A Study of the Electrical Conductivity and Transition Points of Sodium Carbonate

P. CERISIER AND F. ROUX*

Université de Provence, Centre St Jérôme, Laboratoire de Thermodynamique, Rue Henri Poincaré, 13397 Marseille, Cédex 4, France

The electrical conductivity of Na_2CO_3 has been measured between 270 and 830°C under different atmospheres: air, argon, nitrogen, and carbon dioxide. The conductivity depends on atmosphere owing to superficial decomposition of Na_2CO_3. The existence of a thermal transformation at 620°C seems confirmed. The determination of the transport numbers shows that cations only are responsible for the current. From measurements taken on samples containing traces of $CaCO_3$, the migration energy of cation vacancies is inferred.

La conductivité électrique a été mesurée entre 270 et 830°C sous différentes atmospheres: air, argon, azote et gaz carbonique. La conductivité dépend de l'atmosphère à cause d'une décomposition superficielle de Na_2CO_3. L'existence d'une transformation thermique à 620°C semble confirmée. La détermination des nombres de transport montre que seuls les cations sont responsables du passage du courant. Des mesures faites sur des échantillons contenant des traces de $CaCO_2$ on déduit l'énergie de migration des lacunes de cations.

I. Introduction

The electrical conductivity of alkali metal carbonates has, to our knowledge, not been studied so far, except for works of Jaffray and Martin (1) who limited their research to the determination of transition point temperatures, leaving alone the conductivity proper. Up to now, most studies have been carried out on halides. Only position disorder, however, is encountered in the latter whereas in salts containing a polyatomic ion, there is an additional orientation disorder. As a rule, the latter induces one or several transformations (of first or second order) in physical properties and in structure. Consequently, it is possible to study the influence of the crystalline structure upon the electrical conductivity.

* Present address: Laboratoire de Physique Médicale, Faculté de Médecine, Marseille.

The major cause of neglect by investigators of these salts probably lies in the impossibility of obtaining single crystals that can be used for conductivity studies, either because of the thermal instability of these salts or because their crystallization from aqueous solution yields hydrous crystals. Thus it has been decided to use pellets.

II. Experimental

The measuring equipment essentially included a thermostated enclosure under controlled atmosphere. Temperatures were determined to 0.1°C and the absolute precision of measurements was 0.1%. The conductivity of the sample (σ) was measured with alternating current. The ac circuit consisted of a transformer ratio-arm bridge (type B 641, Wayne–Kerr Corporation Ltd.) fed from a 1592-Hz

245

oscillator, an error amplifier, a 90° phase-shifter, a base drive amplifier, and two phase-sensitive detectors, one for capacitance and the other for conductance. A standard voltage derived from a Wien Bridge oscillator was applied to the component under test, and the resulting current was fed by a current transformer to the error amplifier. A current to the error amplifier output was fed back to the original current. The system balanced when these currents were exactly equal.

At 1592 Hz ($\omega = 10^4$) there was no electrode polarization and the absolute precision of measurement was 0.1%.

The salt to be studied was a Prolabo RP product purified by recrystallisation, then reduced to powder and kept *in vacuo* at 200°C for several days to dry out. It was then compressed under a pressure of 7.5×10^8 nm^{-2}. The pellet obtained had a parallelepipedic shape with a thickness of about 2 mm and rectangular faces of 2×1 cm^2.

The electrodes were made of platinum sheet (2×1 cm). In order to ensure good contact between the pellet and electrode, some authors report using a silver paint, but, at the experimental temperature used diffusion between paint and salt occurs. A satisfactory electrical contact between the electrode and the salt may be ensured by mechanical pressure achieved by means of screws. Under these conditions, the contact was not perfect and varied from experiment to experiment, but was constant in the course of a given run: Different pellets pressed from the same salt gave lines which had the same slope (± 0.03 eV) but showed scatter along the conductivity axis of the order of 0.07 log units. This was not a drawback since, in the course of the present paper, we are interested only in changes of slope. After keeping the material around 30°C under the melting point for a day to ensure a good homogeneity, measurements were normally performed at decreasing temperatures, a period of half an hour to an hour being allowed for the sample to reach equilibrium at every temperature.

Our measurements were carried out at 8°C intervals, and comprised more than 80 points for each graph. All these points could not be represented on Figs. 1, 2, and 3 because of insufficient space.

