Thermal Decomposition of Sodium Sesquicarbonate

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Equilibrium decomposition pressure data and x-ray diffraction analyses on sodium sesquicarbonate decomposition products have shown Wegscheider's salt ($3NaHCO_3 \cdot Na_2CO_3$) to be an intermediate. Heat of formation of this salt is 952.9 kcal. (25° C.), as calculated from the measured temperature dependence of the second pressure plateau. First pressure plateau data gave a heat of formation for sodium sesquicarbonate of 639.4 kcal. (25° C.), in good agreement with 641.2 kcal., previously measured by an independent method. A kinetic study of sesquicarbonate decomposition under CO_2/N_2 streams has shown that CO_2 can add to sesquicarbonate under a total pressure of 1 atm. Thus a series of anhydrous mixed alkalies containing $3NaHCO_3 \cdot Na_2CO_3$ and Na_2CO_3 can be produced from sodium sesquicarbonate, where products are pseudomorphous after the parent crystals.

IN THE EARLIEST known reference to sodium sesquicarbonate decomposition, Lescoeur (*4*) measured equilibrium decomposition pressures at 100° C. as a function of product vapor withdrawal. Although the vapors were not collected and measured, there were two distinct pressure plateaus at about 500 and 184 mm. of Hg; the first was interpreted to characterize the formation of an anhydrous form of sesquicarbonate, and the second, destruction of the anhydrous to form Na_2CO_3.

The thermogram of sesquicarbonate decomposition measured by Beck (*2*) gave no clue to the nature of the thermal decomposition. Studies made in connection with the Polish soda ash industry (*6*) showed that sodium sesquicarbonate began to decompose at 55–57° C., but no attempt was made to determine the mechanism.

More recently, Mitkevich (*5*) re-interpreted the data of Yushkevich and Avdeeva (*9*) to suggest that Wegscheider's salt (*8*) is an intermediate in the decomposition of sodium sesquicarbonate according to the scheme

$$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O = \tfrac{1}{3}(3NaHCO_3 \cdot Na_2CO_3) + \tfrac{2}{3}\,Na_2CO_3 + 2H_2O$$

$$\tfrac{1}{3}(3NaHCO_3 \cdot Na_2CO_3) = \tfrac{5}{6}\,Na_2CO_3 + \tfrac{1}{2}\,CO_2 + \tfrac{1}{2}\,H_2O$$

The close agreement between the pressure they obtained for $3NaHCO_3 \cdot Na_2CO_3$, erroneously reported as $4NaHCO_3 \cdot Na_2CO_3$, and the second plateau pressure of Lescoeur was cited as evidence for this mechanism.

The only previous value for the heat of formation of sodium sesquicarbonate (*7*) had been derived from heat of solution data on naturally occurring sodium sesquicarbonate (trona) taken from the Green River, Wyoming, basin.

The present investigation was originally undertaken in order to determine the decomposition pressure over sesquicarbonate as a function of temperature in connection with the thermal decomposition of the solid in contact with aqueous solution (wet calcination). The determination of the mode of sesquicarbonate decomposition and heats of formation from pressure data was a natural extension of the study.

EXPERIMENTAL

Materials. The high purity sodium sesquicarbonate was in the form of air-dried centrifuge cake, (supplied by Intermountain Chemical Co., Green River, Wyo.). A typical analysis on the large, well-defined monoclinic needles is:

Na_2CO_3	46.6% (theor. 46.9)
$NaHCO_3$	37.3% (theor. 37.2)
NaCl	0.02%
Na_2SO_4	0.00%

The needles were lightly ground prior to use in the pressure experiments, but were not sieved or ground for the kinetics study.

Where C.P. Na_2CO_3, $Na_2CO_3 \cdot H_2O$, or $NaHCO_3$ was mixed with the sesquicarbonate, the salts were always ground separately prior to mixing. Only Na_2CO_3 was oven-dried and desiccated.

Naturally occurring Wegscheider's salt was used in the x-ray diffraction study. The mineral contained large amounts of sodium chloride; it was therefore necessary to etch the mineral in either saturated NaCl, or $NaHCO_3$-Na_2CO_3 solutions in order to isolate a higher purity sample for an x-ray powder pattern. Several peaks for Wegscheider's salt in the ASTM pattern (*1*) belong to NaCl, and two important peaks at 2.80 A. and 2.84 A. were not previously reported, probably because of interference from the 2.82 A. peak for NaCl.

The CO_2 and N_2 commercial tank gases used in the atmospheric pressure decomposition experiments were dried but not purified further.

Apparatus. DECOMPOSITION PRESSURES. The usual mercury isoteniscope was unsatisfactory in the present experiments when it became necessary to draw off and collect product vapor. In its place, a three-column apparatus was used, where the two adjacent 6-mm. tubes were used for balancing, and the 12-mm. tube allowed uniform bleeding of gas bubbles through the mercury into the external system.

