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ALTERATION OF KINETICS AND THERMODYNAMICS OF THERMAL DECOMPOSITION OF ALKALINE-EARTH CARBONATES INDUCED BY GRINDING*

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ABSTRACT

The effect of grinding on the kinetics and thermodynamics of thermal decomposition reactions of alkaline-earth carbonates has been studied. Grinding of $MgCO_3$, $SrCO_3$ and $BaCO_3$ leads to a decrease in the activation energy of the reaction which becomes greater as the lattice energy of the salt decreases. These results can be attributed to the mechanically produced lattice disorder that is facilitated with decreasing lattice energy. A decrease in the enthalpy of decomposition has also been noted in the ground samples of $SrCO_3$.

By contrast, the enthalpy and activation energy of thermal decomposition of $CaCO_3$ do not undergo significant alterations. Noticeable changes occur only after quite a long grinding time. This behaviour is probably related to an elimination of the microstrains created during grinding as a result of the phase transformations calcite → aragonite and aragonite → calcite, induced in this salt by grinding.

A compensation effect between the enthalpy and entropy of decomposition and also between the activation energy and frequency factor is observed. These correlations seem to indicate that the reaction takes place through the same activated complex, its thermodynamic constants depending on the nature of the cation. Thus, the decrease in the frequency factor of the reaction as the grinding of the salt continues, might be related to an increase in the carbonate ion entropy.

INTRODUCTION

Mechanical processes, such as grinding, constitute one of the most important procedures for preparing active solids. Although the primary object of these processes is size reduction, it is well known that they also alter the chemical properties of solids. Recently, Lin et al[1]. have reviewed the changes in the state of solids induced during

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prolonged grinding. These changes are classified into four general groups related to changes in surface properties, amorphization and decrystallization, polymorphic transformations and mechano-chemical reactions. In the case of carbonates these two latter phenomena have been widely reported in the literature. Polymorphic transitions of calcite into aragonite and vice versa induced in a ball mill by prolonged grinding have been fully documented[2-5]. Also solid state decomposition of carbonates, such as zinc and cadmium carbonates, which have relatively low decomposition temperatures, has been described[6, 7]. When a carbonate has a higher decomposition temperature, e.g. magnesium carbonate, a decrease in the decomposition temperature has been observed during prolonged grinding. However, few, if any, systematic investigations have been carried out concerning the influence exerted by grinding on kinetic and thermodynamic stabilities in connection with thermal decomposition reactions.

Alkaline-earth carbonates provide a particularly interesting subject for carrying out a comparative study of the effect of grinding on the kinetics and thermodynamics of decomposition of these carbonates. Thermogravimetric curves can be used to obtain both kinetic and equilibrium data. Alterations in structure and surface properties of the samples studied here have been described elsewhere[8, 9].

MATERIALS AND METHODS

Magnesite from Navarra (Spain) was used. This carbonate exhibits the following chemical composition: SiO_2 1.76%; Fe_2O_3 1.12%; Al_2O_3 0.32%; CaO 0.98%; MgO 45.35%; loss on ignition 50.50%. Calcium, strontium and barium carbonate D'Hemio a.r. were also used.

The ground samples were prepared in a Colorecord 20 A planetary mill with a speed of 400 r.p.m. The mill is equipped with a steatite jar (capacity 300 cm^3, $\phi = 11$ cm) containing 20 balls ($\phi = 20$ mm). Samples of 2–3 g were ground for different periods of time.

TG curves were obtained with a Chan Electrobalance model RG, connected with a conventional vacuum system. The temperature was measured with a cromel–alumel thermocouple placed outside the electrobalance tube, very close to the sample.

RESULTS AND DISCUSSION

As already mentioned, different examples of mechanically induced reactions in carbonates have been reported in the literature. Molchanov et al.[10] and others authors[11] have found that grinding of ankerite, dolomite and calcite results in final products of metal oxides and CO_2. In our case, the X-ray diffraction powder analysis of the ground samples shows that this conversion is not produced during mechanical treatment. Results obtained for $CaCO_3$ show that successive transformations of calcite → aragonite and aragonite → calcite take place in the ball mill as a consequence of grinding[8]. In the case of ground samples of $MgCO_3$, $SrCO_3$ and $BaCO_3$,

