Two phases in a commercial anhydrous sodium carbonate by air contact

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Abstract

Two phases have been detected by XRD measurements in a commercial sodium carbonate in air contact: Na₂CO₃·H₂O and pure Na₂CO₃. TG, DTG and DSC analysis evidenced that the water loss is taking place in two steps: a first strongest mass fall is of 8.5% in the temperature range 64-113 °C and the second mass loss is of 1.4% recorded in the range 130-460 °C. The melting process begins at 831.8 °C and it is finished at 852.0 °C, having its maximum point at 843.6 °C as seen on DSC curve. The concentrations of the two phases has been calculated both from XRD and thermal measurements. Specific heat capacity for anhydrous sodium carbonates exhibits a metallic behavior from 400 to 574 K then, from 574 K to 806 K a clear decrease is occurred. By extrapolating the linear fit, in the range temperature 400.43-403.19 K, for the specific heat capacity of the anhydrous sodium carbonates, we calculated a value of 1.073 J g⁻¹K⁻¹ at 20 °C. A metallic behavior is also observed for the mixture of the two phases before the beginning of dehydration process.

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1 Introduction

The anhydrous sodium carbonate, Na₂CO₃, is a sodium salt of carbonic acid, is a white, odorless powder that absorbs moisture from the air, has an alkaline taste, and forms a strongly alkaline water solution [1]. Sodium carbonate is domestically well known for its everyday use as a water softener. It can be extracted from the ashes of many plants. It is synthetically produced in large quantities from salt (sodium chloride) and limestone by a method known as the Solvay process. Concerning the first principal sources to produce sodium carbonate we mention, for example, that nearly all the domestic consumption of Na₂CO₃ in US or in Turkey is provided by the mining production since 1938 when it was discovered large natural deposits of the mineral named "trona" or trisodium hydrogendicarbonate dehydrate (Na₃HCO₃CO₃·2H₂O).

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Another source (predominated in Europe and elsewhere) to produce sodium carbonate is given by several "halophyte" (salt-tolerant) plant species and seaweed species (e.g. Salsola soda or barilla plant) that can be processed to yield an impure form of sodium carbonate, termed "soda ash".

Commercially-viable routes to synthesizing soda ash from salt and other chemicals were also intensified to ensure the population needs. In this contest, we have to mention the French chemist Nicolas Leblanc who, in 1791, patented a process for producing sodium carbonate from NaCl salt, sulfuric acid, calcium carbonate (CaCO₃), and coal (C). First, sea salt (sodium chloride) was boiled in sulfuric acid to yield sodium sulfate and hydrogen chloride gas, according to the chemical equation. Next, the sodium sulfate was blended with calcium carbonate and coal, and the mixture was burnt, producing calcium sulfide in conformity with the adequate reactions [1]-[2]:

Despite to air pollution given by HCl and CaS, the Leblanc process remained the major production method for sodium carbonate until the late 1880s [1].

In 1861, the Belgian industrial chemist Ernest Solvay developed a new method to convert sodium chloride to sodium carbonate using ammonia. The Solvay process centered around a large hollow tower. At the bottom, calcium carbonate (limestone) was heated to obtain CaO and to release carbon dioxide:

At the top, a concentrated solution of sodium chloride and ammonia entered the tower. As the carbon dioxide bubbled up through it, sodium bicarbonate precipitated [2]:

 $NaCl + NH_3 + CO_2 + H_2O \longrightarrow NaHCO_3 + NH_4Cl$

The sodium bicarbonate was then converted to sodium carbonate by heating it, releasing water and carbon dioxide:

 $2 \text{ NaHCO}_3 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$

The Solvay process, recycles its ammonia, because it is regenerated from the ammonium chloride by treating it with the lime (calcium hydroxide).

Consequently, because it consumes only brine and limestone, and has calcium chloride as its only waste product, the Solvay process is becoming substantially more economical than the Leblanc process. Thus by 1900, the Solvay process come to dominate the world in sodium carbonate production.

Finally we describe the Hou's process, developed by Chinese chemist Hou Debang in 1930s. The earlier steam reforming byproduct carbon dioxide was pumped through a saturated solution of sodium chloride and ammonia to produce sodium bicarbonate via the following reactions [2]:

 $NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$

 $NH_4HCO_3 + NaCl \longrightarrow NH_4Cl + NaHCO_3$

The sodium bicarbonate was collected as a precipitate due to its low solubility and then heated to yield pure sodium carbonate similar to the last step of the Solvay process. More sodium chloride is added to the remaining solution of ammonium and sodium chlorides; also more ammonia is pumped at 30-40°C to this solution. The solution temperature is then lowered to below 10°C. Solubility of ammonium chloride is higher than that of sodium chloride at 30°C and lower at 10°C. Due to this temperature dependent solubility difference and the common-ion effect, ammonium chloride is precipitated in a sodium chloride solution.

