

ON THE DISSOCIATION MECHANISM OF CARBONATES AND THEIR ISOMORPHOUS MIXTURE

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The thermal decomposition processes of carbonate minerals are analyzed by comparison of the notions on chemical bonds in crystals and modern concepts on solid-phase reactions. It is shown that depending on the mechanism of thermal dissociation, the carbonate minerals most widespread in nature may be divided into two groups: first, CaCO_3 , SrCO_3 and BaCO_3 , characterized by decomposition temperatures close to the equilibrium values and undergoing recombination on cooling; and second, MgCO_3 , MnCO_3 , FeCO_3 and ZnCO_3 , with dissociation temperatures exceeding the equilibrium values by $\sim 250^\circ$ and recombining only at high partial pressures of CO_2 (above 1000 bar).

The frequent occurrence of carbonate minerals in nature, and the relative simplicity of their investigation by thermoanalytical methods, have resulted in a large number of experimental and theoretical studies, involving identification of carbonates via their thermal decomposition curves obtained by various methods (DTA, TG, DTG, etc.), determination of their thermodynamic parameters, studies of the effects of the experimental conditions on the thermal dissociation, etc. However, even though factual material has been accumulating for almost a century, serious contradictions still arise in the interpretation of the results of thermal studies, and a number of questions connected with the mechanism of thermal dissociation (e.g. the reasons for the recombination of some carbonate minerals at atmospheric pressure, for the decomposition of isomorphous mixtures of carbonates in one or more stages, etc.) remain unclear. The theoretical preconditions for solving such questions, and methodological recommendations for interpreting the results of thermoanalytical studies, may be obtained by means of the model proposed below for the mechanism of thermal dissociation of carbonates, based on the comparison of our notions on chemical bonds in crystals with the modern concepts on solid-phase reactions.

A comparison of the results of theoretical calculations relating to the conditions of thermodynamic equilibrium for the decomposition reaction $\text{MCO}_3_{\text{cryst.}} \rightarrow \text{MO}_{\text{cryst.}} + \text{CO}_2\uparrow$ (Fig. 1), and the dissociation temperatures experimentally observed for the carbonate minerals occurring most frequently in nature permits their division into two groups.* Group I, represented by CaCO_3 , BaCO_3 , SrCO_3 and others, is characterized

*Carbonates whose dissociation yields intermediate products which vary in composition (PbCO_3 and some rare earth metal carbonates) should be classified in a separate group. This paper will not deal with the particular features of the thermal dissociation of these compounds.

by the close agreement of the calculated and experimental temperatures. For Group II (MgCO_3 , MnCO_3 , FeCO_3 , ZnCO_3 and others), experimentally measured decomposition temperatures exceeding the calculated values by more than 250° are typical.

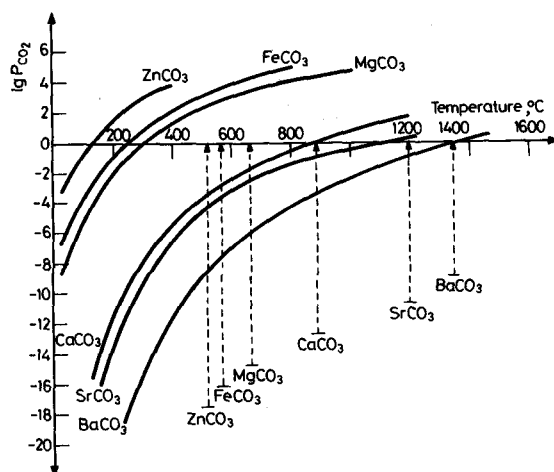


Fig. 1 Dependence of the thermodynamic equilibrium of the reaction $\text{MO} + \text{CO}_2 \rightleftharpoons \text{MCO}_3$ on temperature and pressure. (Experimental decomposition temperatures of carbonates in air according to [1] are indicated by arrows)

The classification of carbonate minerals according to their behaviour during heating practically coincides with the classification based on their crystal systems: carbonates having a rhombic structure and an elementary cell coordination number of 9 (the group of aragonite and calcite) belong in Group I, while carbonates having a trigonal structure and a coordination number of 6 (the magnesite group) belong in Group II.

