

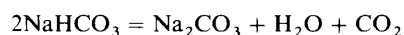
Investigation of the Formation of Wegscheiderite, $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$

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The reaction of sodium carbonate with water vapour and carbon dioxide has been studied in the temperature range 343–368 K in pure carbon dioxide, and at pressures of water vapour between 1×10^4 and $5 \times 10^4 \text{ N m}^{-2}$. The products of reaction, sodium hydrogencarbonate and/or wegscheiderite, vary with temperature and pressure, and stability fields are presented. Reaction mechanisms for the formation of wegscheiderite are probably diffusion controlled but are complicated by side reactions. The rate of formation of wegscheiderite is very dependent on the partial pressure of water vapour: analysis of this dependence suggests that sodium carbonate monohydrate is the most likely intermediate.

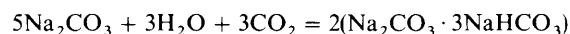
In the manufacture of sodium carbonate by the Solvay process, sodium hydrogencarbonate is heated:¹



In practice, the hydrogencarbonate is slightly damp, and, for reasons of heat balance, some reaction product is recycled, so that various side reactions are possible between carbonate, hydrogencarbonate, water and carbon dioxide. Depending on conditions, these may result in the formation of sodium carbonate monohydrate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), sodium sesquicarbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), or wegscheiderite ($\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$). The rates of formation and subsequent decomposition of these compounds are important in the overall efficiency of the calcination stage of the process. Previous work on the decompositions of some of these compounds has been published.^{2,3,4}

Wegscheiderite has been relatively little studied in comparison with the other compounds in the Na_2CO_3 – NaHCO_3 – H_2O system. Its natural occurrence⁵ and crystallography have been examined,⁶ and its thermal decomposition has recently been studied.⁴ Conditions for its preparation⁷ have been outlined, but little systematic work on the preparation has been done.

The aim of the present work is to investigate the formation of wegscheiderite at atmospheric pressure by the reaction of anhydrous sodium carbonate with carbon dioxide and water:



in order to approximate to the conditions applying during the industrial calcination of sodium hydrogencarbonate.

Experimental

Mass gain *vs.* time measurements were used to study the rates of the reaction of sodium carbonate. Sample masses were $30 \text{ mg} \pm 10\%$ throughout and mass increases were measured using a CI Mark 2 electrobalance and a chart recorder (sensitivity 40 mg f.s.d.). A constant temperature was maintained around the sample chamber by pumping water through an insulated water jacket from a thermostatically controlled tank. The atmosphere in the sample chamber was controlled by bubbling carbon dioxide (99.5%) at a constant rate through thermostatted distilled water before allowing it to flow into the sample chamber. A counter-current of dry nitrogen was passed through the balance head to prevent water vapour affecting the instrument. Additionally, at high partial pressures of water, heating tapes were used to prevent condensation occurring outside the sample zone. Reaction temperatures remained constant to $\pm 1 \text{ K}$. The reaction was

timed from when carbon dioxide was allowed to flow directly into the sample chamber. The products of all of the experimental runs were identified by X-ray diffractometry (Philips PW1050 goniometer, modified to step-scanning by Hiltonbrooks Ltd., using $\text{Cu-K}\alpha$ radiation). SEM photographs (ISI Model SS40) of the starting material and selected products were also obtained.

Results

Reaction Products

X-Ray powder diffractometry provided the best means for product identification by comparing powder patterns for samples of anhydrous sodium carbonate, wegscheiderite, sodium sesquicarbonate and sodium hydrogencarbonate with those obtained from each product. The only products of the reaction under the conditions specified were wegscheiderite and sodium hydrogencarbonate. Fig. 1 summarises the temperature and pressure conditions for each run, and the products as determined by X-ray diffractometry.