The Chinese name of Hou's process means "Coupled Manufacturing Alkali Method": Hou's process is coupled to the Haber process and offers better atom economy by eliminating the production of calcium chloride since ammonia no longer needs to be regenerated. The by-product ammonium chloride can be sold as a fertilizer. Sodium carbonate is a compound that could be find either in hydrate form or in anhydrous form and has multiple domestic and industrial uses. One of the application is as pH regulator to maintain stable alkaline conditions of the photographic film developing agents [1]. It is also known as a common additive in municipal pools used to neutralize the corrosive effects of chlorine and to raise pH.

From multiple domestic uses, we mention its quality to be very good as water softener in laundering, useful in removing the grease, oil and wine stains, as descaling agent in boilers, in dyeing with fiber-reactive dyes, sodium carbonate (often under a name such as soda ash fixative or soda ash activator) is used to ensure proper chemical bonding of the dye with cellulose (plant) fibers, typically before dyeing (for tie dyes), mixed with the dye (for dye painting), or after dyeing (for immersion dyeing). Sodium carbonate is a food additive (E500) used as an acidity regulator, anti-caking agent, raising agent, and stabilizer.

In chemistry, it is often used as an electrolyte, because it acts as a very good conductor in the process of electrolysis and in addition, carbonate ions are not corrosive to the anodes. It is also used as a primary standard for acid-base titrations because it is solid and air-stable, making it easy to weigh accurately.

The procedure named sodium carbonate test is used in the qualitative cation analysis to distinguish between Cu, Fe and Ca/Zn/Pb. When the sodium carbonate solution is added to the salt of the Cu²⁺ ion it is obtained a blue precipitate of copper (II) carbonate; a dirty green precipitate iron(II) carbonate indicates the presence of Fe²⁺ ion; a yellowbrown precipitate of iron(III) oxide indicates Fe³⁺ ion. A white precipitate indicates Ca²⁺, Zn²⁺ or Pb²⁺ ions but there is an impossibility to distinguish between them. Sodium carbonate, in a solution with common salt, may be used for cleaning silver [1]-[2].

Used in toothpastes, sodium carbonate acts as a foaming agent and an abrasive, and contribute to temporarily increase mouth pH.

In this work we presents the XRD analysis and thermal analysis of a commercial analydrous sodium carbonate of initial 99.5% purity used in reactive analysis, that by air contact it is becoming a two phases mixture compound.

2 Experimental results and discussion

2.1 XRD analysis

The experiments were made with a commercial material [3] used for reactive analysis by chemists, named anhydrous Na_2CO_3 (ANCO) of a initial 99.5 % purity, that has accumulated a quantity of water when it has been kept several days in an open vessel.

In order to determine the concentration of the two expected components of the mixture (anhydrous and hydrate sodium carbonates) we have chosen two methods of analysis existent in our laboratories: XRD analysis and Thermal analysis, respectively.

X ray diffraction (XRD) measurements were performed on powder samples, with a Shimadzu XRD-6000 X-ray Diffractometer, equipped with a precision vertical goniometer and a scintillation detector [4]-[5]. The functioning parameters of the X-ray tube (A-40-Cu type) were established at a voltage of 30 kV and a current of 30 mA. A continuous scan measurement has been chosen as operation mode in a geometry ($\theta/2\theta$) seetting a scan speed of 2 deg/min and a scan range from 15 deg to 50 deg. Divergence slit was of 1.0000 deg, scattering slit was of 1.0000 deg, and receiving slit of 0.1500 mm. All the

hardware control including measurement operations was exercised through the computer. Measurement and data processing took place at the same time (multi-task).



Figure 1: XRD for mixture of hydrate (H) and anhidrous (A) sodium carbonates

Due to hygroscopic properties of the ANCO compound, when is in air contact, two principal phases have been evidenced on XRD spectrum of the analysed powder as observed in Figure 1.

One of the mixture components should be the hydrate sodium carbonate $(Na_2CO_3 \cdot H_2O)$ phase, which was indexed as orthorhombic structure, whose peaks are denoted by letter H in the XRD spectrum. A similar orthorhombic structure is that given by the card co8-0448 from 2001 JCPDS-International Centre for Diffraction Data (PCPDFWIN v. 2,2) and in ref. [6]. We have calculated the lattice parameters by using the characteristic formula for the orthorhombic system:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

where, d_{hkl} are the interplane distances, h, k, l are the Miller indices and a, b, c are the lattice constants [7]. We obtained the following values:

a=10.693 Å, b=5.258 Å, c=6.485 Å

The, diffraction angles, the relative intensities, the interplane distances and the Miller indices for the main peaks of the hydrate $Na_2CO_3 \cdot H_2O$ phase (HNCO) are given in Table 1.

