compression the arbitrary equations found to fit these curves are

$$
\begin{aligned}
(F + 0.15)\,(A + 36.6) &= 452 && \text{(I)}\\
(F + 0.15)\,(A - 32.2) &= 556 && \text{(II)}\\
(F + 0.15)\,(A - 41.2) &= 771 && \text{(III)}\\
(F + 0.15)\,(A - 510) &= 925 && \text{(IV)}\\
(F + 0.15)\,(A - 540) &= 1210 && \text{(V)}\\
(F + 0.15)\,(A - 2350) &= 3470 && \text{(VI)}
\end{aligned}
$$

From the "b" term in these two dimensional van der Waals equations we note that the ease of partial immersion of the chains varies inversely as the chain length, whereas the ease of immersion is about equal for the acid and neutral succinates (IV and V) of nearly the same chain length. The maximum pressure withstood by the films before collapse sets in does not vary appreciably with the chain length and is in the neighborhood of 2.5 dyne/cm.

This work was carried out in the Laboratory of Colloid Science, The University, Cambridge, England, under the direction of Professor E. K. Rideal, to whom the author is greatly indebted.

Summary

It is shown that the polymeric acid and neutral ethylene succinates form a regular series of stable unimolecular films on dilute acid substrates. The films are similar to vapor expanded films of fatty acid esters. Evidence is presented for the assumption that the molecular chains are flexible and can be closely packed before immersion on compression occurs. The closeness of approach is found to be 5.85 Å. units comparable with the value 5.25 Å. obtained from x-ray data.

RIDLEY PARK, PA. RECEIVED AUGUST 21, 1933

[CONTRIBUTION FROM THE LABORATORIES OF THE COLUMBIA DIVISION OF THE PITTSBURGH PLATE GLASS COMPANY AND OF NEW YORK UNIVERSITY]

Aqueous Solubility of Salts at High Temperatures. II. The Ternary System Na_2CO_3–$NaHCO_3$–H_2O from 100 to 200°

BY WILLIAM F. WALDECK,[1] GEORGE LYNN[2] AND ARTHUR E. HILL

An earlier publication[3] from these laboratories gave measurements of the solubility of sodium carbonate in water up to 348°. The present investigation introduces a third component, sodium bicarbonate, up to temperatures of 200°, beyond which the work could not be carried with accuracy because of the very high pressures involved, causing large loss of carbon dioxide in amounts which could not be estimated exactly.

Apparatus and Methods

The solubility measurements were made in bombs of Allegheny metal as shown in Fig. 1, having a capacity of 135 cc. These bombs differ in construction from those used previously[3] in having the sampler set in from the top, which makes the apparatus less unwieldy and permits the insertion of several in the thermostat at one time; they also lack the relief valves of the earlier construction. The details as to threading, springs, washers, etc., may be had from the earlier paper, as also the details of the air thermostat used. The salts used were of the highest commercial grade, the bicarbonate, however, always containing a small percentage of normal carbonate which was determined by analysis and allowed for in the calculations; the two salts and water were weighed into the bomb by the method of difference, so that the exact composition of the complex could be used as one of the necessary two points for determining the composition of the solid phase by the method of extrapolation.[4] After equilibrium had been attained at the temperature of the thermostat and time had been allowed for the settling of the solid, a sample of solution was allowed to enter the sampler by opening its needle valve. After the system had reached room temperature the sampler was removed and weighed, the contents washed out and analyzed for total alkali by titration with methyl orange and xylene cyanole FF as indicator and for carbon dioxide by absorption in soda lime, which gave data for calculation of the complete composition. A small but noticeable amount of iron was leached from the bombs at 190° and above, appearing at first as a bluish opalescence; on exposure to the air this became oxidized and precipitated as what was apparently ferric hydroxide; where the amounts made it advisable, this was filtered off before the analysis. The presence of small amounts of chromium in the samples was mentioned in the earlier publication.

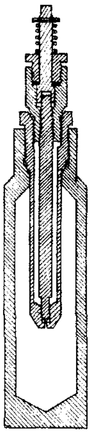

Fig. 1.

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[1] The experimental work of this paper is from the thesis of Mr. Waldeck, presented in partial fulfilment of the requirements for the degree of Ph.D. at New York University, June, 1933.

[2] Mr. Lynn coöperated throughout the completion of this work, which has been written up since his death.

[3] Waldeck, Lynn and Hill, THIS JOURNAL, **54**, 928 (1932).