The doped samples were prepared by intimately mixing Na_2CO_3 and $CaCO_3$ powders prior to the fabricate ion of the pellet. We used, as a doping agent, calcium carbonate labelled with calcium-45, a β^- active isotope, after checking that the radioactivity introduced had no influence upon the conductivity. The radiosalt was prepared by Saclay Department of radio elements (C.E.A.) from a Johnson Matthey product, ultrapure. The maximum solubility of the salt was achieved by maintaining the pellet at high temperature for approximately 1 day before starting the measuring. From these measurements the quantity of impurities actually present in the pellet was determined in the following way. The sample, after being weighed, was dissolved in 250 cm^3 of distilled water, 0.1 cm^3 of that solution was evaporated on an aluminum disc, and the radioactivity was measured. It was then easy to obtain the percentage of calcium carbonate by comparison with a standard test solution.

III. Transition Points—Influence of the Atmosphere

The number of transition points of Na_2CO_3 and their nature have been studied by differential thermal analysis (*2–5*) dilatometry (*1, 6*) and X-ray scattering (*5–7*). The experiments have usually been carried out under air atmosphere, sometimes under CO_2. The authors are unanimous in concluding that transitions do exist at 360 and 485°C, but, on the other hand, the presence of a transition between 570 and 620°C is very controversial. Hence, we believed it interesting to go further into the study, using the electrical conductivity and specifying the influence of the atmosphere. Consequently, we worked successively under confined air, argon, nitrogen, and carbon
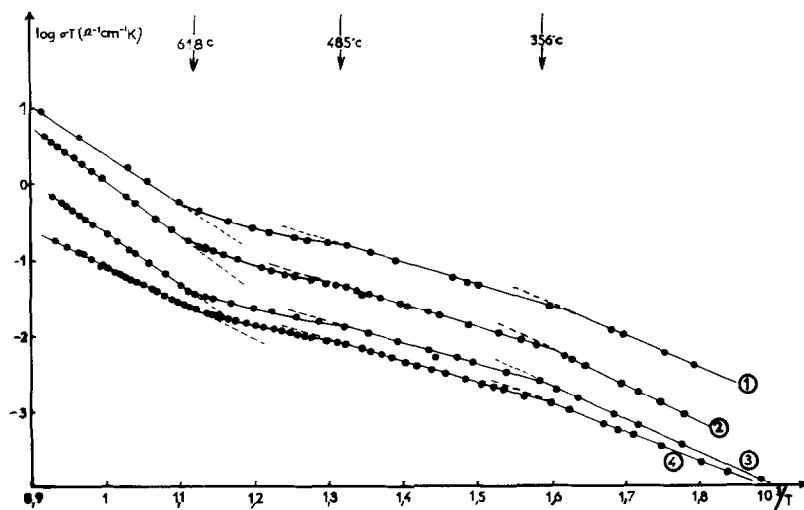
FIG. 1. Electrical conductivity of pure sodium carbonate under different atmospheres, 1, air; 2, Ar; 3, N$_2$; 4, CO$_2$.

dioxide. The corresponding log σT vs $(10^3/T)$ curves have been plotted on Fig. 1. By examining them, the existence of transition points clearly appears at temperature of 356, 486, and about 618°C, whatever the surrounding atmosphere. The existence of the first two points can be easily explained by the change of crystal structure of the Na$_2$CO$_3$ from the monoclinic system (phase γ) for the range of room temperature to 356°C into another monoclinic structure from 356° to 468°C (phase β), and finally to the hexagonal system (phase α) for the range up to fusion. The transition at 618°C is discussed below after study of electrical conductivity.

The curves of Fig. 1 are all similar but the measured conductivities are very different and depend on the atmosphere. They decrease in the following way.

$$\sigma \text{ (air)} > \sigma \text{ (Ar)} > \sigma \text{ (N}_2) > \sigma \text{ (CO}_2).$$

This phenomenon has not been systematically studied because the aim of this work was only the study of the existence of transition points under different atmospheres. It is therefore not explained hence. Several phenomenons can cause the differences in σ. Among these, for instance, gas moisture, surface adsorption on pellets, modifications of

contacts between sample, and electrodes because of the formation of new compounds (oxides) etc. One can also mention partial decomposition of sodium carbonate according to the reaction

$$\text{Na}_2\text{CO}_3 \rightleftharpoons \text{Na}_2\text{O} + \text{CO}_2 \text{ (g)}$$
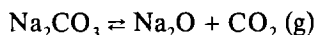
for which partial pressure measurements have been reported by Lebeau (8). In fact, titrations carried out on pellets after different experiments have not demonstrated such decomposition suggesting that the latter is slight and affects only the surface part of the pellet. However, such a pyrolysis seems to be assumed by most authors who, in recent years, investigated carbonates at elevated temperatures (9, 10).