The second phase is the anhydrous sodium carbonate (Na₂CO₃), which is belonging to the monoclinic system, being indexed in conformity with the card c11-1130 [8] from 2001 JCPDS-International Centre for Diffraction Data (PCPDFWIN v. 2,2) and the relation between the interplane distances, d_{hkl} , the Miller indices, h, k, l the lattice constants, a, b, c and β angle [7]:

$$\frac{1}{d_{hkl}^2} = \frac{1}{\sin^2\beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac} \right)$$

$2\theta/\deg$	I_{rel}	d_{hkl}/\mathring{A}	hkl
16.58	9	5.3467	200
16.82	12	5.2584	010
21.54	4	4.1254	201
27.46	7	3.2457	211
32.20	100	2.7725	202
32.98	14	2.7138	012
33.40	34	2.6806	311,400
33.78	22	2.6513	112
34.12	26	2.6292	020
35.14	65	2.5531	120
36.16	18	2.4716	401
36.60	15	2.4525	212
37.84	82	2.3757	121
40,264	18	2,2274	411
41.4	31	2.1812	312
43.82	28	2.0627	402
45.08	15	2.0111	321
48.30	18	1.8745	420

Table 1: XRD data for hydrate sodium carbonate

The lattice constants were the following: a=8.907 Å, b=5.239Å, c=6.043Å, $\beta = 101.3 \deg$.

XRD pattern of anhydrous sodium carbonate show the deformation suffered by the crystalline network through the loss of crystallization water.

In Table 2 we give the diffraction angles, the relative intensity and the Miller indices for the main peaks of the monoclinic anhydrous Na_2CO_3 phase.

To evaluate the concentration of the two phases we chosen the (402) peak of HNCO (hydrate sodium carbonate) positioned at $2\theta = 43.82$ deg, having the integral intensity of 7.35 a.u. and the peak (221) of ANCO (anhydrous sodium carbonate) located at $2\theta = 44.38$ deg having the integral intensity of 4.41 *a.u.* The following formula is used to calculate the percentage of the HNCO compound ([9]-[11]).

$$f_{HNCO} = \frac{I_{HNCO}(402)}{I_{HNCO}(402) + I_{ANCO}(221)} \cdot 100$$

The results of XRD show that the concentrations of the mixture components are: 62.16 % for HNCO and 35.83% for ANCO.

2.2 Thermal analysis

Thermal analysis measurements (TG, DTG, DTA and DSC) of the mixture of hydrate and anhydrous sodium carbonate were carried out in dynamic air atmosphere (150 cm³ min⁻¹). A horizontal "Diamond" Differential/Thermogravimetric Analyzer from PerkinElmer Instruments was used during the measurements. The thermogravimetric and enthalpic calculations were performed within the specialized software Pyris.

2θ	I_{rel}	hkl
23.5	2	111
25.96	7	111
27.56	10	201
30.06	53	002
32.92	14	202
34.12	26	020
34.44	25	112
35.16	66	310
37.5	8	021
39.84	31	202
41.12	25	401
41.4	31	$\overline{2}21$
44.38	11	221
46.5	13	402

Table 2: XRD data for anhydrous sodium carbonate

An initial mass of 3.648 mg was heated in air, with an increasing rate of 10 K min⁻¹, from room temperature (RT) to 1000 °C. As has been shown by the results of XRD measurements, the presence of the two phases are evidenced also on the thermal diagrams. The results of mass variation for the powder sample in the range RT-500 °C are given on TG curve in Figure 2.



Figure 2: TG curve of the hygroscopic sodium carbonate from RT to 500°C

The strongest mass loss from hydrate sodium carbonate is seen on the TG as well on DTG curves.

In fact, one can observe on TG curve presented in the temperature range from RT to 500 °C in Figure 2, that the total loss of crystallization water is taken place from 64 °C to 460.0 °C in two steps: the first mass loss of 0.311 mg (8.5%) is seen as a very sharp fall on TG curve, detected also by DTG and DSC that is occurring in the range 64.0 - 113.0 °C; then the mass is decreasing only with 0.051 mg (1.4%) (with a very small rate) in the

range 130.0-460 °C.

The total mass loss is of 0.362 mg. A simple algebraic calculation permits us to obtain the mass (percentage) corresponding to the two components of the mixture: 2.494 mg (68.37%) of hydrate sodium carbonates (Na₂CO₃·H₂O) and 1.154 mg (31.63%) of anhydrous Na₂CO₃.