[4] Schreinemakers, *Z. physik. Chem.*, **11**, 81 (1893); Bancroft, *J. Phys. Chem.*, **6**, 178 (1902); for the algebraic method see Hill and Ricci, THIS JOURNAL, **53**, 4305 (1931).

Through the work of Freeth,[5] Hill and Bacon[6] and Wegscheider and Mehl[7] the ternary system is well understood up to the temperature of 100°, at which point this work was begun. The results are given in Table I and shown in Fig. 2.

TABLE I

Na_2CO_3–$NaHCO_3$–H_2O AT 100°

Original complex Wt. % Na_2CO_3	Original complex Wt. % $NaHCO_3$	Solution Wt. % Na_2CO_3	Solution Wt. % $NaHCO_3$	Solid phases
0.4	27.1	1.2	18.5	$NaHCO_3$
7.9	23.9	8.7	16.0	$NaHCO_3$
12.1	22.6	12.7	14.4	$NaHCO_3 + 3NaHCO_3 \cdot Na_2CO_3$
13.2	22.2	14.6	13.9	$NaHCO_3$ (metastable)
14.0	21.3	15.3	13.8	$NaHCO_3$ (metastable)
15.4	20.9	13.4	14.4	$3NaHCO_3 \cdot Na_2CO_3$
18.2	20.8	16.5	11.9	$3NaHCO_3 \cdot Na_2CO_3$
18.4	18.3	16.5	12.0	$3NaHCO_3 \cdot Na_2CO_3$
20.5	16.8	19.3	10.7	$3NaHCO_3 \cdot Na_2CO_3$
21.8	17.2	21.0	9.8	$3NaHCO_3 \cdot Na_2CO_3$
24.0	16.2	21.1	9.7	$3NaHCO_3 \cdot Na_2CO_3 + NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$
26.2	13.4	27.7	8.8	$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$
26.3	12.1	23.6	8.2	$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$
27.8	10.5	25.3	7.1	$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$
27.5	10.6	25.1	7.2	$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$
28.8	10.1	26.7	5.9	$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$
29.5	8.6	27.9	5.2	$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$
29.4	8.7	27.7	5.3	$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$
32.0	5.4	29.1	4.2	$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O + Na_2CO_3 \cdot H_2O$
32.9	3.1	29.2	3.4	$Na_2CO_3 \cdot H_2O$
35.2	2.2	29.9	2.3	$Na_2CO_3 \cdot H_2O$
..	..	30.7	..	$Na_2CO_3 \cdot H_2O$

As will be seen in Fig. 2, all but four of the determinations (omitted from the graph) give tie-lines which extrapolate satisfactorily to the solid phases. The solids are four in number, the monohydrate of sodium carbonate, trona ($NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$), the salt $3NaHCO_3 \cdot Na_2CO_3$, first found by Wegscheider and Mehl[8] and later patented by Cocksedge,[9] and the bicarbonate. These with the anhydrous Na_2CO_3 are the only solid phases which we have found within the entire temperature range investigated; the salt $Na_2CO_3 \cdot 2NaHCO_3 \cdot 2H_2O$, for which Wegscheider and Mehl[7] found admittedly incomplete indications in their isotherm at 90°, has not been found. The curve for the bicarbonate was carried over into the metastable field. The curve for trona is not greatly changed from its dimensions at lower temperatures. In the experimental work, satisfactory results on the trona curve could not be obtained by use of mixtures of the two components, probably because it crystallizes about the particles of solid sodium carbonate and prevents their complete transformation; the use of pure crystallized trona in this field obviated the difficulty. The curve for Wegscheider's double salt has increased greatly in length as compared with the curve at 85–90°, at about which temperature Wegscheider found it to form.

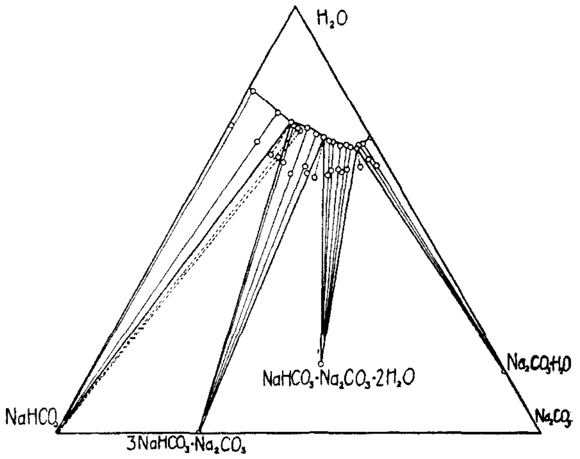

Fig. 2.—Isotherm at 100°.