Finally it may be mentioned that the phenomenon is reversible: If after having been performed under carbon dioxide, the experiment is repeated with the same sample under air atmosphere, the same results are found as on graph 1. If the sample was once more introduced into a CO$_2$ atmosphere, the conductivity decreased and approached that of 4. In the same way, if we operated first under argon, then under CO$_2$, a drop in the values of the conductivity was noticed from graph 2 towards graph 4.

Following the above, we operated under an atmosphere of CO_2 for the measurements of the conductivity in order to prevent the decomposition of Na_2CO_3.

IV. Transport Numbers

As electrical current is due to migration of ions, it is interesting to know the ratio of current carried by each type of ion, i.e., the transport number (t_+ for cations, and t_- for anions).

Our device consisted essentially of three identical pellets put in series in a circuit including a coulometric current source. The current varied between 100 and 300 μA; the time electrolysis, between 24 and 72 hr. The mass variation of anodic compartment ranged between 18 and 25 mg for test temperatures varying between 550 and 680°C. In all cases the t_+ values was found equal to 1 ± 0.01.

The determination of t_- which could verify the previous result is not possible, as it is necessary to oxidize the sodium deposited at the cathode in order to prevent its rediffusion into the pellets. As, under our experimental conditions, several sodium oxides appear as well as a platinum oxide in unknown proportions, the determination of t_- is not feasible.

In conclusion, we may say that the value $t_+ = 1$ confirms the hypothesis that may be

formulated considering only the respective volumes of the ions present. The anions supposedly having a cylinder-shaped volume, are very bulky ($(V \simeq 66$ Å$^3)$ with respect to the cations) ($V \simeq 4$ Å^3) and their contribution to electrical current is either nonexistent or negligible. This result is corroborated to a certain extent by the experimental determination of the diffusion coefficients of anions and cations in liquid (Li, Na, K)CO_3 which shows that the ratio of diffusion coefficients D_+/D_- is about 10 (10).

V. Electrical Conductivity

All graphs of Fig. 2 present three changes in slope. According to the temperature, four regions can be distinguished: A γ-phase region corresponding to room temperature up to 356°C; a β-phase region from 356 to 485°C; an αII region from 485 to about 618°C, and an αI region from 618°C to melting. All results can be interpreted by applying the well-known simple theory of electrical conductivity in ionic crystals. The basic concepts on point defects in ionic crystals and on ionic conductivity have been treated in many articles and textbooks. A survey of the historical aspects as well as for a bibliography is given in the famous encyclopedia article by Lidiard (11) up to 1956, and in the review article by Süptitz and Teltow (12) (up to 1967).
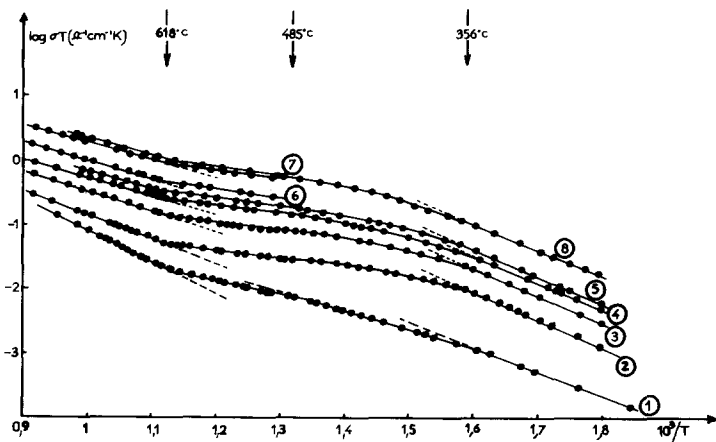

FIG. 2. Electrical conductivity of pure and doped Na_2CO_3, 1, Na_2CO_3 pure; 2, 1.1×10^{-5} $CaCO_3$; 3, 4.2×10^{-5} $CaCO_3$; 4, 3.25×10^{-5} CaCO; 5, 5.15×10^{-5} $CaCO_3$; 6, 5.6×10^{-4} $CaCO_3$; 7, 8.9×10^{-4} $CaCO_3$; 8, 9.3×10^{-4}.