The attainment of equilibrium in carbonate-bicarbonate systems, known to be slow (*3*), was greatly accelerated by the use of a special stirring magnet encased in glass tubing and covered with smooth glass "spikes." The spikes prevented the magnet from riding atop the solids and packing them. The magnet was activated by a large horseshoe magnet acting through the bottom of the constant temperature oil bath in which the entire bulb-isoteniscope assembly was immersed. Without stirring, equilibrium in a 90° C. system, for example, would not be attained over a two-week period; with stirring the same system would reach constant pressure in about 48 hours. Approximately 12 grams of solid was stirred in a 50-ml. bulb (Figure 1).

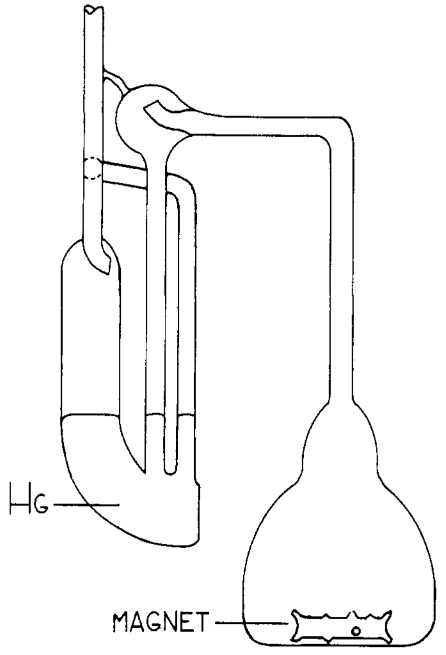

Figure 1. Sample bulb and modified isoteniscope

Levelling of the mercury was accomplished with the aid of fine needle valves, and observed by focussing a cathetometer through a window in the bath insulation. Balancing was reproducible to within ±0.2 mm. Barometer and manometer readings were corrected for temperature, meniscus, and capillarity.

SESQUICARBONATE-CO_2 Reactions. A Rinco evaporator was modified by drilling a hole through the steel axis and introducing a J-type thermocouple wire which measured the temperature of the rotating solids at the outside of the gas inlet. The 500-ml. Morton flask containing the solids was fitted with a ground glass adapter which held the ring-sealed gas inlet tube and at the same time allowed exit gases to escape into the atmosphere. The rotating flask was lowered into a constant temperature oil bath until it was immersed about two-thirds of the way. Preheating of the metered inlet CO_2-N_2 gas mixtures was unnecessary. Condensation of water in the outlet annular space was prevented by the use of an infrared lamp. Reaction temperatures were followed on a Honeywell-Brown recorder.

Analytical Methods. CARBONATE, BICARBONATE ASSAY. Because of the absence of gross impurities in the reaction mixtures, it was possible to improve upon the precision and accuracy of the usual barium carbonate precipitate titration method by decomposing the sample in a 260° C. tube furnace, and measuring weight loss and CO_2 and H_2O evolved.

X-RAY DIFFRACTION ANALYSIS. All samples were run on a Phillips diffractometer using nickel-filtered copper $K\alpha$ radiation (1.54 A.) at 35 kv. and 20 ma. A one-degree-per-minute scanning speed was used. Intensity values given in the tables were corrected for background radiation by subtracting an average value found on either side of the peak in question. The interplanar spacing values, d, were determined at maximum peak height.

RESULTS AND DISCUSSION

Table I. Total Equilibrium Pressures over Stirred Sodium Sesquicarbonate–Salt Mixtures

T, ° C.	p, MM. Hg	T, ° C.	p, MM. Hg
10:1 sesqui: Na_2CO_3		5:5:1 sesqui: $Na_2CO_3 \cdot H_2O:Na_2CO_3$[d]	
40.5[a]	13.8	60.1[a]	59.5
50.7[a]	24.5	80.1[a]	193.5
60.4[a]	48.0	99.9[a]	574.3
70.1[a]	93.9	110.3[a]	910.4
80.1[a]	169.1	115.3[a]	1100.4
90.1[a]	296.7	105.3[b]	760.8
100.0[a]	510.1	95.0[b]	446.5
111.9[a]	907.1	8:2:1 sesqui:$NaHCO_3$:Na_2CO_3	
99.9[a]	504.1	60.0[a]	56.3
110.0[a]	839.7	82.1[a]	198.4
105.0[b]	642.6	100.0[a]	513.1
100.0[b]	507.2	90.0[b]	304.4
97.0[b]	431.9	81.2[b]	195.8
95.9[b]	408.7	75.0[b]	135.2
95.1[b]	389.2	70.1[b]	101.9
85.1[b]	232.1	59.9[b]	56.6
74.9[b]	130.2	10:1:1 sesqui:$NaHCO_3$:Na_2CO_3	
65.1[b]	77.0	41.9[a]	16.6
47.3[b]	28.9	60.1[a]	55.0
10:1 sesqui:$Na_2CO_3 \cdot H_2O$[c]		40.4[a]	26.1
40.6[a]	21.6	60.1[a]	68.3
60.0[a]	56.2	80.1[a]	188.1
84.2[a]	216.7	100.3[a]	538.6
97.2[a]	501.6		