With the information at present available as to the carbonates of sodium, it may be shown that the simplest system capable of including them all would be a system of tetra-carbonates, as follows:

$H_8(CO_3)_4$	carbonic acid
$Na_4H_4(CO_3)_4$	sodium bicarbonate
$Na_5H_3(CO_3)_4$	Wegscheider's salt
$Na_6H_2(CO_3)_4$	trona
$Na_8(CO_3)_4$	normal carbonate

The next complete isotherm was studied at 150°, as shown in Table II and Fig. 3.

TABLE II

Na_2CO_3–$NaHCO_3$–H_2O AT 150°

Original complex Wt. % Na_2CO_3	Original complex Wt. % $NaHCO_3$	Solution Wt. % Na_2CO_3	Solution Wt. % $NaHCO_3$	Solid phases
0.6	40.0	2.5	26.8	$NaHCO_3$
4.4	35.9	5.1	26.4	$NaHCO_3$
..	..	8.4	25.6	$NaHCO_3 + 3NaHCO_3 \cdot Na_2CO_3$
12.8	29.9	10.0	23.6	$3NaHCO_3 \cdot NaHCO_3$
13.8	25.1	12.3	21.6	$3NaHCO_3 \cdot NaHCO_3$
15.4	24.9	13.8	20.0	$3NaHCO_3 \cdot NaHCO_3$
19.4	20.8	18.3	17.3	$3NaHCO_3 \cdot NaHCO_3$
..	..	20.7	15.4	$3NaHCO_3 \cdot Na_2CO_3 + NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$
27.4	17.4	22.4	11.9	$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$
..	..	23.1	10.2	$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O + Na_2CO_3$
25.2	15.3	20.9	15.9	Na_2CO_3 (metastable)
29.8	6.7	24.4	7.4	Na_2CO_3
33.6	3.1	25.9	3.4	Na_2CO_3
..	..	27.5	..	Na_2CO_3

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(5) Freeth, *Trans. Royal Soc.* (London), **223A**, 35 (1922).

(6) Hill and Bacon, THIS JOURNAL, **49**, 2487 (1927).

(7) Wegscheider and Mehl, *Monatsh.*, **49**, 283 (1928).

(8) Wegscheider and Mehl, *Verhandlungen der Gesellschaft deutscher Naturforscher und Aerzte*, 85 Versammlung zu Wien, Sept. 1913, 11 Teil, I Haelfte, p. 366.

(9) Cocksedge, U. S. Patent 1,583,660; also 1,473,259, 1,503,481, 1,583,661, 1,583,662, 1,583,663.

At this temperature the stable form of sodium carbonate is unhydrated; the transition temperature is 112.5 ± 1°.[3] The solubility of the carbonate decreases with the temperature while that of the bicarbonate increases, which accounts for the marked extension of the solubility curve of the carbonate and the corresponding shrinkage of that for the bicarbonate as the temperature rises. The curve for Wegscheider's salt reaches its maximum length at about this temperature. The decomposition pressure of solutions high in bicarbonate has doubtless reached a high figure, involving a considerable loss of carbon dioxide to the gas space and thereby invalidating the accuracy of the points taken for the original complex; for this reason the extrapolation of the tie-line for the figures of line 2 fails to pass through the composition represented by $NaHCO_3$. It will be noted that this error, which of course introduces no uncertainty as to $NaHCO_3$ as the solid phase, becomes less as the solutions become higher in content of Na_2CO_3; but the region over which this error prevails becomes greater and greater as the temperature rises, and is given discussion and estimation later on.

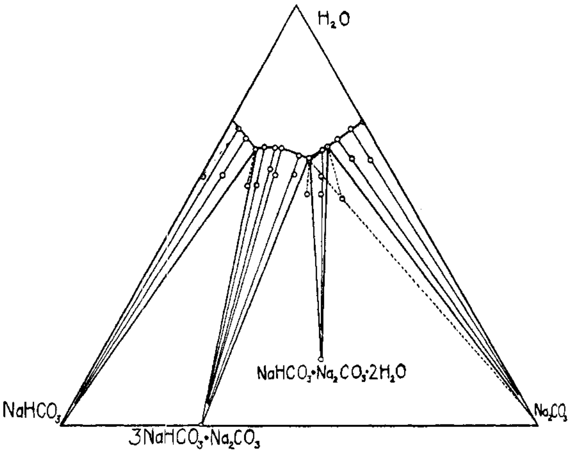

Fig. 3.—Isotherm at 150°.