Reaction Mechanisms for the Formation of Wegscheiderite

Reduced-time plots were derived from the experimental α - t curves (where α is the proportion of the complete reaction) by using reduced time values, $t_R = t/t_{0.5}$, where $t_{0.5}$ is the time at which 50% mass gain has occurred, *i.e.* when $\alpha = 0.5$. The experimental reduced-time plots were directly compared with theoretical reduced time curves for different mechanisms.⁸

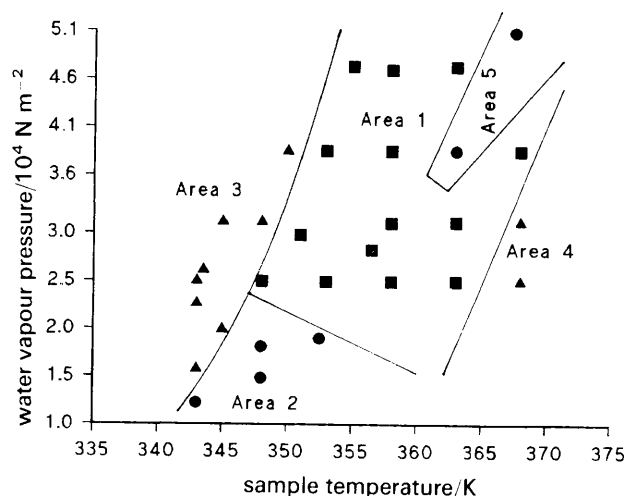


Fig. 1 Variation of reaction product with temperature and water vapour pressure. ▲, Hydrogencarbonate only; ■, wegscheiderite only; ●, mixed wegscheiderite/hydrogencarbonate

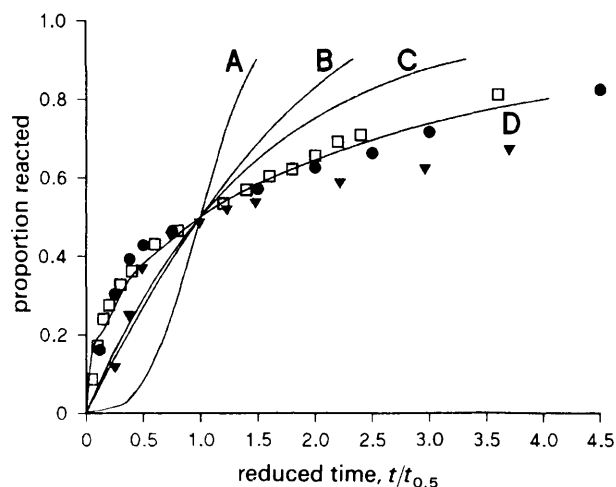


Fig. 2 Reduced-time plots for the formation of wegscheiderite. A, Avrami-Erofev equation, $n = 3$, $-\ln(1 - \alpha) = kt^3$; B, contracting disc equation, $[1 - (1 - \alpha)^{1/2}] = kt$; C, first-order equation, $-\ln(1 - \alpha) = kt$; D, Jander's equation, $[1 - (1 - \alpha)^{1/3}]^2 = kt$. ●, data from run 9; □, data from run 12; ▼, data from run 27

This method normally indicates the 'best fit' between experimental results and the theoretical models. In this work the method was only used where a single product was obtained.

The fit between experimental data and models was not good, but it can be said that the curves were deceleratory, and that probably some form of diffusion was rate-controlling. Typical reduced-time curves are shown in Fig. 2, with model equations for comparison. One feature worthy of comment is that several of the weight-gain curves did not reach high values of α , despite long reaction times. The limiting values decreased with increasing temperature and pressure; these are incorporated into Table 1.

Reaction Rates for the Formation of Wegscheiderite

Rate constants, k , for the reaction were derived from the half-times used in the reduced-time calculations, $k = 1/t_{0.5}$. Table 1 is a compilation of the half-life times and rate constants for the runs where wegscheiderite was obtained.