[a] Ascending temperature series. [b] Descending temperature series. [c] Reverts to sesqui–Na_2CO_3 curve below 85° C., then cakes at 97° C. in spite of stirring. [d] Reverts to sesqui–Na_2CO_3 curve above 100° C.

Decomposition Pressures and Mechanism. Equilibrium decomposition pressures for several salt mixtures are given in Table 1. As expected, reabsorption of gases upon lowering the temperature was slow, but was accelerated by lowering in 1° or 2° steps to avoid caking of the stirred solids. Results on the unstirred mixtures are not reported; although pressures remained virtually constant after as long as one week, they cannot be considered as equilibrium values because of the observed encrustation. In fact, liquid formed over an unstirred sesquicarbonate -$NaHCO_3$ mixture at about 75° C.

Curve 1 in Figure 2 represents the best straight line that can be drawn through the higher temperature data for the sesquicarbonate-Na_2CO_3 mixture. Ascending temperature points fall slightly below, and descending points, slightly above this line below about 40° C. Addition of $Na_2CO_3 \cdot H_2O$ to the system resulted in a pressure increase but did not appreciably alter the slope of the curve (Curve 2). Thus over-all decomposition schemes involving $Na_2CO_3 \cdot H_2O$ can be eliminated:

$$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O = \tfrac{3}{2} Na_2CO_3 \cdot H_2O + \tfrac{1}{2} CO_2 + H_2O$$

$$\tfrac{3}{2} Na_2CO_3 \cdot H_2O = \tfrac{3}{2} Na_2CO_3 + \tfrac{3}{2} H_2O \qquad (1)$$

$$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O = \tfrac{1}{3} (3NaHCO_3 \cdot Na_2CO_3) + \tfrac{2}{3} Na_2CO_3 \cdot H_2O + \tfrac{4}{3} H_2O$$

$$\tfrac{1}{3} (3NaHCO_3 \cdot Na_2CO_3) = \tfrac{5}{6} Na_2CO_3 + \tfrac{1}{2} CO_2 + \tfrac{1}{2} H_2O$$

$$\tfrac{2}{3} Na_2CO_3 \cdot H_2O = \tfrac{2}{3} Na_2CO_3 + \tfrac{2}{3} H_2O \qquad (2)$$

Equation 1 is univariant because CO_2 and H_2O can be expressed as the single component H_2CO_3, and could have been expected to give rise to a regular log p vs. $1/T$ curve. Equation 2 is invariant, however, existing only at a single temperature where the pressure curves of Equations 2a and 2b intersect.

$$\mathrm{Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O = \tfrac{1}{3}(3NaHCO_3 \cdot Na_2CO_3) + \tfrac{2}{3}\, Na_2CO_3 + 2H_2O}$$

$$\mathrm{\tfrac{1}{3}(3NaHCO_3 \cdot Na_2CO_3) = \tfrac{5}{6}\, Na_2CO_3 + \tfrac{1}{2}\, CO_2 + \tfrac{1}{2}\, H_2O} \qquad (2a)$$

$$\mathrm{Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O = \tfrac{1}{3}\,(3NaHCO_3 \cdot Na_2CO_3) + \tfrac{2}{3}\, Na_2CO_3 \cdot H_2O + \tfrac{4}{3}\, H_2O}$$

$$\mathrm{\tfrac{1}{3}(3NaHCO_3 \cdot Na_2CO_3) + \tfrac{1}{3}\, H_2O = \tfrac{5}{6}\, Na_2CO_3 \cdot H_2O + \tfrac{1}{2}\, CO_2} \qquad (2b)$$

A mechanism involving $NaHCO_3$ such as Equation 3 can be eliminated because such a system is invariant.

$$\mathrm{Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O = Na_2CO_3 + NaHCO_3 + 2H_2O}$$

$$\mathrm{NaHCO_3 = \tfrac{1}{5}(3NaHCO_3 \cdot Na_2CO_3) + \tfrac{1}{5}\, CO_2 + \tfrac{1}{5}\, H_2O}$$

$$\mathrm{\tfrac{1}{5}(3NaHCO_3 \cdot Na_2CO_3) = \tfrac{1}{2}\, Na_2CO_3 + \tfrac{3}{10}\, CO_2 + \tfrac{3}{10}\, H_2O} \qquad (3)$$

The fact that $NaHCO_3$ addition to decomposing sesquicarbonate raises the pressure and leaves the slope virtually unchanged (Curve 3) makes it improbable that $NaHCO_3$ is involved. But the most obvious proof that $NaHCO_3$ is not an intermediate in the thermal decomposition is that the known total equilibrium decomposition pressure of $NaHCO_3$ (*3*) exceeds that of sesquicarbonate (Curve 1).