The results at 170° are given in Table III and Fig. 4.

At this temperature the losses of carbon dioxide become increasingly apparent, and since their amount varies with the volume of the gas space left in the apparatus, we have the difference in results of lines 1 and 2, both undertaken with the same complex. The figures for the isothermally invariant points are the mean of from two to four determinations, varying several tenths of one per cent. from each other. It is a matter of interest that the field of stability for trona, through its regular movement toward the left of the diagram with rise of temperature, has caused the salt to pass through a temperature range of congruent solubility and again out of it; at 150° and all lower temperatures the salt is incongruently soluble, at about 160° it is congruently soluble, and at 170° it has again passed into a region of incongruent solubility, this latter being a region of excess of bicarbonate. In an earlier publication[6] the prediction was made that the salt would show congruent solubility at high temperatures.

TABLE III

Na_2CO_3–$NaHCO_3$–H_2O AT 170°

Original complex Wt. % Na_2CO_3	Original complex Wt. % $NaHCO_3$	Solution Wt. % Na_2CO_3	Solution Wt. % $NaHCO_3$	Solid phases
0.7	48.0	3.6	31.7	$NaHCO_3$
.7	48.0	4.7	31.6	$NaHCO_3$
..	..	7.5	31.2	$NaHCO_3 + 3NaHCO_3 \cdot Na_2CO_3$
10.1	33.5	9.7	28.4	$3NaHCO_3 \cdot Na_2CO_3$
..	..	13.5	24.3	$3NaHCO_3 \cdot Na_2CO_3 + NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$
22.5	22.2	18.4	19.7	$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$
..	..	18.9	18.3	$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O + Na_2CO_3$
25.4	15.3	19.3	16.3	Na_2CO_3
..	..	26.0	..	Na_2CO_3

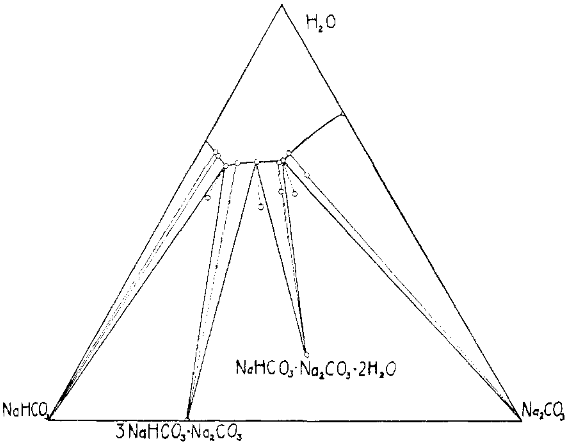

Fig. 4.—Isotherm at 170°.

The results at 190° are given in Table IV and Fig. 5.

At this temperature the carbon dioxide pressure from pure bicarbonate solutions is probably of the order of 1000 lb. per sq. in. estimated from data given in the next paragraph. No effort to bring this into calculation at 190° was made. Line 1 represents an effort to secure a point as near the bicarbonate axis as possible by filling the gas space with carbon dioxide gas by adding

TABLE IV

Na_2CO_3–$NaHCO_3$–H_2O AT 190°

Original complex Wt. % Na_2CO_3	Original complex Wt. % $NaHCO_3$	Solution Wt. % Na_2CO_3	Solution Wt. % $NaHCO_3$	Solid phases
($NaHCO_3$ + CO_2 gas)		1.7	36.8	$NaHCO_3$
1.0	50.0	4.8 ± 0.8	35.6 ± 1.5	$NaHCO_3$
..	..	7.0 ± .4	35.0 ± 1.5	$NaHCO_3$ + $3NaHCO_3{\cdot}Na_2CO_3$
..	..	10.2 ± .0	33.0 ± 0.1	$3NaHCO_3{\cdot}Na_2CO_3$ + $NaHCO_3{\cdot}Na_2CO_3{\cdot}2H_2O$
18.4	30.8	13.7	28.9	$NaHCO_3{\cdot}Na_2CO_3{\cdot}2H_2O$
..	..	16.7 ± .1	25.5 ± .4	$NaHCO_3{\cdot}Na_2CO_3{\cdot}2H_2O$ + Na_2CO_3
24.5	19.2	17.2	20.7	Na_2CO_3
28.9	10.0	19.7	11.6	Na_2CO_3
..	..	24.2	..	Na_2CO_3

1 to 2 g. of solid carbon dioxide. Figures are included showing the variation in analytical results at the isothermally invariant points.