(1) Pure Salt

The activation energies were equal to 0.96, 0.47, 0.56, and 0.75 eV in the regions αI, αII, β, and γ respectively.

(2) Doped Samples up to $C = 10^{-3}$

Generally the slope of log σT vs $1/T$ curves give the migration energy of cation vacancies (U_v) (11, 12). In the γ region, $\log \sigma T$ vs $10^3/T$ is represented by parallel straight lines. Hence the activation energy of cation vacancies is $U_v = 0.78 \pm 0.03$ eV.

In the β region, log σT is not linear. The slope of the curves decrease when T increase, but for a given temperature all the curves have the same slope within the precision of the measurements. The activation energy 0.29 $\pm$ 0.03 eV. This value is equal, within the limits of the measurement, to the one determined in the β region at about 485°C (0.30 eV from (1)). Thus, the passage from the monoclinic system to the hexagonal system has practically no influence upon the activation energy of the cation vacancies. In the αI region the curves (3–8) are parallel and their slope is 0.52 $\pm$ 0.03 eV.

(3) Doped Samples above $c = 10^{-3}$

When the $CaCO_3$ mole fraction reaches 10^{-3}, the log $\sigma T = f(10^3/T)$ curves differ from previous ones, presumably owing to the presence of an eutectic in the pellets of Na_2CO_3 (13). We can notice on Fig. 3 that the position of the curves practically does not depend on the concentration in impurities and that the transformations at 485b and 618°C are no longer apparent.

(4) Discussion

The main conclusions which can be drawn from these results are

(a) it is possible to form solid homogenous solutions of calcium carbonate in sodium carbonate when $c < 10^{-3}$;

(b) in the γ region the activation energies of the pure salt and of the doped samples are equal. For the pure salt, the extrinsic conductivity due to residual impurities and to grain boundaries is measured (11, 12).

(c) in the β and αII regions the slopes of the pure salt and of the doped samples are not equal, but the variation between the values (0.15 eV at most) is not significant. Hence, we may think that, there again, we measure, in the case of the pure salt, an extrinsic conductivity due to residual impurities and grain boundaries;

(d) in the αI region the slopes vary beyond 0.4 eV; it is likely that the measured conductivity corresponds to the intrinsic region. However, it is not possible to draw definition conclusions on the conduction mechanism in Na_2CO_3.
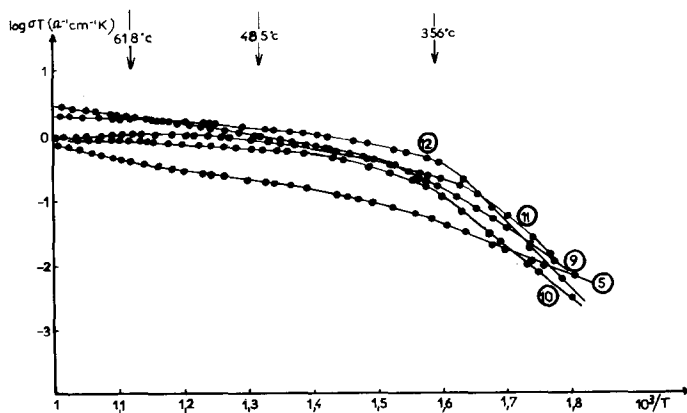

FIG. 3. Electrical conductivity of Na_2CO_3 + $CaCO_3$, 9, 1.1 × 10^{-3} $CaCO_3$; 10, 1.2 × 10^{-3} $CaCO_3$; 11, 4.3 × 10^{-3} $CaCO_3$; 12, 8 × 10^{-3} $CaCO_3$.

Let W be the energy of formation of the defects and U_v the migration energy of the cation vacancies. Several cases may be considered.

If the ionic disorder is of the Schottky type, the slope of the curve log T is equal to $-(W/2 + U_v)$ since $t_+ = 1$, $W = 0.86$ eV is inferred.

If the disorder is of the Frenkel type and cation vacancies are the main current carriers, the same conclusion is drawn. On the other hand, if the displacement of the interstitial ions is the chief contribution to the current, the corresponding activation energy is lower than 0.53 eV and $W > 0.86$ eV.

The hypothesis of Frenkel disorder seems the more probable, as a Schottky disorder must perturb the crystalline network more, bearing in mind the volumes of the ions present.