Consideration of the simplest of all mechanisms,

$$\mathrm{Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O = \tfrac{3}{2}\, Na_2CO_3 + \tfrac{1}{2}\, CO_2 + \tfrac{5}{2}\, H_2O} \qquad (4)$$

indicates that there is no way of distinguishing it from that suggested by Mitkevich (*5*) on the basis of decomposition pressures alone:

$$\mathrm{Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O = \tfrac{1}{3}(3NaHCO_3 \cdot Na_2CO_3) + \tfrac{2}{3}\, Na_2CO_3 + 2H_2O}$$

$$\mathrm{\tfrac{1}{3}(3NaHCO_3 \cdot Na_2CO_3) = \tfrac{5}{6}\, Na_2CO_3 + \tfrac{1}{2}\, CO_2 + \tfrac{1}{2}\, H_2O} \qquad (5)$$

The log *p vs.* $1/T$ slope does not offer a means of distinction because Equation 4 is simply the net reaction for Equation 5. It remains for pressure-composition data to resolve the question. Equation 4 will give rise to a single pressure *vs.* water withdrawal plateau which falls off at a 2.5 mole ratio of water to sesquicarbonate. Equation 5 should show two distinct plateaus,—one which drops off after two moles of water have been given off, and the other at 2.5.

Table II gives pressure values corresponding to the weight of water vapor drawn off and condensed, for sesquicarbonate samples held at 90° C. and 100° C.; two distinct plateaus are evident in each case. At 100° C., the second plateau fell off slightly before the theoretical 2.5 H_2O-sesquicarbonate mole ratio was reached owing to an accidental bleeding in the series. The 90° C. data show well defined breaks at 2.0 and 2.5

Thus the simpler decomposition mechanism of Equation 4 would seem to give way to the process of Mitkevich which involves a Wegscheider's salt intermediate. However, an initial evolution of two moles of water could also account for the formation of a true anhydrous sodium sesquicarbonate, as proposed by Lescoeur:

$$\mathrm{Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O = Na_2CO_3 \cdot NaHCO_3 + 2H_2O} \qquad (6)$$

Furthermore, chemical assay for carbonate-bicarbonate on a mixture sampled at a point beyond the first pressure plateau would fail to distinguish between Equations 5 and 6. Therefore, resort was made to x-ray diffraction analysis of a mixture obtained by bleeding gases from a sesquicarbonate sample held at 90° C. until the first transition was reached; water evolved was not measured. Chemical analysis showed 67.1% Na_2CO_3, 32.5% $NaHCO_3$. This can be interpreted either as 46.5% Wegscheider's salt + 53.6% Na_2CO_3; or as 73.9% $Na_2CO_3 \cdot NaHCO_3$ + 26.1% Na_2CO_3.

X-ray diffraction data in Table III show that Wegscheider's salt is indeed present along with Na_2CO_3 as the only other component. The pattern for the Green River mineral used in the proof compares well with that of the ASTM standard, except that some peaks in the latter properly belong to NaCl (Table IV). Also, two important peaks at 2.80 A. and 2.84 A. are not found in the standard pattern, possibly because they were obscured by a 2.82 A. NaCl peak.

A semiquantitative estimate of the relative concentrations in the unknown was made by using Na_2CO_3 peaks and salt peaks not common to each other:

Wegscheider's salt (salt peaks only)	49±7%
Na_2CO_3 (Na_2CO_3 peaks only)	40±7%

Table II. Decomposition Pressures over Sodium Sesquicarbonate

Withdrawal of Product Vapors

Pressure (MM. of Hg)	Moles H_2O/ Mole Sesqui	Pressure (MM. of Hg)	Moles H_2O/ Mole Sesqui
$T = 100°$ C.		$T = 90°$ C.	
500.5	. . .	295.6	0.505
504.3	1.58	295.9	0.908
286.9	1.99	297.5	1.733
191.2	2.00	299.5	1.962
192.9	2.40	98.5	2.071
96.0	2.44	96.6	2.103
58.3	2.45	95.4	2.367
		94.4	2.397
		72.7	2.529