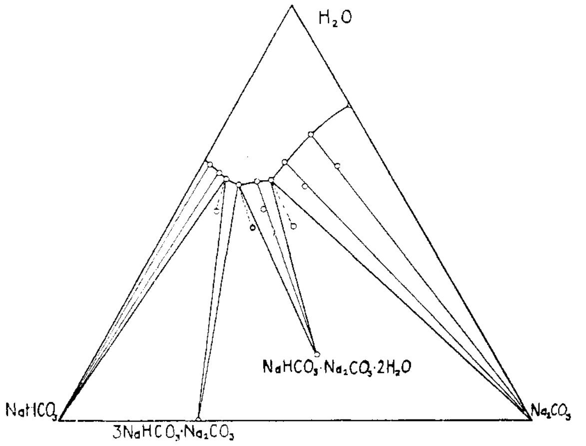

Fig. 5.—Isotherm at 190°.

The results at 200° are shown in Table V. As will be seen from Fig. 6, there is but one double salt found; it would be quite impossible to determine from the uncorrected figures, invalidated by large loss of carbon dioxide, which double salt remains of the two known to exist at 190°. To determine the amount of this loss, so that proper correction could be made, a sample containing 1% Na_2CO_3, 67% $NaHCO_3$ and 32% H_2O was heated at 200° in the usual manner in the bomb described in our earlier work,[3] which permitted a measurement of the pressure. This was found to be 1325 lb. per sq. in.; diminished by the pressure of water vapor at this temperature and also by that due to residual air, the approximate volume of which was known, the

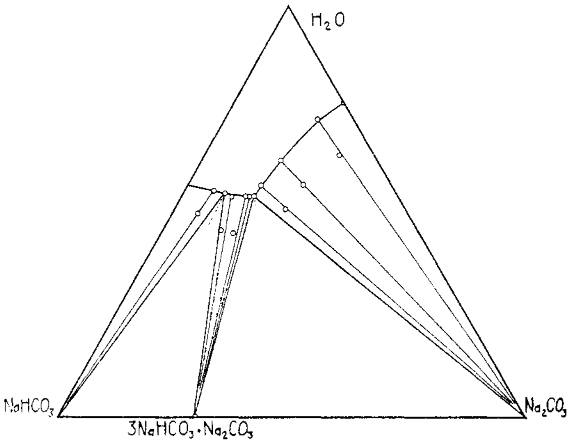

Fig. 6.—Isotherm at 200°.

TABLE V

Na_2CO_3–$NaHCO_3$–H_2O AT 200°

Original complex Wt. % Na_2CO_3	Original complex Wt. % $NaHCO_3$	Solution Wt. % Na_2CO_3	Solution Wt. % $NaHCO_3$	Solid phases
1.0 + 4.6	50.0	6.1 ± 0.9	38.6 ± 1.1	$NaHCO_3$
..... .	..	9.0 ± 0.6	36.4 ± 0.7	$NaHCO_3$ + $3NaHCO_3{\cdot}Na_2CO_3$
12.4 + 1.5	42.1	10.9	35.6	$3NaHCO_3{\cdot}Na_2CO_3$
12.6 + 1.5	43.3	12.6	33.5	$3NaHCO_3{\cdot}Na_2CO_3$
12.7 + 1.5	44.4	13.0	32.4	$3NaHCO_3{\cdot}Na_2CO_3$
14.6 + 0.9	40.0	13.8	32.2	$3NaHCO_3{\cdot}Na_2CO_3$
13.8 + 1.1	42.6	14.7	31.3	$3NaHCO_3{\cdot}Na_2CO_3$
14.9 + 0.8	40.4	14.6	31.4	$3NaHCO_3{\cdot}Na_2CO_3$
..... .	..	15.4 ± 0.5	30.5 ± 0.6	$3NaHCO_3{\cdot}Na_2CO_3$ + Na_2CO_3
23.8	25.5	15.7	27.7	Na_2CO_3
24.8	18.5	16.9	20.3	Na_2CO_3
28.8	7.1	19.9	7.5	Na_2CO_3
..	..	23.3	..	Na_2CO_3

carbon dioxide pressure was 1120 lb. Another determination was made with a complex of 15% Na_2CO_3, 45% $NaHCO_3$ and 40% H_2O, giving a corrected pressure of 190 lb. per square inch. Taking the gas space in our regular bomb as 30 cc. it became possible to calculate the loss of carbon dioxide and the gain in sodium carbonate content of the solutions within the range given. These corrections are added to the composition taken in column 1 of Table V; when they are taken into account, the usual extrapolations run in satisfactory manner. They indicate that trona has disappeared from the system between 190 and 200°; its upper transition temperature may therefore be placed as 195 ± 5°. Wegscheider's salt is still stable at 200°.