VI. Transition at 620°C

About 620°C a change slope can be observed for the pure and doped samples (up to $c = 10^{-3}$) and under various atmospheres. For the doped samples above $c = 10^{-3}$ there is no slope change as the latter, and the $(\alpha \rightleftharpoons \beta)$ transition at 485°C are hidden by another effect (such as the presence of an eutectic). This transition in the neighborhood of 620°C has not been observed by Reisman (3, 4) who explains the "anomalous heat effects" by the presence of Cl^- impurities. But the RP Prolabo contains less than 2.10^{-5} Cl^- and the Johnson Mattey specpure less than 10^{-6} Cl^-. Another possible explanation is the presence of oxides in the pellet (oxides possibly formed during the making of pellets) but Reisman (3, 4) demonstrated that sodium oxides have no effect on D.T.A. curves at 620°C. these facts seem to prove the existence of an intrinsic point transition at about 620°C.

This transition in the electrical properties appears without from any change in structure. An analogous phenomenon has been ob served in $NaNO_3$ by different processes and more

particularly by electrical conductivity (14). $NaNO_3$ crystallizes in the rhombohedric system from room temperature up to melting. In addition, we observe a first transition at 150°C and a second one at 275°C which may be explained by progressive appearance of orientational disorder of the ion NO_3^-. The type of disorder as commonly considered is an oscillation of NO_3^- about the c axis, the amplitude of which increases with temperature and leads to a rotation of the anion at 275°C. Such a phenomenon obviously has an impact upon the physical properties and especially upon the electrical conductivity and the crystalline parameters.

In the case of Na_2CO_3 the use of X-ray diffraction has made it possible to know the polymorphism of the salt, but there is still little information about the orientation of CO_3^{2-}. We only know that in the γ phase, there is, as a first approximation, an oscillation around the CO bond. In fact, because of the existence of secondary lines, we must admit that it is not a matter of oscillation but of "well-ordered" orientations varying over a given period of the crystalline network. In $Na_2CO_3 \cdot 10$ H_2O there is, on the other hand, an oscillation of CO_3 about the trigonal axis. In the absence of information on the α phase we may assume, in analogy to $NaNO_3$, that there is progressive orientational disorder which appears at 485°C and ends at about 618°C. Different types of orientation disorder may be considered: oscillation, rotation around a CO bond, in the CO_3 plane, or around the carbon atom. The progressive aspect of the transition is underlined by a fact that may be observed on Fig. 1 between 486° and 620°C (αII region). The variation of log σT is not linear: It corresponds to a faster increase with temperature up to 620°C. Furthermore, the latter value is not well defined: 618 ± 5°C has been found and Khlapova (5) has pointed out that according to the treatment undergone by the sample, the temperature of transition may vary from 570 up to 620°C.

References

1. J. JAFFRAY AND M. MARTIN, *J. Phys. Rad.* **14**, 553 (1953).
2. S. MAKAROV AND M. P. SCHULGINA, *Bull. Acad. Sci. USSR* **5**, 691 (1940).
3. A. REISMAN, F. HOLTZBERG, AND E. BANKS, *J. Amer. Chem. Soc.* **80**, 37 (1958).
4. A. REISMAN, *J. Amer. Chem. Soc.* **80**, 3558 (1958); **81**, 7 (1959).
5. A. N. KHLAPOVA, *Dokl. Akad. Nauk. SSSR* **116**, No. 6, 978–982 (1957).
6. E. BROUNS AND J. W. VISSER, *Acta Crystallogr.* **17**, 614 (1964).
7. G. C. DUBBELDAM AND P. M. DE WOLFF, *Acta Crystallogr. B* **25**, 2665 (1969).
8. LEBEAU, *Ann. Chim. Phys.* **6**, 425 (1905).
9. R. L. SASS AND R. S. Scheuerman, *Acta Crystallogr.* **15**, 77 (1962).
10. R. L. FREDERICK AND E. L. WILLIAMS, *J. Electrochem. Soc.* **116**, 4, 454 (1969).
11. A. B. LIDIARD, "Handbuch der Physik," Vol. 20, p. 246, Springer–Verlag, Berlin (1957).
12. P. SÜPTITZ AND J. TELTOW, *Phys. Stat. Sol.* **23**, 9 (1967).
13. P. NIGGLI, *Z. Anorg. Allgem. Chem.* **106**, 131 (1919).
14. P. CERISIER, Thesis, Aix-Marseilles (1970).