Table III. X-Ray Diffraction Analysis

Na_2CO_3		Wegscheider's Salt[a]		Decomp. Product	
d, A.	I/I_i[b]	*d*, A.	I/I_i[b]	*d*, A.	I/I_i[b]
. . .	. . .	3.68	107	3.69	8
. . .	. . .	3.50	11	3.51	6
3.43	15	. . .	. . .	3.43	6
3.23	18	3.25	7[c]	3.23	6
. . .	. . .	3.11	15	3.11	7
. . .	. . .	3.09	13	3.09	7
2.97	100	2.96	140	2.97	43
. . .	. . .	2.95	125	. . .	. . .
. . .	. . .	2.92	14	2.92	11
. . .	. . .	2.84	39	2.84	10
. . .	. . .	2.82	24[c]	2.81	10
2.72	28	2.73	8	2.73	8
. . .	. . .	2.66	38	2.67	11
. . .	. . .	2.65	24	2.65	15
2.62	42	2.63	13	2.63	15
2.61	46	2.60	8	2.61	15
2.55	67	2.55	15	2.55	25
. . .	. . .	2.48	14	2.48	7
. . .	. . .	2.45	13	2.46	6
2.37	100	. . .	. . .	2.37	28
2.34	10	2.33	8	2.34	6
2.26	48	. . .	. . .	2.26	14
. . .	. . .	2.22	68	2.23	11
2.20	35	. . .	. . .	2.20	13
. . .	. . .	2.10	21	2.10	8
2.04	13	2.07	6	2.04	6
1.96	34	1.95	4	1.96	10
1.93	6	1.928	10	. . .	. . .
. . .	. . .	1.915	10	1.92	6
1.89	32	. . .	. . .	1.89	13
. . .	. . .	1.722	21	. . .	. . .
. . .	. . .	1.719	13	. . .	. . .
1.71	14	1.710	8	1.71	6
1.68	13	. . .	. . .	1.68	6

[a] Mineral sample, 2.24% NaCl; remainder, 30.0% Na_2CO_3(theor. 29.6%); 69.9% $NaHCO_3$ (theor. 70.4%).
[b] I_i intensity of 2.97A. Na_2CO_3 peak set to 100.
[c] NaCl has peaks at these points.

Table IV. Comparison of X-Ray Diffraction Pattern for Wegscheider's Salt with ASTM Standard

Experimental[a]		ASTM Values (*1*)	
d, A.	I/I_t[b]	*d*, A.	I/I_t[b]
. . .	. . .	4.30	40
3.68	76	3.67	40
3.50	8	. . .	. . .
3.25	5[c]	3.26	20[c]
3.09	9	. . .	. . .
2.96	100	2.96	100
2.95	89	. . .	. . .
2.92	10	. . .	. . .
2.84	28	. . .	. . .
2.82	17[c]	. . .	. . .
2.80	8	. . .	. . .
2.73	6	. . .	. . .
2.66	27	. . .	. . .
2.65	17	. . .	. . .
2.63	9	2.63	80
2.60	6	. . .	. . .
2.55	11	. . .	. . .
2.48	10	. . .	. . .
2.45	9	2.43	60
2.33	6	2.31	20
2.22	49	2.20	60
2.10	15	2.08	50
2.00	6[c]	1.99	50B[c]
1.93	7	. . .	. . .
1.915	7	. . .	. . .
1.906	7	1.89	60
1.77	6	1.80	40
1.722	15	. . .	. . .
1.719	9	1.72	60B
1.710	6	. . .	. . .
1.63	7[c]	1.62	40[c]

[a,b,c] Same as Table III.

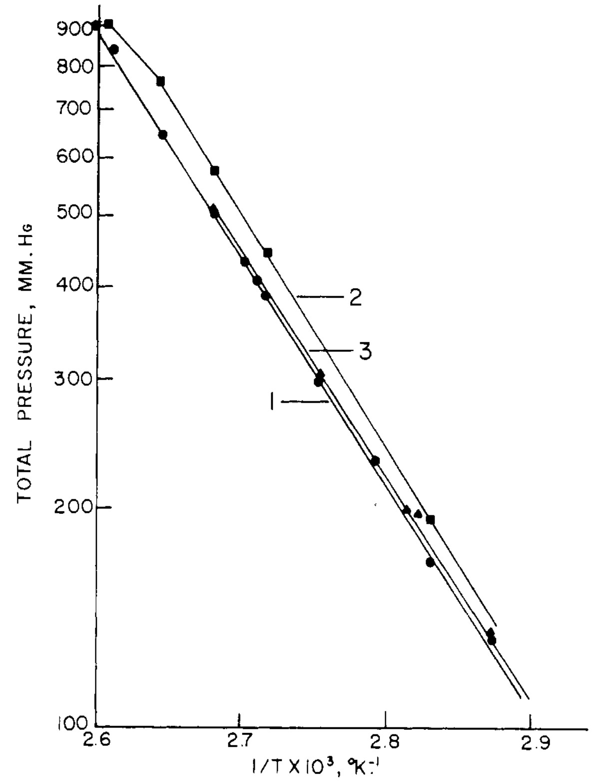

Figure 2. Sodium sesquicarbonate decomposition pressures

1—10:1 Sesqui:Na_2CO_3
2—5:5:1 Sesqui:$Na_2CO_3 \cdot H_2O$:Na_2CO_3
3—8:2:1 Sesqui:$NaHCO_3$:Na_2CO_3