Figure 3: DSC curve obtained on heating from RT to 1000 °C

In Figure 3 is given DSC curve, where two endothermic processes could be observe. The first is only the water loss from the hydrate component of sodium carbonate, the second thermal process is evidently the melting of the anhydrous sodium carbonate associated with a decomposition.

The melting process of anhydrous sodium carbonate, detected on DSC curve, begins at 831.5 °C and is finished at 852.0 °C, having the maximum point at 843.6 °C.



Figure 4: Detailed process of water crystalization loss from hydrate sodium carbonate

In Figure 4 are given some details from DSC diagram in order to see the first thermal

event corresponding to the water vaporization, a clear endothermic process occurring when the crystallization water is losing from the one of the component of the mixture named hydrate sodium carbonates (HNCO). From Figure 4 one can see that the strongest de-

hydration process of the mixture begins at 82.54 °C and is finished at 110.69 °C, the temperature of the peak being localized at 96.09 °C. The enthalpy variation in this endothermic process was calculated within the framework of the specialized software Pyris, obtaining a value of $\Delta H=210.425$ J/g.



Figure 5: Specific heat capacity for the anhydrous sodium carbonate. The inset show the specific heat capacity for the two phases mixture.

In Figure 5 are shown the curves representing the temperature dependences of the calculated specific heat capacity of the anhydrous sodium carbonate in the range temperature 400-800 K and, in inset of the Figure 5, the specific heat capacity of the two phases mixture.

Specific heat capacity was calculated using the following formula [7], [5]:

$$c_p = \frac{1}{m} \frac{\delta Q}{dT} = \frac{1}{m} \frac{(\delta Q/d\tau)}{(dT/d\tau)}$$

where, $(\delta Q/d\tau)$ is the heat flux, given by the DSC curve, *m* is the sample mass and $(dT/d\tau) = 10 \text{ K min}^{-1}$ is the heating rate of the sample.

We have seen that from 400 K to 569 K the anhydrous sodium carbonate has a metallic behavior for the c = f(T), the compound having a good stability in the range 400-479 K and then the rate of the increasing of specific heat capacity with temperature is becoming smaller.



Figure 6: Linear fit of the data giving the specific heat capacity over absolute temperature in the range 400.42-403.19K

A linear fit (Figure 6) of the specific heat capacity over temperature obtaining in the range temperature 400.42-403.19 K, in conformity with the equation,

$$c = -38.92_{err:0.58} + 0.1364_{err:0.0014}T$$

permits us, by extrapolation, to obtain for the heat capacity at 20 °C a value of $\mathbf{c}_{20^{\circ}C} = 1.073 \ kJ \cdot Kg^{-1} \cdot K^{-1}$, that is close to 1.042 $\mathrm{Jg}^{-1}K^{-1}$ found in the literature [12]. In the range 479-800 K is recorded an evident decrease of heat capacity as a function

of absolute temperature.

Concerning the temperature dependence of the specific heat capacity for the mixture of hydrate and anhydrous sodium carbonates, before the dehydration process, we have seen a metallic behavior (the inset of Figure 5) in the range temperature RT-350 K.

3 Conclusions

An anhydrous sodium carbonate of 99.5% purity prepared for reactive analysis was investigated after the air contact. A mixture of two phases have been detected by XRD analysis and by thermal analysis. One of them is the hydrate sodium carbonate (68.37%) that was indexed as belonging to the orthorhombic system with the following lattice parameters: a=10.693 Å, b=5.258 Å, c=6.485 Å . In a smaller percentage of about 31.63% is present in the mixture the anhydrous sodium carbonate, which was found to have a monoclinic structure; whose parameters are: a=8.907 Å, b=5.239 Å, c=6.043 Å, $\beta = 101.3$ deg . Thermogravimetric measurements also allowed to us making the evaluating of the percentages of the two phases from the mixture. The analysis of DSC curve helps us to identify the temperature range of dehydration process (from 64 °C to 460.0 °C), the strongest endothermic process with $\Delta H=210.425$ J/g, being centered on 96.09 °C, when a huge quantity of crystallization water is lost. The maximum point of the endothermic melting process for the anhydrous sodium carbonate was located at 843.6 °C. Specific heat capacity for anhydrous sodium carbonates exhibits a metallic behavior from 400 to 569 K, then a decrease of the specific heat capacity until the melting process is occurred. A metallic behavior is also observed for the mixture of the two phases before the first endothermic process (water vaporization) is occurred. A value of 1.073 $Jg^{-1}K^{-1}$ of the specific heat capacity at 20°C has been obtained, that is quite close to that given by the literature.

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