It is also known that the synthesis of Group I carbonates from MO and CO_2 at atmospheric pressure proceeds within a wide temperature range, while Group II minerals can only be synthesized at very high CO_2 pressures (exceeding 1000 bar), and consequently practically no recombination of these oxides with CO_2 will occur during thermoanalytical investigations.

It appears obvious that such large differences in the structures of crystals belonging in Groups I and II, and in their behaviour on heating, must be due to differences in the properties of the metals forming them. In carbonate minerals, ionic bonds are known to exist between the carbonate group and the cation, the degree of ionicity depending on the structure of the electron shell in the metal forming the carbonate.

The interionic distances in ionic crystals are the resultants of the equilibrium between the attraction of the oppositely charged ions and the repulsion of the identically charged ions forming the structure. This equilibrium is defined on the one hand by the geometrical dimensions of the initial atoms, and on the other by the tendency of

the atoms to form ions. The geometrical dimensions of ions are characterized by the ionic radii and by the distance between the centre of the ion and the minimum value of the electron density. The tendency of an atom to form an ionic bond, i.e. its ability to donate or accept an electron, is usually characterized by the notion of electronegativity. However, the formal concepts of ionic radii and electronegativity characterize one and the same physical phenomenon, namely the resulting field of interactions, including both coulombic interactions and strong and weak interactions. It is therefore reasonable to introduce a generalized energy parameter γ to evaluate the properties of the bond. This parameter represents the ratio of the ionization energy of the outermost electron to its orbital radius [2].

The relative characteristics of the metals forming carbonates are listed in Table 1. They demonstrate that the highest share of ionic bonds appear in carbonates formed by Ba, Sr and Ca, where the difference between the energy of the valency electrons in the next-lower level is high, and the ionic radii are large, whereas Mg, Fe and Zn are characterized by smaller ionic radii and high ionization energies, and hence less pronounced donor properties.

Table 1 Comparison of the properties of metal ions forming carbonate minerals (from [2])

Ion	Coord. number	Ionic radius, Å	Electronegativity	Generalized energetic parameter, γ
Ba ²⁺	9	1.61	0.9	6.45
Sr ²⁺	10	1.46	1.0	8.29
Ca ²⁺	6	1.14	1.0	10.99
Mg ²⁺	6	0.86	1.2	18.79
Fe ²⁺	6	0.75	1.7	18.81
Zn ²⁺	6	0.89	1.6	21.64

The difference in the electronic properties of metals forming carbonates and manifested in their differing shares of ionic bonds may be illustrated on the example of the electron density distributions in essentially ionic (NaCl) and essentially covalent (InSb) crystals.

These distributions in NaCl [3] and in InSb [4] are illustrated in Figs 2a and 2b; in the interstices between Na and Cl, the electron density decreases to $0.1 \text{ a}/\text{Å}^3$, whereas in indium antimonide crystals interstitial parts with electron densities as high as 0.3 to $0.3 \text{ a}/\text{Å}^3$ (so-called bridges) exist, forming potential barriers for diffusion by the interstitial mechanism. The electron density distribution in carbonate minerals is intermediate between the two cases represented in the figures, with the electron density increasing from Ba to Zn in proportion to the electronegativity.

Let us now consider the above features of the chemical bonds in carbonates in the mechanism of their decomposition reaction. The start of the dissociation process is characterized by the formation of nuclei of the new phase at the lattice points with greatest defects (ion vacancies, interstitial elements, dislocations, Smekal fissures, etc.)