The agreement between chemical and x-ray data shows that a true anhydrous sodium sesquicarbonate does not exist, and Mitkevich is correct in concluding that the detection of $4NaHCO_3 \cdot Na_2CO_3$ by Yushkevich and Avdeeva was erroneous.

Heats of Formation. In another series of experiments, gases were withdrawn from decomposing sesquicarbonate until well within the second plateau region, and the temperature dependence was followed. Table V gives the ascending and descending temperature pressures. The heat of decomposition was estimated from the best straight line through the data points, which is represented by $\log p = 11.8651 - 3574/T$. From these data, and Curve 1 of Figure 2, represented by $\log p = 10.9387 - 3075/T$, the heats of formation of sodium sesquicarbonate and of Wegscheider's salt were calculated (Table VI). There is good agreement between the present value for sesquicarbonate and that of Torgeson (*7*), obtained by an independent method.

Dynamic Pressure Measurements. When relatively stable intermediates are formed during the decomposition, it is sometimes possible to observe a halt in the vapor pressure–time curve. Measurements were made on stirred and unstirred salt mixtures from the instant when the bulb assembly was lowered into the constant temperature bath. An independent measurement of the heating curve showed that about 10 minutes were required for the solids to reach bath temperature. Figure 3 shows the results at 100° C. and again illustrates the importance of stirring.

There is a marked plateau for $NaHCO_3$ at approximately 40% of equilibrium pressure, indicating the relative stability of the intermediate Wegscheider's salt where approximately ⅖ of the total equilibrium pressure would be exhibited according to

$$NaHCO_3 = \tfrac{1}{5}(3NaHCO_3 \cdot Na_2CO_3) + \tfrac{1}{5}CO_2 + \tfrac{1}{5}H_2O.$$

For unstirred sesquicarbonate the equilibrium vapor pressure is actually exceeded for a time, indicating that the forward step in the decomposition is faster than the reaction of Wegscheider's salt with water and Na_2CO_3:

$$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O \rightleftarrows \tfrac{1}{3}(3NaHCO_3 \cdot Na_2CO_3) + \tfrac{2}{3}Na_2CO_3 + 2H_2O$$

Decomposition Under CO_2/N_2 Streams. In order to shift the CO_2-evolution reactions to the left, CO_2 diluted with N_2 was passed over thermally decomposing sesquicarbonate using the Rinco apparatus described above. With 100% CO_2, reaction temperatures rose to a peak (below the 130° C. bath temperature), dropped to a trough, and then rose slowly again to bath temperature. An unexpected rise in bicarbonate assay led to the postulate of a bicarbonate

Table V. Second Plateau Pressures

Pressure (mm. of Hg)	Temp., ° C.
53.5[a]	80.0
193.3[a]	100.2
592.0[a]	120.0
193.3[b]	100.0
64.0[b]	80.0

[a] Ascending temperature. [b] Descending temperature.

Table VI. 25° C. Heats of Formation from Decomposition Pressures

	Δ*H*, kcal.	Source
Sodium	639.4	This work
Sesquicarbonate	641.2	Torgeson (*7*)
Wegscheider's salt	952.9	This work

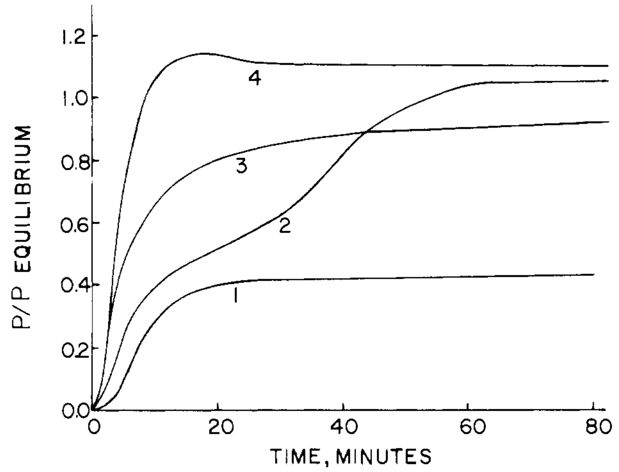

Figure 3. Decomposition pressure-time curves for $NaHCO_3$ and $Na_2CO_3 \cdot 2H_2O$ at 100° C.