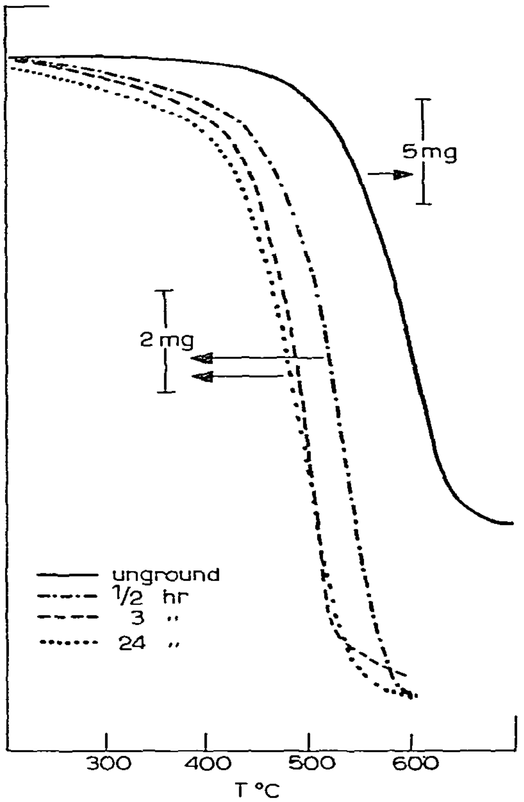

Fig. 1. TG curves of $MgCO_3$, ground for different periods of time.

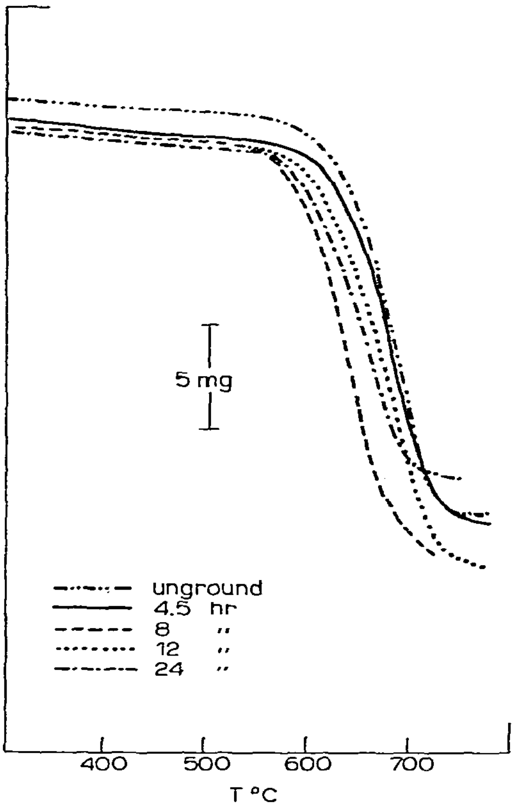

Fig. 2. TG curves of $CaCO_3$, ground for different periods of time.

a broadening of the diffraction lines is observed. Such a broadening is probably related to a decrease in coherent diffraction domains and an increase in the microstrains induced in the crystals during grinding.

A kinetic study has been carried out from TG curves obtained with a heating rate of 12°C min^{-1}, under high vacuum (10^{-4} Torr) and using sample weight of 30–50 mg. Under these conditions, the influence of the pressure of CO_2 on decomposition rate is reduced and the problems arising from heat transfer are minimized. Therefore, the kinetic parameters obtained are independent of the experimental conditions and can be considered representative of the structural nature of the solid. The TG curves of milled samples, except that of $CaCO_3$, showed a shift in the decomposition temperature to lower values as the mechanical treatment increased. In this salt there was no correlation between these latter parameters, either upon increasing or decreasing the initial temperature of decomposition as the grinding continued. Figures 1 and 2 are two examples which illustrate this behaviour.

Because the isothermal kinetic data of unground samples fit the "contracting sphere model", which describes the reaction as a phase-boundary process, TG curves have been analysed according to this mechanism. Moreover, the decomposed fraction at the inflexion point of these curves, α_m, where the reaction rate reaches a maximum value, exhibits a value in the range of 0.66–0.68. These values lie in the range calculated by different authors[12, 13] for a two-third order mechanism. According to these considerations, the equation which describes the decomposition mechanism of alkaline-earth carbonates undergoing different mechanical treatment can be expressed as

$$\frac{d\alpha}{dt} = A\, e^{-E/RT} (1 - \alpha)^{2/3} \tag{1}$$

where α is the fraction decomposed at time t, and E and A the activation energy and frequency factor of the reaction, respectively.