SEM Micrographs

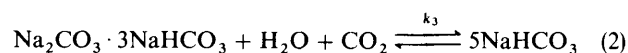
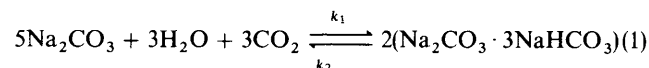
Fig. 3(a) shows anhydrous sodium carbonate, the reactant for all experimental runs. A uniform pore structure is observable in the material. Fig. 3(b) is of material from a run in which only wegscheiderite was formed. The product morphology is very different from that of the reactant, and much reduced porosity is evident. Fig. 3(c) illustrates a product in which

only sodium hydrogencarbonate was formed at low temperature. The change in crystal morphology is very pronounced: the product crystals are much larger with smoother faces. Again, the porosity is much reduced. Fig. 3(d) is from the area of high temperature formation of hydrogencarbonate. Crystal growth is obvious, and is greater than at low temperatures [Fig. 3(c)]. Fig. 3(e) is from the area of low-temperature formation of mixed product. The product is not well defined, and porosity is low. Fig. 3(f) serves to indicate the formation of larger crystals (of sodium hydrogencarbonate?) alongside smaller (wagscheiderite?) crystals, as an example of a mixed product formed at high temperatures and high relative humidities. The differences between these and Fig. 3(e) (low-temperature formation) are obvious. Further photographs obtained from runs under different experimental conditions indicate that the degree of porosity of the product changes at different partial pressure values. It is evident that the fastest reactions give the least porous products.

Discussion

Reaction Scheme

From a study of Fig. 1, much of the overall reaction pattern can be represented by the following reactions:



where k_1 , k_2 and k_3 are rate constants.

Effect of Temperature and Water Vapour Pressure on Reaction Product

Fig. 1 can be readily subdivided into five 'product areas':

Area (1) Wegscheiderite Formation

Wegscheiderite is the only product and this can be accounted for in terms of the rate of conversion of wegscheiderite to sodium hydrogencarbonate being very slow, *i.e.* k_3 is small relative to k_1 . The higher temperature runs gave low conversions, suggesting an increasing amount of the back-reaction, *i.e.* k_2 is becoming comparable with k_1 at higher temperatures.

Area (2) Low-temperature Wegscheiderite/Sodium Hydrogencarbonate mixtures

Both wegscheiderite and hydrogencarbonate are being formed, but the rate of conversion to sodium hydro-

Table 1 Half-life times and rate constants for wegscheiderite formation

run no.	sample temperature/K	$P(\text{H}_2\text{O})$ $/10^{-4} \text{ N m}^{-2}$	half-life time/s	rate constant, k , $/10^{-4} \text{ s}^{-1}$	limiting α value
28	368	3.854	1530	6.53	0.82
26	363	4.734	795	12.6	0.75
25	363	3.116	1020	9.80	0.80
27	363	2.500	2430	4.11	0.71
14	358	4.696	2580	3.88	0.78
31	358	3.854	540	18.5	0.98
33	358	2.500	1620	6.1	0.95
9	356.5	2.830	1200	8.33	0.93
15	355	4.734	3600	2.78	0.78
12	353	3.854	3000	3.33	0.81
20	353	2.500	1170	8.55	0.97
8	351	2.983	600	16.7	0.98
18	348	2.500	570	17.5	0.94

