

272. *The System Sodium Carbonate–Calcium Carbonate–Water.*

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THE above system has been investigated as a preliminary to the study of the four-component (reciprocal salt pair) system lime–sodium carbonate–water. The double salt $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3$ (Niggli, *Z. anorg. Chem.*, 1916, **98**, 241) and its dihydrate (pirssonite) and pentahydrate (gaylussite) (Groth, "Chemische Krystallographie," 1908, vol. 11, pp. 219, 222) are known; these are stated under certain conditions to play an important part in the manufacture of caustic soda by the causticising process. Wegscheider and Walter (*Monatsh.*, 1907, **28**, 633) have investigated the conditions under which gaylussite and pirssonite are formed and decomposed, but it is obvious from their description that equilibrium was never established, probably owing to the lack of efficient stirring. Pratolongo (*Atti R. Accad. Lincei*, 1925, **1**, 238) reports similar experiments at "the ordinary temperature."

EXPERIMENTAL.

The system has been completely investigated at 15°, 25°, 35°, 37.5°, and 45°, and partially at 20°, 30°, 39°, 55°, 65°, 75°, 85°, and 95°, sufficient work being done at these latter temperatures to fix the compositions of solutions at certain triple points.

At the lower temperatures, up to 45°, tubes containing suitable amounts of the three components were rotated in the thermostat for 7–14 days. With efficient stirring, no difficulties due to the non-establishment of equilibrium were encountered. In those regions in which gaylussite is the stable solid phase, metastable equilibria of calcium carbonate or of pirssonite can readily be obtained by heating mixtures of the components to 45° for a day, cooling to the desired temperature, inoculating with pirssonite, and then stirring to attain equilibrium.

Sodium carbonate was determined in the liquid phase by titration with acid; the other component, calcium carbonate, was present in too small amounts to be detected. A known weight of the moist solid was dissolved in a known amount of acid and, after the evolution of carbon dioxide, the solution was weighed and aliquot portions taken for the determination of calcium, by precipitation as oxalate and conversion into carbonate (Willard and Boldyreff, *J. Amer. Chem. Soc.*, 1930, **52**, 1888), and of total carbonates by back titration with baryta. The results obtained are quoted in the following table, analyses being expressed as g. of the carbonate per 100 g. of solution or moist solid. All results quoted are the mean of two concordant determinations.

Temp.	Soln.		Moist solid, %.		Solid phases.	Temp.	Soln.		Moist solid, %.		Solid phases.
	Na ₂ CO ₃ , %.	Na ₂ CO ₃ , %.	Na ₂ CO ₃ , %.	CaCO ₃ , %.			Na ₂ CO ₃ , %.	Na ₂ CO ₃ , %.	Na ₂ CO ₃ , %.	CaCO ₃ , %.	
15°	8·91	6·01	32·38	C.	35°	23·10	30·04	17·29	G.		
	12·10	7·08	39·50	C.		28·01	33·33	22·61	G.		
	14·11	10·57	29·82	C, G.		30·09	34·11	23·00	G.		
	14·11	18·88	33·37	C, G.		32·88	44·92	14·03	G, H.		
	14·12	35·72	23·45	G, D.		32·89	36·72	21·76	G, H.		
	16·78	32·58	27·10	G.*		37·5	18·14	9·55	46·81	C.	
	17·24	31·76	25·52	G.*			19·87	11·91	40·45	C.	
20	22·51	32·97	25·94	G.*	20·33	11·20	43·62	C.			
	14·81	14·21	31·14	C, G.	20·53	17·53	35·18	C, G.			
	14·81	21·45	32·78	C, G.	20·53	28·03	30·22	C, G.			
	14·82	26·50	28·48	C, G.	21·38	32·84	26·14	G.			
25	6·86	3·10	58·71	C.	23·16	32·72	24·71	G.			
	12·33	6·50	47·03	C.	26·32	34·00	26·36	G.			
	13·03	6·39	48·21	C.	29·26	34·33	25·51	G.			
	14·65	7·88	48·21	C.	31·29	34·61	24·26	G.			
	14·85	9·32	35·95	C.	32·43	37·53	25·05	G, P.			
	15·81	17·11	35·09	C, G.	32·43	38·90	25·49	G, P.			
	15·81	23·04	25·10	C, G.	32·68	39·84	24·21	P.			
	15·83	36·78	33·88	G.	21·48	18·84	32·24	C, P.*			
	16·49	32·02	26·35	G.	21·49	29·63	31·26	C, P.*			
	17·54	31·04	24·06	G.	24·62	34·28	20·03	P.*			
	18·03	31·42	24·39	G.	27·81	37·39	23·46	P.*			
	19·52	31·81	24·70	G.	29·58	38·59	25·23	P.*			
	20·30	32·04	24·97	G.	31·37	38·86	23·81	P.*			
	22·63	42·20	27·92	G, D.	32·97	41·82	22·31	P, M.			
22·64	43·29	30·99	G, D.	32·97	45·45	20·89	P, M.				
30	19·84	13·32	33·07	C.*	39	21·26	19·13	35·46	C, G.		
	20·52	17·36	30·68	C, P.*		21·26	28·43	25·81	C, G.		
	20·52	26·18	25·92	C, P.*		23·46	32·63	24·61	G.		
	21·14	33·81	22·63	P.*		25·72	34·51	24·62	G, P.		
	16·20	9·74	40·43	C.		25·74	35·57	23·67	G, P.		
	17·42	17·90	30·31	C, G.		27·35	37·24	24·02	P.		
	17·42	22·66	26·14	C, G.		45	11·40	6·61	40·47	C.	
	18·78	31·64	24·34	G.			18·15	10·34	41·31	C.	
	20·05	12·76	36·59	C.*			21·09	11·64	43·67	C.	
	20·90	18·34	30·28	C, P.*			22·18	19·21	36·46	C, P.	
20·90	23·51	29·14	C, P.*	22·19	25·77	30·82	C, P.				
21·68	36·02	26·20	P.*	23·74	34·61	22·04	P.				
35	7·00	3·91	45·00	C.	25·64	36·68	24·31	P.			
	16·90	9·15	44·01	C.	27·87	36·72	21·60	P.			
	18·91	14·51	23·00	C.	30·31	37·91	22·25	P.			
	19·49	27·90	30·88	C, G.	32·15	38·49	21·13	P.			
	19·49	18·21	31·67	C, G.	32·46	44·36	19·48	P, M.			
	20·86	30·68	21·14	G.	32·47	41·32	20·30	P, M.			