For determining the kinetic parameters the Coats and Redfern's integral method has been used. This approach gives reliable results and has been recommended by several authors[14–16] in preference to other integral or differential methods of kinetic analysis. Thus, kinetic analysis of TG curves, such as those included in Figs. 1 and 2, has been carried out by the kinetic equation

$$\log [1 - (1 - \alpha)^{1/3}] - 2 \log T = \log \frac{AR}{3\,E\beta} - \frac{E}{2.3\,RT} \tag{2}$$

Bearing in mind the above considerations, kinetic parameters of alkaline-earth

TABLE 1

KINETIC PARAMETERS FOR THERMAL DECOMPOSITION OF ALKALINE-EARTH CARBONATES, UNDERGOING DIFFERENT MECHANICAL TREATMENTS

Compound	*Time of grinding (h)*	*E (kcal mole^{-1})*	*A (seg^{-1})*
$MgCO_3$	0	29	7.7×10^7
	0.5	24	2.0×10^6
	3	24	3.2×10^6
	10	25	1.4×10^7
	24	25	2.2×10^7
$CaCO_3$	0	39	1.6×10^9
	4.5	39	1.2×10^9
	8	37	5.2×10^8
	12	33	3.4×10^7
	24	32	6.8×10^7
$SrCO_3$	0	60	1.0×10^{12}
	2	49	4.3×10^9
	6	41	7.3×10^7
	8	40	3.0×10^7
$BaCO_3$	0	62	2.0×10^{11}
	2	45	1.4×10^8
	4	42	4.1×10^7

carbonates, deduced from eqn. (2) and referred to the surface reaction, are included in Table 1.

The method which allows the calculation of the equilibrium constant for the thermal decomposition of alkaline-earth carbonates has been extensively described elsewhere[18]. The procedure is based upon the overlapping of the TG curves corresponding to the reaction of formation and decomposition of the salt by changing the heating rate in an appropriate way. Figures 3 and 4 illustrate the behaviour of alkaline-earth oxides when they are heated under a known CO_2 pressure. At the peak temperature, the rate of formation of carbonate and its reverse become equal and the system reaches equilibrium. Under these conditions, the measured pressure of CO_2 would be the equilibrium constant of the thermal reaction at this temperature. Unfortunately, it has not been possible to extend this study to $MgCO_3$ and $BaCO_3$, due to the difficulties of the MgO recarbonation and the high stability of $BaCO_3$. In this salt, the temperature required for the equilibrium constant measurements was higher than that allowed by our experimental system. From the corresponding TG curves of the different CaO–$CaCO_3$ and SrO–$SrCO_3$ samples, the equilibrium pressures of CO_2 have been determined at different temperatures. Thermodynamic parameters — enthalpy and entropy of decomposition — are obtained from the Clausius–

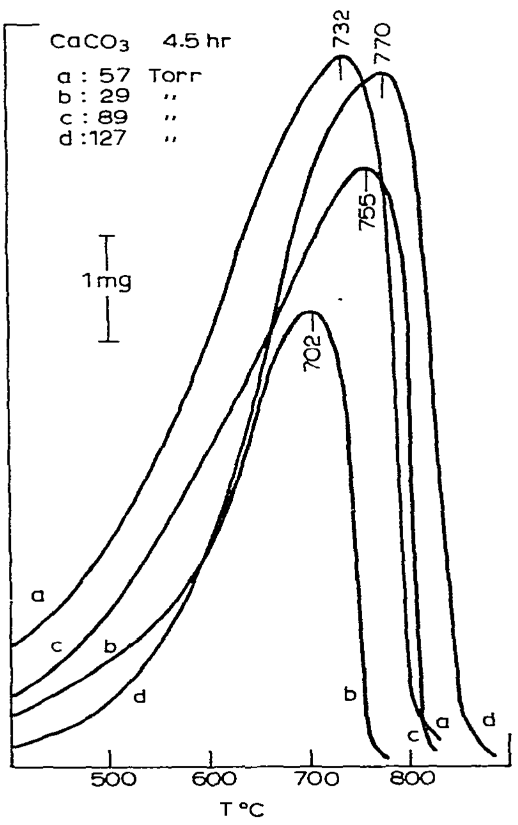

Fig. 3. TG curves of a sample of CaO–$CaCO_3$ obtained at different CO_2 pressures. The sample has been ground for four and a half hours. Heating rate has been changed until overlapping has been reached.