1—$NaHCO_3$, stirred
2—$NaHCO_3$, unstirred
3—$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, stirred
4—$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, unstirred

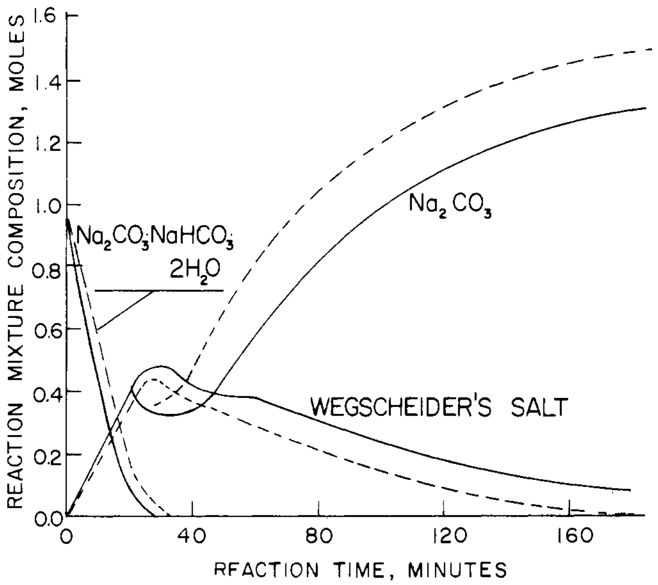

Figure 4. Reaction of sodium sesquicarbonate with CO_2
—— 100 mole % CO_2
------- 50 mole % CO_2

rich complex, inasmuch as maximum vapor pressures occurring at peak temperature were insufficient to stabilize $NaHCO_3$ itself. The logical reaction to consider is

$$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O + \tfrac{2}{5}CO_2 = \tfrac{3}{5}(3NaHCO_3 \cdot Na_2CO_3) + \tfrac{8}{5}H_2O$$

where the heat of reaction can now be calculated from the results above as −13.1 kcal. at 25° C. According to chemical analysis on a 28.5-minute run sample, 84% Wegscheider's salt and 16% Na_2CO_3 should have been present. X-ray diffraction analysis showed 86±7% salt, in good agreement with the postulate. In Table VII, analytical results have been expressed in terms of undecomposed sesquicarbonate, Wegscheider's salt, and Na_2CO_3.

Representative reaction results are shown in Figure 4, where sesquicarbonate is seen to disappear rather rapidly, Wegscheider's salt experiences a maximum, and Na_2CO_3 builds as water vapor is removed from the system.

Theoretically, it is possible to make Wegscheider's salt from sodium sesquicarbonate in 100% yields, without the formation of $NaHCO_3$. Attempts to do this at 115° and 120° C. using 100% CO_2 at atmospheric pressure showed that the temperature peak encountered earlier was the special case of a reaction plateau, where the carbonate, bicarbonate, and water assay varied little over the plateau. Although x-ray diffraction showed Wegscheider's salt and Na_2CO_3, it was evident from weight recovery data that 100% Wegscheider's salt was not produced. Instead, the data are in excellent quantitative agreement with the expression obtained by adding the equations:

$$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$$
$$= \tfrac{1}{3}(3NaHCO_2 \cdot Na_2CO_3 + \tfrac{2}{3}Na_2CO_3 + 2H_2O$$

$$Na_2CO_3 ; NaHCO_3 \cdot 2H_2O + \tfrac{2}{5}CO_2 = \tfrac{3}{5}(3NaHCO_3 \cdot Na_2CO_3) + \tfrac{8}{5}H_2O$$

to give:

$$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O + \tfrac{1}{5}CO_2 =$$
$$\tfrac{7}{15}(3NaHCO_3 \cdot Na_2CO_3) + \tfrac{1}{3}Na_2CO_3 + \tfrac{9}{5}H_2O$$

where the calculated heat for the net reaction is −19.7 kcal. at 25° C. Superatmospheric pressure CO_2 is required to produce the salt quantitatively, by supressing the initial evolution of water. Under the conditions described, the reaction products—all pseudomorphs after the parent crystals—can be represented by the general formula:

$$[(\tfrac{7}{5} - x)(3NaHCO_3 \cdot Na_2CO_3) + (1 + \tfrac{5}{2}x)(Na_2CO_3)]\ 0 \leqq x \leqq \tfrac{7}{5}$$

Table VII. Reaction of Sodium Sesquicarbonate with Carbon Dioxide

Atmospheric Pressure; Bath Temperature = 130° C.