Solid phases: C = CaCO₃; G = Na₂CO₃, CaCO₃, 5H₂O (gaylussite); P = Na₂CO₃, CaCO₃, 2H₂O (pirssonite); D = Na₂CO₃, 10H₂O; H = Na₂CO₃, 7H₂O; M = Na₂CO₃, H₂O.

* denotes metastable equilibrium.

At the higher temperatures, 55° and above, suitable amounts of the three components were stirred in a bottle fixed in the thermostat. From time to time, small amounts of sodium carbonate were added until, after 24 hours' stirring, pirssonite could be detected in the moist solid by microscopic examination. After analysis of the solution, a further amount of sodium carbonate was added, and the solution analysed after 24 hours', and again after 48 hours' stirring. Water was then added and the solution again analysed after 24 hours. The four analyses of the solution were always in satisfactory agreement, proving that equilibrium is obtained under these conditions. The results obtained in this series of experiments are given below.

Analyses of solutions at the triple point CaCO₃-pirssonite-solution.

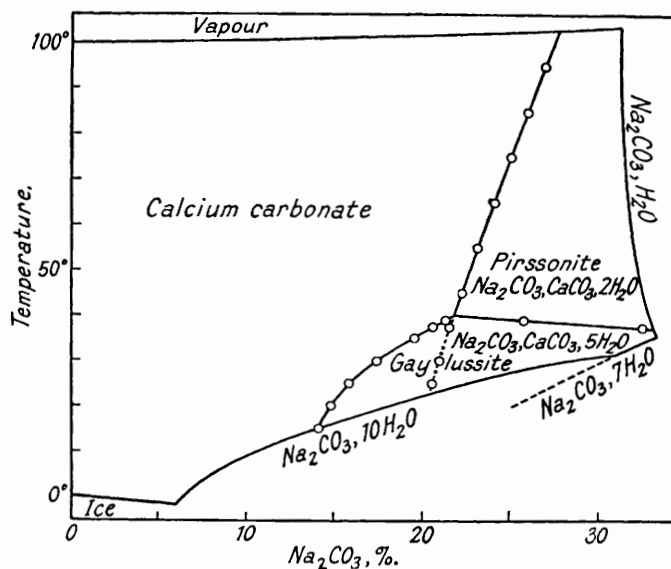
Temp.	55·0°	65·0°	75·0°	85·0°	95·0°
Na ₂ CO ₃ , %	23·07	24·02	24·93	25·87	26·81

DISCUSSION.

In the fig. are shown the temperatures and concentrations of solutions in equilibrium with the various solid phases. The representation of a three-component system at a series of temperatures usually requires the use of three co-ordinates, but in this case, since the concentration of calcium carbonate in the solution is too small to be measurable,

two co-ordinates are sufficient. Data for the solubility of the various hydrates of sodium carbonate, and for the boiling and freezing points of its solutions, used in constructing the fig., are taken from International Critical Tables.

As can be seen from the fig., dilute solutions of sodium carbonate are in equilibrium with calcium carbonate, while more concentrated solutions react with it to form gaylussite or pirssonite, according to the temperature. Gaylussite is in equilibrium with pirssonite at 37–40°, the exact temperature depending on the concentration of the sodium carbonate solution with which they are in contact. At 15° the concentration of the solution at the triple point calcium carbonate–gaylussite–solution is identical, within the limits of experimental error, with that of a saturated solution of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$; consequently, gaylussite is only stable at, or below, 15° in contact with an aqueous solution when this is supersaturated with respect to the decahydrate. The equilibrium calcium carbonate–pirssonite–solution can readily be followed in the metastable region below 40° where gaylussite is the stable solid phase.



Wegscheider and Walter (*loc. cit.*) suggest that the anhydrous double salt is formed at about 60°, but our experiments do not support this suggestion; the anhydrous double salt does not appear to be formed under any conditions in the range covered by our experiments, and has hitherto only been prepared with certainty at high temperatures in the absence of water.

The temperatures and concentrations of the solution at the following quadruple points—invariant points at atmospheric pressure—have been determined from the figure:

	Temp.	Na ₂ CO ₃ , %.
CaCO ₃ –gaylussite–Na ₂ CO ₃ · 10H ₂ O–solution	15·0°	14·11
CaCO ₃ –pirssonite–Na ₂ CO ₃ · 10H ₂ O–solution	22·5	20·4
CaCO ₃ –gaylussite–pirssonite–solution	40·0	21·7
Gaylussite–pirssonite–Na ₂ CO ₃ · H ₂ O–solution	37·3	33·0
CaCO ₃ –pirssonite–solution–vapour	103·2	27·5

Attempts were made to determine the temperatures of some of these quadruple points with a dilatometer, but these were unsuccessful owing to the slowness with which the change takes place when efficient stirring is impossible.

We desire to thank Mr. R. O. Jones for suggesting this topic.

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[Received, June 28th, 1933.]