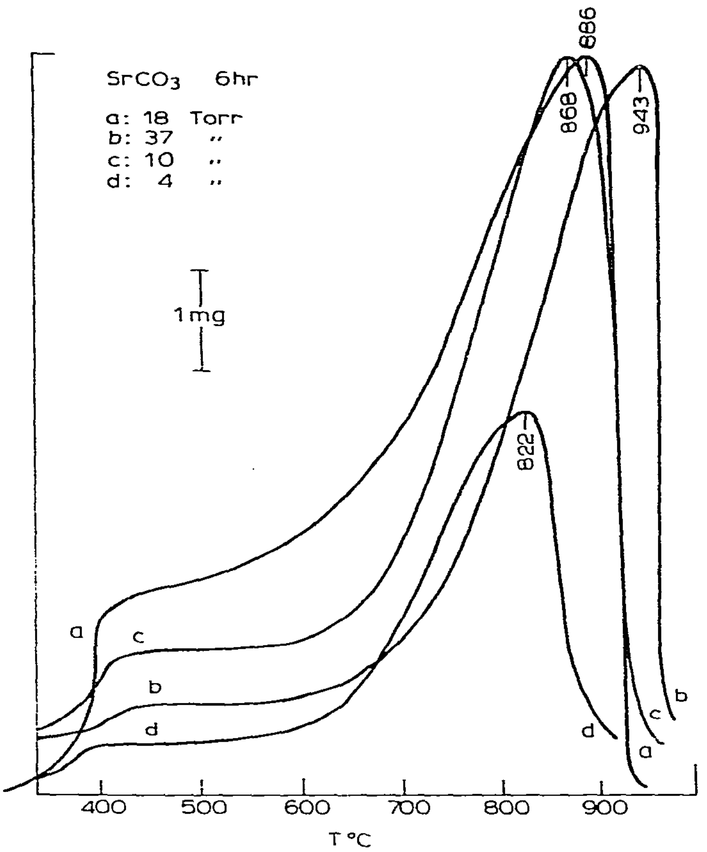

Fig. 4. TG curves of a sample of SrO–$SrCO_3$ obtained at different CO_2 pressures. The sample of $SrCO_3$ has been ground for six hours. Heating rate has been changed until overlapping has been reached.

TABLE 2

THERMODYNAMIC CONSTANTS FOR THE THERMAL DECOMPOSITION REACTIONS OF $CaCo_3$ AND $SrCo_3$, UNDERGOING DIFFERENT MECHANICAL TREATMENTS

Compound	*Time of grinding (h)*	ΔH^0 *(kcal mole^{-1})*	ΔS^0 *(cal mole^{-1})*
$CaCO_3$	0	41	34
	4.5	41	35
	8	41	35
	12	36	31
	24	37	32
$SrCO_3$	0	63	47
	2	57	42
	6	51	36
	8	51	36

Clapeyron equation by plotting the logarithm of the CO_2 equilibrium pressure versus $1/T$. The results obtained are summarized in Table 2.

A comparative study of the effect of grinding on kinetic and thermodynamic parameters of the thermal decomposition reactions of alkaline-earth carbonates will be further elaborated. The results included in Table 1 and 2 show that the activation energy obtained is close to the enthalpy of decomposition. In the samples of $CaCO_3$ and $SrCO_3$, where it has been possible to determine both parameters, the changes induced by mechanical activation show a similar trend, as can be observed by plotting the activation energy of $CaCO_3$ and $SrCO_3$ against the enthalpy of decomposition (see Fig. 5).

As shown in Table 1, grinding of $MgCO_3$, $SrCO_3$ and $BaCO_3$ leads to a diminution of the activation energy of the thermal decomposition reaction. This becomes greater as the molecular weight of the salt increases. This behaviour can be explained because, as the molecular weight of these carbonates increases, their lattice energy decreases, making the displacement of the ions from their equilibrium lattice positions easier (see Table 3, which includes the lattice energy of alkaline-earth carbonates deduced from Kapustinkii equation[19]). Consequently, there is probably an increase in the stored deformation energy induced by the grinding process across the series $MgCO_3$, $SrCO_3$ and $BaCO_3$.