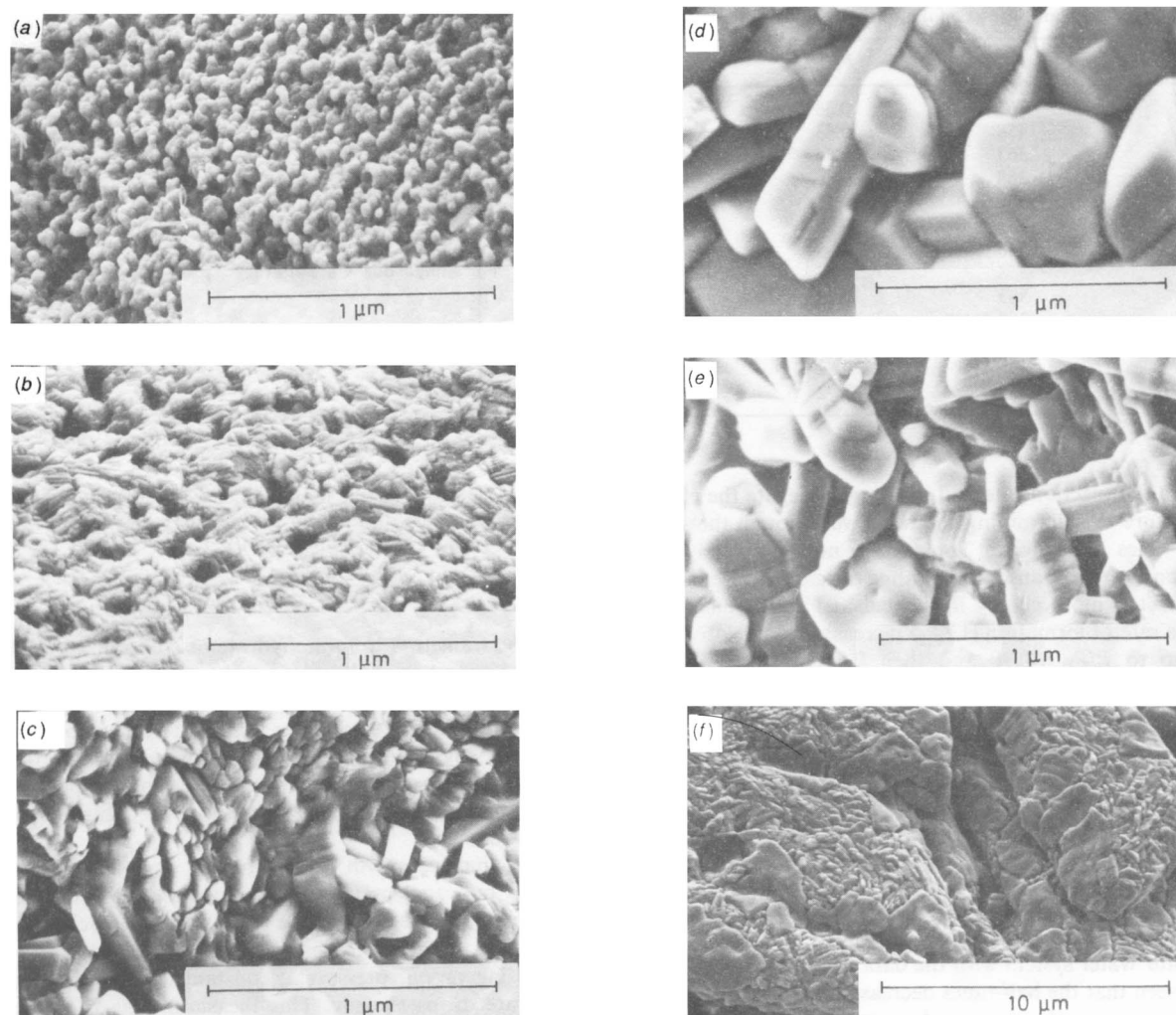


Fig. 3 SEM micrographs: (a) sodium carbonate starting material; (b) wegscheiderite; (c) sodium hydrogencarbonate, low temperature; (d) sodium hydrogencarbonate, high temperature; (e) mixed product, low temperature; (f) mixed product, high temperature

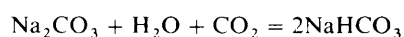
gencarbonate is slow, *i.e.* k_3 and k_1 are comparable, but $k_1 > k_3$. k_2 is low.

