

ON THE HYDRATES OF SODIUM CARBONATE

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Sodium carbonate forms at least three stable hydrates, the mono-, hepta-, and decahydrates. Besides these there have been described a large number of other hydrates which are probably unstable. The existence of these other hydrates has been called into question by various writers.

In the course of some work on the system $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-H}_2\text{O}$ the writer obtained several hydrates of sodium carbonate and is able to affirm definitely the existence of the hemipentahydrate $\text{Na}_2\text{CO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$.

This hydrate was first described by Morel¹ and has also been obtained by Professor W. C. Blasdale² who describes it as follows: "This salt usually separates in the form of needles but occasionally as long 4-sided or flattened 8-sided prisms terminated by a single pair of planes intersecting at 134° . The percentages of water in the different preparations were 31.04, 31.30, 32.10, 31.54, 29.90, and 30.46. Many samples contained potassium in the form of the carbonate up to 4%. The theoretical percentage of H_2O is 29.80 and the variations in its composition are due to a limited amount of solid solution formation."

In evaporating a solution of sodium and potassium carbonates in equimolecular proportion at 25°C several hydrates of sodium carbonate are the first crystalline products to form. If these crystals are left in contact with the solution and evaporation is continued a mass of the double salt $\text{NaKCO}_3 \cdot 6\text{H}_2\text{O}$ is finally obtained the earlier formed crystals again disappearing. If, however, some of the early crystals are removed the bulk composition is displaced and the double salt may fail to form.

At room temperature (ca. 18°) the first crystals are obtained at a concentration of about 21.3 mols each of K_2CO_3 and Na_2CO_3 to 1000 mols of water. These crystals are of some hitherto undescribed metastable hydrate of sodium carbonate which will not be further considered here. As evaporation continues the composition of the solution is displaced towards higher proportions of K_2CO_3 , and $\text{Na}_2\text{CO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ forms in good crystals from solutions over a

¹ J. Morel, Sur un nouvel hydrate de carbonate de sodium, *Bull. Soc. Fran. Min.*, vol. 12, p. 546, 1889.

² W. C. Blasdale, *Jour. Am. Chem. Soc.*, vol. 45, p. 2936, 1923.

wide range of concentrations. For instance, crystals of the hemipentahydrate were obtained from a solution having the composition 100.2 mols K_2CO_3 and 19.5 mols Na_2CO_3 per 1000 mols of H_2O .

CRYSTALLOGRAPHY

The crystals of $Na_2CO_3 \cdot 2\frac{1}{2}H_2O$ so obtained were very well developed. They were up to several centimeters in length, acicular and often in sheaf-like arrangement. Several of these crystals were measured on the two-circle goniometer. They were found to be orthorhombic and showed a strong development of the prism zone with four or five end faces. The forms (110), (010), (101) and (011) are always present. Several other forms, occur sporadically. In composition these crystals show the same variations mentioned by Blasdale.

The crystallography of this hydrate has been described by Morel.³ The angles measured by the writer agree well with the axial ratio, $a:b:c=0.794:1:0.439$, given by him, as shown in table 1 comparing measured angles with angles calculated from the given axial ratio.

TABLE 1.

	Measured	Calculated
101 \wedge 101	57° 57'	57° 52'
011 \wedge 011	47° 44'	47° 24'
110 \wedge 110	76° 27'	76° 54'
010 \wedge 011	66° 17'	66° 18'
010 \wedge 110	51° 46'	51° 33'
010 \wedge 110	51° 47'	51° 33'

Wegscheider⁴ has suspected that the crystals described by Morel belonged to the monohydrate. He points out that the angle $m:m=108^\circ 6'$ given by Morel is probably due to a misprint and should be $103^\circ 6'$,⁵ in which case it differs by only $2^\circ 14'$ from the corresponding angle for thermonatrite. There is no question that Wegscheider is correct in suspecting the misprint, but still the difference between the angles of the monohydrate and the hemipentahydrate is too great to allow his interpretation. The average

³ J. Morel, *op. cit.*

⁴ Notiz ueber die Hydrate des Natrium Carbonats, *Zeitsch. f. anorg. Chem.*, vol. 73, p. 256-258, 1912.

⁵ In modern usage this angle would be given as the supplement, $76^\circ 54'$.

value for the angle $110 \wedge \bar{1}\bar{1}0$ found on crystals of the hemipentahydrate was $76^\circ 41'$. This departs from the value given by Morel by $13'$, whereas it departs from the value for thermonatrite by $2^\circ 27'$. It seems to the writer that the correctness of Morel's crystallographic data for the hemipentahydrate, having due regard for the aforementioned misprint, is thus well established.