Reaction Time, Minutes	Reaction Mixture Composition, Moles, Normalized		
	Sesqui.	Weg. Salt	Na_2CO_3
	100% CO_2 at 2.25 l./min.		
0.0	1.00	0.00	0.00
20.0	0.095	0.39	0.41
28.5	0.00	0.48	0.31
40.0	0.00	0.42	0.33
60.0	0.00	0.38	0.55
73.3	0.00	0.33	0.67
180.0	0.00	0.08	1.30
	50% CO_2-50% N_2 at 3 l./min.		
0.0	1.00	0.00	0.00
28.5	0.03	0.44	0.36
49.5	0.00	0.34	0.65
72.7	0.00	0.24	0.90
185.5	0.00	0.00	1.51
	25% CO_2-75% N_2 at 3 l./min.		
0.0	1.00	0.00	0.00
20.0	0.30	0.24	0.45
31.4	0.05	0.28	0.78
52.0	0.01	0.09	1.29
83.0	0.00	0.00	1.50
	100% N_2 at 3 l./min.		
0.0	1.00	0.00	0.00
22.0	0.31	0.16	0.62
38.0	0.01	0.12	1.24
61.0	0.00	0.00	1.49
95.0	0.00	0.00	1.49

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Second Virial Coefficients of Mixtures of Nonpolar Molecules from Correlations on Pure Components

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The empirical correlations of the second virial coefficient of pure compounds as a function of temperature are shown to be satisfactory for mixtures of gases. From the London theory of dispersion attraction, the Lennard-Jones potential energy function, and the theory of corresponding states, the critical-pressure and critical-temperature characteristic of an unlike pair interaction are obtained in terms of the critical values of the two species involved in the pair interaction. These unlike pair critical values are used directly in the empirical relationships for pure compounds to obtain the second virial coefficient of a mixture of two or more molecular species. The average of the absolute per cent deviation of the calculated cross coefficient from its experimental value in 21 binary systems is 9.7 per cent.

THE SECOND virial coefficient depends on the interaction between only two molecules at a time. Statistical thermodynamics allows one to calculate the second virial coefficient from a knowledge of the isolated pair potential energy. Recently, Hudson and McCoubrey (*10*) have shown that theoretically sound combining rules for the potential energy between nonpolar molecules can be used in the statistical calculation of the second virial coefficient.

An alternate procedure for calculating the second virial coefficient in mixtures is to use empirical corresponding state correlations for pure components together with mixing rules to obtain the critical-constants characteristics of the interaction of an isolated pair. Heretofore the simple geometric mean assumption for the energy of interaction and the arithmetic mean rule for the characteristic intermolecular distance have been used to obtain the critical temperature and the critical volume, respectively, for a mixture (*1*, *7*). Prausnitz and Gunn (*18*) have used empirical combining rules for the energy of interaction and the single-component correlations of Pitzer and Curl (*14*) to calculate virial coefficients in mixtures. This last method requires a restatement of Pitzer's correlations in terms of the critical volume rather than in terms of the critical pressure as it originally appears.

Empirical correlations of second virial coefficients, B, are in the form of B/V_c *vs.* reduced temperature, T/T_c, or BP_c/RT_c *vs.* T/T_c. The use of correlations of this sort, obtained on pure components, for the calculation on the virial coefficients of mixtures requires values for V_{c12}, P_{c12}, and T_{c12}. These parameters are the critical constants characteristic of interaction of unlike molecules 1 and 2. The purpose of this work is to show that T_{c12} and P_{c12} for the unlike isolated pair interaction are not, in general, given by the geometric mean rule. These parameters may, however, be estimated from the critical properties of the pure components. The parameters so obtained give reliable values for the second virial coefficient of mixtures from correlations for single component systems.

CRITICAL CONSTANTS FOR UNLIKE MOLECULAR PAIRS

Hudson and McCoubrey (*10*) have shown from the London theory of dispersion forces and the Lennard-Jones 6, 12 potential energy function that corresponding state theory requires that the critical temperature characteristic of an unlike pair of interacting molecules be given by

$$T_{c12} = (T_{c11}T_{c22})^{1/2} f_I f_s^6 \qquad (1)$$

where

$$f_s = 2(V_{c11}/V_{c22})^{1/6}/[1 + (V_{c11}/V_{c22})^{1/3}] \qquad (2)$$

$$f_I = 2(I_1/I_2)^{1/2}/(1 + I_1/I_2) \qquad (3)$$

It can also be shown (*11*) that the characteristic critical pressure for unlike pair interactions is

$$P_{c12} = (P_{c11}P_{c22})^{1/2} f_I f_s^9 \qquad (4)$$

and that

$$V_{c12} = (V_{c11}V_{c22})^{1/2}/f_f^3 \qquad (5)$$

Equation 5 is merely a transformation of the arithmetic mean rule for V_{c12}:

$$V_{c12} = [(V_{c11}^{1/3} + V_{c22}^{1/3})/2]^3 \qquad (6)$$

Equations 1 and 4 are the mixture rules for evaluating the characteristic critical constants for an unlike isolated pair.