Area (3) Low-temperature/High-pressure Sodium Hydrogencarbonate Formation

Formation of sodium hydrogencarbonate in this region occurred as a single-stage reaction, with the exception of two runs ($P_1 = 3.85 \times 10^{-4} \text{ N m}^{-2}$, $T_1 = 350 \text{ K}$; $P_2 = 3.12 \times 10^{-4} \text{ N m}^{-2}$, $T_2 = 348 \text{ K}$) which are on the edge of the field, and which gave wegscheiderite as intermediate in a two-stage reaction. This suggests that hydrogencarbonate is not formed directly from sodium carbonate, and further justifies the use of eqn. (1) and (2).

Area (4) High-temperature/Low-pressure Sodium Hydrogencarbonate Formation

These conditions are those under which wegscheiderite has been shown to decompose,⁴ *i.e.* k_2 is large. However, the direct thermal decomposition produces carbonate, not hydrogencarbonate; the hydrogencarbonate produced in this case is probably formed directly from sodium carbonate due to the high pressure of carbon dioxide:



Area (5) High-temperature Wegscheiderite/Sodium Hydrogencarbonate Mixtures

The occurrence of a mixed product under these conditions, close to the centre of the wegscheiderite stability region,

cannot be explained in terms of the scheme above. Other possible explanations (water/carbon dioxide ratios, for example) were considered, without success.

Effect of Temperature and Pressure on Wegscheiderite Formation

Examination of Table 1 shows that the temperature/pressure behaviour of the rate of formation of wegscheiderite is complicated. It can be seen that, *e.g.* at $2.5 \times 10^{-4} \text{ N m}^{-2}$ the rates decrease with temperature, while at pressures close to $4.7 \times 10^{-4} \text{ N m}^{-2}$ the rates increase over essentially the same temperature range. Similar complicated behaviour can be seen in the effect of varying pressure at constant temperature: at 363 K the rates increase with increasing pressure, while at 353 K the rates decrease. Such behaviour is more complicated than straightforward kinetic or mass action effects would suggest.

Effect of Relative Pressure on Rate of Wegscheiderite Formation

Table 2 lists the experimental data, not as a function of water vapour pressure or temperature, but with respect to the relative water vapour pressure, P/P_0 , where P is the experimental water vapour pressure and P_0 is the equilibrium vapour pressure of water at the temperature of the run. It shows a grouped series of partial pressures, across a range of temperatures, which are paralleled by groups of similar half-times. This indicates that the relative pressure has a major

Table 2 Half-time as a function of relative pressure

run no.	T/K	P/P ₀	t _{0.5} /s
27	363	0.36	2430
33	358	0.43	1620
25	363	0.44	1020
28	368	0.46	1530
9	356.5	0.51	1200
20	353	0.53	1170
18	348	0.65	570
31	358	0.67	540
26	363	0.68	795
8	351	0.70	600
12	353	0.81	3000
14	358	0.82	2580
15	355	0.92	3600

effect on the reaction rate and can largely negate the effect of temperature in determining the rate, even though the groups of half-times indicated in Table 2 are not completely internally consistent, because of the range of temperature covered. This effect is more clearly illustrated in Fig. 4 which shows that the rate of formation ($1/t_{0.5}$) increases with relative pressure, up to $P/P_0 \approx 0.70$ and then falls extremely quickly. Again, such behaviour is more complicated than simple mass action effects would suggest; the most likely complication would be brought about by sorption of water by either reactant or products.