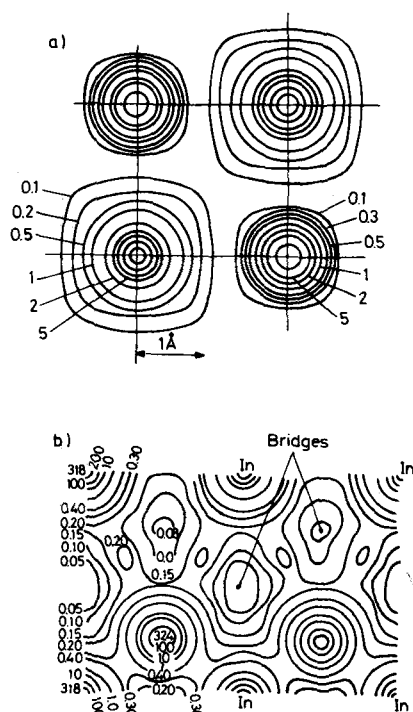


Fig. 2 Distribution of electron density in sodium chloride (a) and indium antimonide (b) crystals

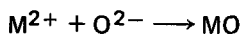
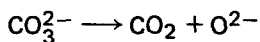
[5], where local energy fluctuations will be sufficient to accumulate the activation energy required. For the reaction to proceed further, it is necessary that the CO_3^{2-} ions be capable of diffusing through the crystal structure.

Diffusion in the crystal lattice takes place by the shift of defects of various types; the most frequent mechanisms of volume diffusion are connected with interstitial crystal elements and vacancies (Schottky and Frenkel defects).

Structural defects may be regarded as energetically excited states of the crystal lattice, involving changes in the filling of the lattice points. The concentration and localization of defects depend on the temperature and pressure of the environment and on the properties of the object under study, these being defined above all by the forces of atomic interaction (chemical bonds and density of packing, i.e. the ratio of the ionic radii). Atomic defects in the crystal may become ionized, this actually taking place usually on temperature rise. In solid-phase reactions a chemical potential gradient develops, with the result that the defects move towards the reaction interface; however, since the defects are charged, their interaction with the field of the crystal lattice may either promote the reaction or retard it.

Consequently, for the dissociation of carbonates, conditions are necessary under which the splitting of one of the carbon-oxygen bonds in the CO_3^{2-} ion, the forma-

tion of the CO_2 molecule, and its removal from the carbonate structure are possible, i.e.



The energy consumption in carbonate thermal decomposition may be represented as the sum of the consumptions for defect formation, defect diffusion, and splitting of one carbon-oxygen bond in the anion. While the latter is constant at constant pressure, the energy required for defect formation and diffusion may change during the reaction, since the defect formation energy depends on the distortion of the lattice caused by its transformation, and the diffusion energy depends on the lengths of the path in the initial material and in the newly-formed product.

The mechanism of thermal decomposition may be described by various models; however, in the case of the thermal dissociation of carbonates, the model of Wagner [6] appears most realistic. This model regards this reaction as the two-way diffusion of the particles of the initial material and the product being formed, in opposite directions.

In our opinion, for the case of carbonate decomposition (or recombination) the events taking place are the diffusion of the CO_3^{2-} anions to the interface of the solid and gas phases, the formation of CO_2 molecules and O^{2-} anions at this interface, and the diffusion in the opposite direction of O^{2-} across the layer of the reaction product. This assumption appears most probable, since the other variant (the splitting of a carbon-oxygen bond in the CO_3^{2-} group directly at the lattice point, and the escape of CO_2 into the interstice, with further diffusion to the interface) is energetically disadvantageous; to split a carbon-oxygen bond within the lattice, a substantial distortion of the field around the lattice point occupied by the dissociating anion is required (i.e. an association of defects must be formed). This latter variant is also possible, however, if dislocations and small-angled boundaries of grains of crystals are present.

The correctness of the above assumption is experimentally confirmed by the data on the decomposition of carbonate minerals at various CO_2 pressures. If CO_2 molecules were being formed within the crystal structure, the dissociation temperature *versus* pressure relationship would be adequate for the carbonates of Group I and Group II. However, for Group I, the relationship is as presented in Fig. 1, whereas for Group II the relationship is much weaker and is defined by the dependence of the diffusion of anionic defects on the CO_2 pressure.

