) gives H = 1.09×10^{-10}, from which we then find Ca = 1.66×10^{-4}; $CO_3 = 0.56 \times 10^{-4}$; $H_2CO_3 = 1.10 \times 10^{-4}$; OH = 1.10×10^{-4}; $H_2CO_3 = 4.0 \times 10^{-8}$. An inspection of the figures shows that a solution formed from pure water and $CaCO_3$ would contain only 34 per cent. as much free CO_3 as the Ca present would represent. The remaining 66 per cent. of the CO_3 would have united with water to give HCO_3 and an equal concentration of OH. To form such a solution 16.6 mg. of $CaCO_3$ per liter of water would be required if practically complete ionization be assumed. We have calculated from the measurements of Kohlrausch[1] of the conductivity of pure water saturated with $CaCO_3$ that 12 mg. of the substance are dissolved by 1 l. of water. In so doing we have considered the hydrolysis to be 66 per cent. The agreement is only fair; the cause of the difference is not apparent.

Strontium and barium carbonates have been studied in the same way as calcium carbonate. In the case of strontium carbonate, nine experiments have been made at pressures between 0.05 and 1.1 atmospheres. The equilibrium constant $k = 1.29 \times 10^{-2}$, with an average deviation from the mean of 1.2 per cent. This value leads by equation (7) to the solubility product $Sr \times CO_3 = k_3 = 1.567 \times 10^{-9}$. With barium carbonate, eleven experiments were made at pressures between 0.2 and 30 atmospheres. The graph for $BaCO_3$ is very similar to that for $CaCO_3$; a maximum solubility, $Ba(HCO_3)_2 = 0.028$, is reached at a concentration of $H_2CO_3 = 0.727$, corresponding to a calculated CO_2 pressure of about 22 atmospheres. The solubility of $Ba(HCO_3)_2$ is 7.3 g. per liter or 0.73 g. in 100 cc. of water. For $BaCO_3$ the equilibrium constant was found to be $k = 2.24 \times 10^{-2}$; average deviation from mean = 0.8 per cent. The solubility product $Ba \times CO_3 = k_3 = 8.1 \times 10^{-9}$.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

EQUILIBRIUM BETWEEN SODIUM CARBONATE, SODIUM BICARBONATE AND WATER.

[SECOND PAPER.]

BY HERBERT N. MCCOY AND CHARLES D. TEST.

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Several years ago one of us made a study of the system carbonates of sodium, carbon dioxide and water,[2] for solutions of decinormal to normal

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[1] *Z. physik. Chem.*, 44, 236 (1903).

[2] McCoy, *Amer. Chem. J.*, 29, 437 (1903).

concentration. We have now extended this work to include solutions in equilibrium with solid phases. All experiments were carried out at 25° ± 0.02. Forty grams of pure sodium bicarbonate and about 200 cc. of water were rotated in a 25° thermostat until equilbrium was reached (usually 24 to 48 hours). Small portions of the clear solution were then analyzed by Winkler's method for carbonate content and by titration in the presence of methyl orange for sodium. About 15 g. of normal sodium carbonate decahydrate were then added to the residual mixture of saturated solution containing solid bicarbonate; the whole again rotated until a new state of equilibrium were reached and again analyzed. The results obtained by a continuation of this method are shown in the accompanying graph, where the ordinates are gram of sodium per cc. of solution and the abscissas are percentages of total sodium in form of bicarbonate in the solution. The following table gives the numerical data for points A, B, C, and **D**.

	Percentage of sodium as bicarbonate.	Grams of sodium per liter.	Grams of bicarbonate per liter.	Grams of carbonate per liter.
A..........	100.00	27.02	98.7	0.0
B..........	12.89	108.0	50.8	216.6
C..........	5.92	127.6	27.6	276.3
D..........	0.00	119.9	0.0	276.4

The point A represents the solubility of pure sodium bicarbonate in water. AB is the solubility curve for solutions containing increasing proportions of normal carbonate in equilibrium with sodium bicarbonate as the solid phase. At B 12.9 per cent. of the sodium in solution is in the form of bicarbonate and 87.1 in form of carbonate. At this point a new solid phase appears. It consists of long needles. There are therefore four-phases present at the point B: vapor, solution, solid bicarbonate and the needles. The addition of more and more solid sodium carbonate to this four-phase system at B did not change the composition of the solution until all of the solid bicarbonate had disappeared. The solution then contained less than 12.9 per cent. of the sodium as bicarbonate while but one solid phase remained. This consisted of the pure needle form, which after being drained and dried in a centrifuge had the composition $NaCO_3.NaHCO_3.2H_2O$, as shown by the following analysis:

	Calculated.	Found.
Na_2CO_3....................	46.90	46.59
$NaHCO_3$....................	37.17	35.72
$2H_2O$....................	15.93	17.69

The considerable differences between the percentages found and calculated is due to the fact that it was impossible, owing to the nature of the salt, to free the crystals completely from the mother liquor which contained but 10 per cent. of the sodium as bicarbonate.

Between B and C only one solid phase, the double salt, $Na_2CO_3.NaHCO_3.2H_2O$, is present. At C $Na_2CO_3.10H_2O$ is also present, giving again a four-phase system, of which the solution has a fixed composition, with 5.9 per cent. of the sodium as bicarbonate. Solutions containing smaller proportions of the sodium as bicarbonate give the line CD, the solid phase being $Na_2CO_3.10H_2O$.