OPTICAL EXAMINATION

All crystalline products obtained during the present study were studied microscopically and it was found that the hemipentahydrate may be distinguished from the other products that can form from the solutions in question with great certainty. The optical properties of $\text{Na}_2\text{CO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, determined in white light, were found to be the following:

Biaxial negative. Indices, determined in white light; $\alpha = 1.435$, $\beta = 1.492$, $\gamma = 1.547$; all ± 0.003 . $2V$ large. Parallel extinction, negative elongation, $X = c$.

The stable hydrate at the temperatures in question is the decahydrate, natron. It was not obtained in the present experiments. Its indices, given by Larsen,⁶ are:

$$\alpha = 1.405 \pm 0.003, \beta = 1.425 \pm 0.003, \gamma = 1.440 \pm 0.003.$$

It will be seen that there is hardly a chance for failure to differentiate between the two microscopically.

The monohydrate was obtained in the course of several trials and could easily be recognized microscopically. Its indices, as well as those of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ from the J. T. Baker Chemical Company, were found to agree well with those given by Larsen⁷ for the mineral thermonatrite; $\alpha = 1.420$ $\beta = 1.506$ $\gamma = 1.524$.

DENSITY RELATIONS

There exists, however, an error in the statement of the density of thermonatrite or of the artificial monohydrate which is repeated in nearly all the text and reference books. The density is given as 1.5–1.6. This is obviously much too low. Concerning this value Saslawsky⁸ says: "Ich persoendlich bin nicht im Zweifel darueber dass das fuer $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ in der Literatur angegebene spez.

⁶ E. S. Larsen, *U. S. Geol. Surv., Bull.* 679, p. 114, 1921.

⁷ *op. cit.*

⁸ J. J. Saslawsky, Die Kontraktion der Minerale, *Zeitsch. f. Krist.*, vol. 59, p. 193, 1923.

Gew., 1.5-1.6, nicht stimmt. Das betreffende spez. Gew. duerfte 2.1-2.3 sein."

The density of the monohydrate was determined by the pycnometer method with benzene to be 2.255 ± 0.002 at 16°C . This is in excellent agreement with the value, 2.235, calculated according to the law of Gladstone and Dale from the refractive indices using the values for "specific refractive energies" given by Larsen.⁹

The density of the hemipentahydrate was also determined using a pycnometer with methyl alcohol and found to be 2.053 ± 0.002 . This also is in excellent agreement with the value, 1.981, calculated from the refractive indices.

Table 2 shows the relation between water content and density of the several hydrates of sodium carbonate. It may be seen that there is a regular decrease in density with increasing water content and that the values determined for the mono- and hemipentahydrate fall well into this series, whereas the value formerly given for the monohydrate would not agree at all with the other values.

TABLE 2.

	Weight percent H ₂ O	Density
Na ₂ CO ₃	00.0	2.533 ^a
Na ₂ CO ₃ · H ₂ O	14.5	2.255 ^b
Na ₂ CO ₃ · 5/2H ₂ O	29.9	2.053 ^b
Na ₂ CO ₃ · 7H ₂ O	54.3	1.510 ^a
Na ₂ CO ₃ · 10H ₂ O	63.0	1.460 ^a

^a From the International Critical Tables.

^b The writer's determination.

The hemipentahydrate of sodium carbonate obtained, as described above, from solutions also containing varying amounts of K₂CO₃ was reexamined after being kept in loosely stoppered bottles for three years. The crystals were still perfectly clear and yielded check results on being examined optically and measured on the goniometer.

Crystals of the hemipentahydrate were suspended in a clear solution of Na₂CO₃ at room temperature. The crystals continued to grow in this solution, and many new crystals in small needles also formed. Both proved to be the hemipentahydrate. At this

⁹ *op. cit.* p. 31.

temperature crystals of the decahydrate should be in equilibrium with a saturated solution of Na_2CO_3 .

The solution in contact with the hemipentahydrate at room temperature had a composition of 3.16 mols Na_2CO_3 per 1000 grams H_2O . The index of refraction of this solution is 1.389, determined in white light. At 20°C $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ is in equilibrium with a solution containing 2.09 mols per 1000 grams of H_2O .¹⁰ These observations agree with Morel's report that he had obtained the hemipentahydrate from very concentrated solutions of solvay soda between 18° and 25°C .

In summary it may be pointed out that several observations agree in indicating the existence of the hemipentahydrate of sodium carbonate as a phase quite distinct from the monohydrate, thermodynamite. These are:

1. Analyses of the material.¹¹
2. Crystallographic data which are characteristic.
3. Optical data which enable its recognition.
4. Density determination in agreement with calculated value.
5. Relation of density to densities of related hydrates in agreement with expectation.

¹⁰ International Critical Tables.

¹¹ Blasdale, *op. cit.*