The high decomposition temperatures of the carbonates of Group I are due to the high deformation energies of the lattice in ionic crystals. However, after the anion has emerged into the interstice, a not very substantial energy is required for its diffusion, since for purely ionic crystals the charge of the electron field at the interstices tends towards zero (cf. Fig. 2). The equilibrium-state temperatures of the carbonates of Group II are significantly lower, due to the appreciable effect of the sharing of

covalent bonds between the ions. However, the anion must overcome a significant energy barrier, resulting from the high electron density in the crystal, to pass into the adjacent interstice and subsequently arrive at the interface of the solid and gas phases. Hence, the rate of reaction in carbonates of Group II is controlled by the rate of diffusion of anionic defects, whereas in carbonates of Group I the rate-controlling factor is their rate of formation. This explains why minerals of Group I dissociate in temperature ranges close to the equilibrium value, and the oxides recombine with CO_2 during cooling in air, while the oxides formed from carbonates of Group II are incapable of recombination under standard DTA conditions, and surplus energy compared to the equilibrium state must be spent for their decomposition.

The same difference in reaction mechanism also appears in thermoanalytical investigations of isomorphous mixtures and double salts of carbonates. The behaviour of a solid solution under DTA conditions (atmospheric pressure, non-isothermal regime) is characterized by a shift of the dissociation temperatures as compared to those of the pure phases, and is defined by the ability of the oxides formed in their decomposition to undergo recombination. The number of steps observed in the thermoanalytical curves depends mainly on the latter circumstance. Isomorphous mixtures of carbonates of Group I or of Groups I and II necessarily dissociate in two stages. For instance, the first stage of dissociation of isomorphous mixtures or double salts of Ca-Mg carbonates consists in the breakdown of the structure and the formation of the respective oxides and CO_2 . However, at this temperature CaO is not stable, as shown by the relationship presented in Fig. 1, and recombines with CO_2 to give CaCO_3 . The second stage of dissociation consists in the decomposition of CaCO_3 .

The thermal dissociation of solid solutions of carbonate minerals of Group II proceeds in one stage, since the metal oxides formed are incapable of recombination with CO_2 under the DTA conditions. A well-known example of such dissociation is the decomposition of minerals belonging to the isomorphous series $\text{MgCO}_3\text{-FeCO}_3$.

Thus, the character of the decomposition curve (the number of steps) in the dissociation of solid solutions yielding metal oxides and CO_2 is defined by the ability of the metal oxides to combine with CO_2 when the carbonate of this oxide is dissociated at higher temperatures.

The theoretical model discussed allows an explanation of the reasons for the recombination of certain carbonate minerals after thermal decomposition. The results of thermoanalytical studies of their isomorphous mixtures and double salts may be interpreted more surely, and the model may also be used to reconstruct the conditions of carbonate formation and the secondary changes occurring in carbonate minerals.

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Zusammenfassung — Die thermischen Zersetzungsprozesse von Carbonatmineralien wurden auf der Basis der Vorstellungen über die chemischen Bindungen in Kristallen und moderner Konzeptionen über Festphasenreaktionen analysiert. Es wird gezeigt, dass die in der Natur weitverbreitetsten Carbonatmineralien, abhängig vom Mechanismus der thermischen Zersetzung, in zwei Gruppen unterteilt werden können: die erste umfasst CaCO_3 , SrCO_3 und BaCO_3 und ist durch Zersetzungstemperaturen nahe den Gleichgewichtswerten und durch Rekombination beim Abkühlen charakterisiert, zur zweiten gehören MgCO_3 , MnCO_3 , FeCO_3 und ZnCO_3 mit Dissoziationstemperaturen, die die Gleichgewichtswerte um etwa 250° überschreiten, und die nur bei hohen CO_2 -Partialdrücken (über 1000 bar) rekombinieren.

Резюме — В статье приводится анализ процессов термического разложения карбонатных минералов, основанный на сопоставлении учения о химических связях в кристаллах с современными представлениями о твердофазных реакциях. Показано, что в зависимости от механизма термодиссоциации, наиболее распространенные в природе карбонатные минералы можно разделить на две группы. Первая группа CaCO_3 , SrCO_3 , BaCO_3 характеризуется температурами разложения, близкими к равновесным значениям и рекомбинируют при охлаждении. Вторая группа MgCO_3 , MnCO_3 , FeCO_3 , ZnCO_3 представлена минералами, температуры диссоциации которых выше равновесного значения на $\sim 250^\circ$, а их рекомбинация возможна только при высоких P_{CO_2} (более 1000 бар).