The mineral trona or urao, which occurs as a natural deposit from the waters of some alkali lakes, is a more or less pure form of the sesquicarbonate, $Na_2CO_3.NaHCO_3.2H_2O$. In earlier times this natural soda was thought to be $Na_2CO_3.2NaHCO_3$ with varying proportions of water. The correct formula was first given by Laurent.[1] Chatard[2] has made an exhaustive study of natural soda, especially as it occurs at Owen's Lake, Calif. His papers contain extensive references to the literature of the subject.[3]

A number of methods for the artificial preparation of the sesquicarbonate are found in the literature.[4]

All are more or less indefinit or involve the addition of a foreign substance, as common salt. Since the sesquicarbonate, in which $33^1/_3$ per cent. of the sodium is in the form of bicarbonate, is stable in contact with aqueous solutions only when these contain between 12.9 and 5.9 per cent. of the total sodium as bicarbonate it is plain why it is decomposed by water and can not be recrystallized in the ordinary way. This fact explains the difficulties that have been encountered in the artificial preparation of the substance.

Our experiments lead to the following method of preparation: 42 g. of bicarbonate and 700 g. of carbonate decahydrate are dissolved in enough water to make one liter of solution. This solution contains about 10 per cent. of its sodium as bicarbonate. Its composition corresponds to a point between B and C on the graph. If now sodium carbonate, bicarbonate and water in the proportions indicated by the formula $Na_2CO_3.NaHCO_3.2H_2O$ be added to the above solution, and the whole shaken at 25°, all of the materials last added will unite to form needles of the sesquicarbonate. The mother liquor may be used repeatedly with new portions of material.

The interpretation of the results from the standpoint of the phase rule is very simple. The system has three components. Since the temperature is fixed (25°) the maximum number of phases is four. This condition is fulfilled at the points B and C. At B, there are in addition

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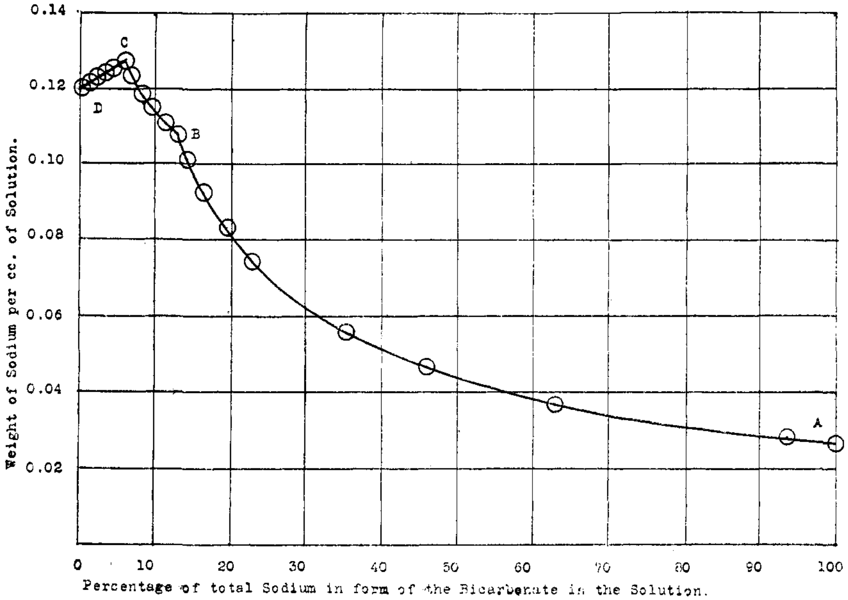
[1] *Ann. chim. phys.*, [3] 36, 348 (1852).

[2] U. S. Geol. Survey., *Bull.* 60, 27 (1887); *Am. J. Sci.*, 38, 59.

[3] See also Lunge, *Z. angew. Chem.*, 1893, 3.

[4] Mondesir, *Compt. rend.*, 104, 1505 (1887); Watts and Richards, D. R. P., 43, 583; Chatard, *Loc. cit.*; Winkler, *Répert.*, 48, 215; *Z. angew. Chem.*, 1893, 445, 599.

to the liquid and vapor phases, two solid phases: bicarbonate and sesquicarbonate. At C, the two solid phases are sesquicarbonate and normal carbonate decahydrate. Each of the three curves represents a three-phase system, each having a vapor, a liquid and a solid phase. Along AB the solid is the bicarbonate; along BC it is the sesquicarbonate; along CD the decahydrate of the normal carbonate. We have made preliminary determinations of the concentration of carbon dioxide in the vapor in equilibrium with solutions of various bicarbonate content. The concentration is high at A and decreases rapidly toward B. When air is drawn through a saturated solution of bicarbonate, in contact with an excess of the solid, the solution loses carbon dioxide: at first rapidly, later very slowly. In six weeks, at 25°, the composition of the solution changed along the curve AB until the solution contained only 18 per cent. of its sodium as bicarbonate. The rate of change was now very slow, but equilibrium had not been reached.



[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 66.]

THE HEAT CONTENT OF THE VARIOUS FORMS OF SULFUR.

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In a systematic calculation of the free energy of the sulfur compounds, we have found it necessary to know, with some degree of precision, the