On cooling to room temperature the bomb which had shown a pressure of 1325 lb. at 200°, and allowing it to stand for several hours, it was found that there remained a high residual pressure of 500 lb. This indicates that the reabsorption of carbon dioxide in the cold system is slow and incomplete. As a result the samples taken for analysis at the higher temperatures should lose carbon dioxide to the gas phase while hot and fail to reabsorb it in its entirety upon cooling; upon the samplers being opened there should be a loss of carbon dioxide. This was found to be the case in the experimental work and is the probable explanation of the variation in analytical results obtained at 190 and 200°, and shown in Tables IV and V.

In addition to the complete isotherms at five temperatures, determinations of the isothermally invariant points were made at five other temperatures, given in Table VI.

TABLE VI

Na_2CO_3–$NaHCO_3$–H_2O

Additional invariant points

Temp., °C.	Solid phases	Wt. % Na_2CO_3	Wt. % $NaHCO_3$
126	Na_2CO_3 + Trona	25.4	8.6
	Trona + $3NaHCO_3 \cdot Na_2CO_3$	20.9	11.8
135	Na_2CO_3 + Trona	25.4	8.2
	Trona + $3NaHCO_3 \cdot Na_2CO_3$	22.0	13.3
143	Na_2CO_3 + Trona	24.6	8.6
	Trona + $3NaHCO_3 \cdot Na_2CO_3$	22.2	14.2
160	Na_2CO_3 + Trona	22.1	10.4
	Trona + $3NaHCO_3 \cdot Na_2CO_3$	20.0	17.4
180	Na_2CO_3 + Trona	18.3	20.7
	Trona + $3NaHCO_3 \cdot Na_2CO_3$	14.9	26.3

It is found that trona is stable in contact with solutions between 21.26°[6] and 195 ± 5°. Whether or not there is a transition to an anhydrous form at high temperatures remains unknown, as our results have not the high accuracy which would distinguish between extrapolations to the two formulas in question. There is, however, nothing in the movements of the invariant points to suggest that a change of phase has occurred.

The Solubility of Sodium Bicarbonate at Higher Temperatures.—By extrapolating our curves in the three-component isotherms to zero concentration of normal carbonate, it is possible to obtain figures of moderate accuracy for the solubility of the pure bicarbonate, under the natural pressure of the system. These are given in Table VII.

TABLE VII

SOLUBILITY OF $NaHCO_3$ IN H_2O UNDER NATURAL PRESSURE OF THE SYSTEM

Temp., °C.	Wt. % $NaHCO_3$
100	19.1 ± 0.2
150	27.2 ± 0.7
170	32.0 ± 1.0
190	37.5 ± 1.0
200	43.0 ± 1.0

These results are shown in Fig. 7, the curve for lower temperatures being taken from "International Critical Tables."

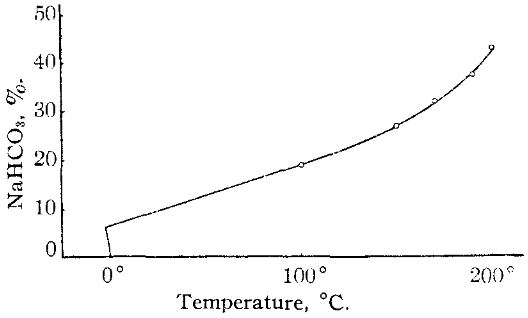

Fig. 7.—Solubility of $NaHCO_3$ in water

Summary

The system Na_2CO_3–$NaHCO_3$–H_2O has been studied between the temperatures 100 and 200°, and isotherms have been drawn for five temperatures. The isothermally invariant concentrations of solutions saturated with two salts have been determined at five other temperatures. Trona is found to be a stable double salt up to 195 ± 5°; Wegscheider's double salt $3NaHCO_3 \cdot Na_2CO_3$ is stable throughout the entire range of temperatures. The solubility of pure $NaHCO_3$ from 100 to 200°, under the natural pressure of the system, has been determined by a method of extrapolation.

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