Sorption of water leading to compound formation would be expected to produce either sodium carbonate monohydrate or sesquicarbonate, and the data which most readily fit the present experimental results are those for monohydrate. Fig. 5 shows data from International Critical Tables,⁹ converted to relative pressures, for the sodium carbonate-water system with the data from Table 2 added. It can be seen that the half-times decrease on crossing the phase boundary from anhydrous carbonate to monohydrate, and then increase sharply as the saturated solution line is reached. This relationship can be rationalised if it is assumed that monohydrate reacts more quickly than the anhydrous compound in the formation of wegscheiderite. When the experimental conditions are below the stability field for monohydrate, the reaction is slow, but once into that field the reaction accelerates. When saturated solution is formed, pore blockage presumably occurs, reducing access of carbon dioxide, and the reaction slows down again. Fig. 5 also shows

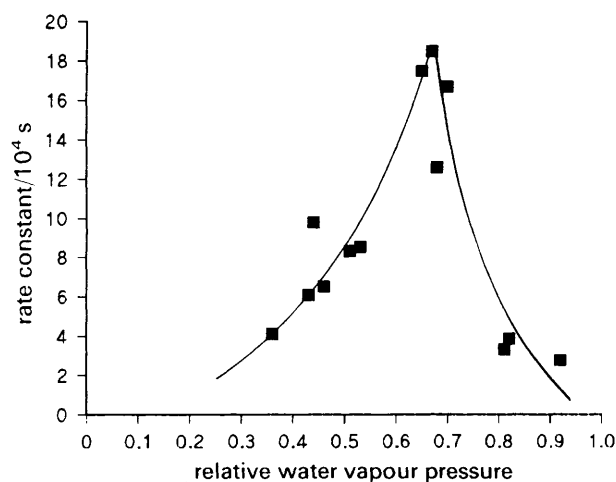


Fig. 4 Rate of formation of wegscheiderite as a function of relative water vapour pressure. Experimental data from Table 1

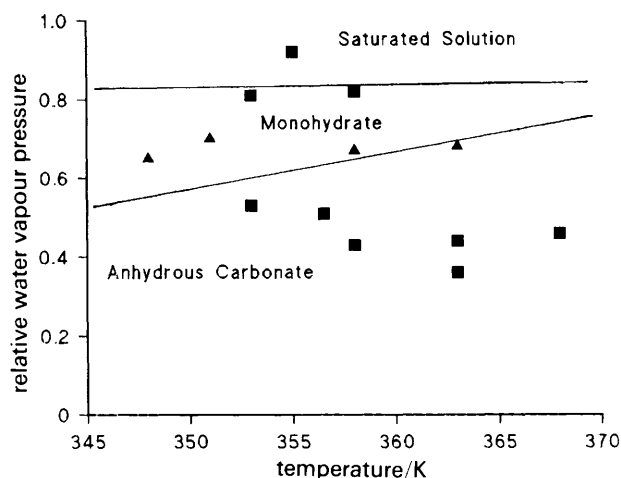


Fig. 5 Rate data for the formation of wegscheiderite superimposed on a partial phase diagram for the sodium carbonate-water system. ■, half-life ca. 10^3 s; ▲, half-life ca. 10^2 s

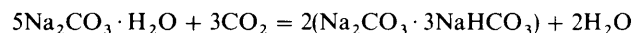
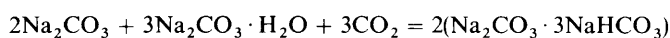
that the transition to monohydrate or solution takes place at relative pressures slightly below the equilibrium values. This suggests that sorption of water is taking place (the amount of water on the surface is greater than that in the vapour phase).

These suggestions can also account for the observed reduction in the values of α with increasing temperature and vapour pressure. There are two reasons for this observation, as follows:

(a) k_2 increases with temperature at constant vapour pressure as indicated previously, producing hydrogen carbonate, but having effects even on the formation of wegscheiderite.

(b) Fig. 4 indicates that at high P/P_0 values, i.e. with increasing vapour pressure at constant temperature, the reaction rate drops sharply. This measured rate is the balance between k_1 and k_2 and if k_1 is reduced more rapidly than k_2 , for reasons outlined above, then the measured degree of conversion will also be reduced.

There are two possible reactions involving monohydrate and producing wegscheiderite:



Of these, the second, a solid-gas reaction, seems more likely than the first, solid-solid, reaction.

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