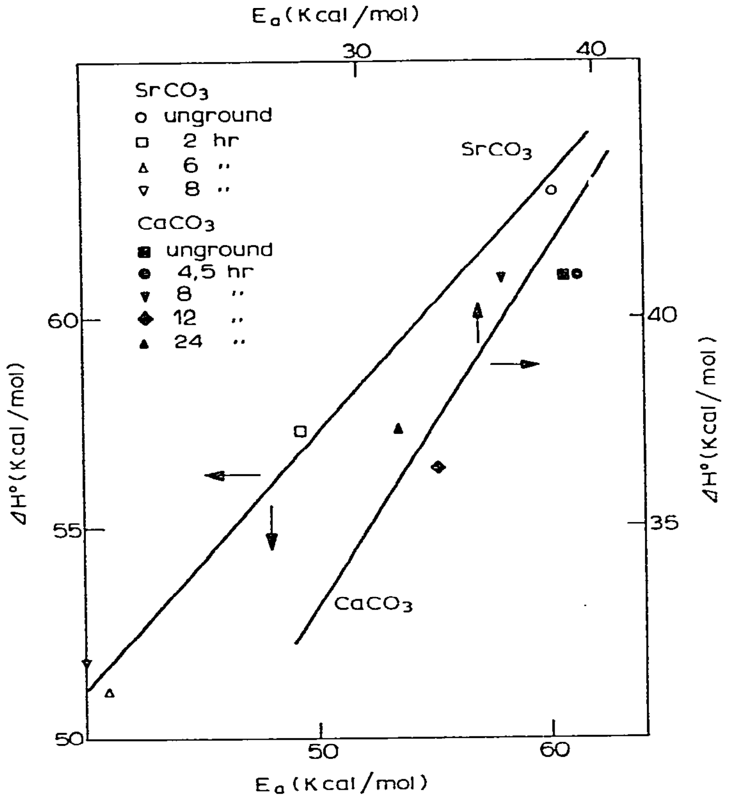

Fig. 5. Relation between activation energy and enthalpy of thermal decomposition reaction of $CaCO_3$ and $SrCO_3$.

TABLE 3

THE LATTICE ENERGY OF THE ALKALINE-EARTH CARBONATES[19]

Compound	*U (kcal mole^{-1})*
$MgCO_3$	760
$CaCO_3$	714
$SrCO_3$	650
$BaCO_3$	625

A pronounced decrease in the thermodynamic parameters of $SrCO_3$ as a result of the mechanical treatment is also shown in Table 2. The increase in thermal reactivity on grinding could be explained in terms of the increase in the surface energy as a result of the fracture of the crystals and the strain energy stored in the lattice due to reticular defects created during the milling run. From the Kelvin equation, we have obtained an approximate value of 0.15 kcal mole^{-1} for the surface energy. This value is notably lower than the energetic changes observed in Tables 1 and 2. On the other hand, a value of 30 kcal mole^{-1} for the stored deformation energy has been calculated from the equation that gives the elastic strain energy per unit length of dislocation[20]. In this calculation we have assumed a dislocation density of 10^{12} cm^{-2}, an average value of the interionic distances of alkaline-earth carbonates for the magnitude of the Burgers vector, and a shear modulus of 10^{12} dynes cm^{-2}[21]. Thus, energy resulting from the imperfections produced by ball-milling might explain the results of Tables 1 and 2.

Different behaviour is found in the case of the mechanical activation of $CaCO_3$. It can be seen from Tables 1 and 2 that kinetic and thermodynamic parameters are found to remain unaltered for short periods of grinding. Our observations are not in agreement with the results obtained by Schrader et al.[22] who studied the effect of grinding on the thermodynamic stability of calcite. These authors have reported 33 and 16 kcal mole^{-1} for the original and the ground material, respectively. We believe that the lack of agreement is probably due to the experimental method used by Schrader et al.[22] for the measurement of the equilibrium constant. The salt is heated in a closed container at a constant temperature and the equilibrium is reached when the pressure of CO_2 remains constant. Stern and Weise[23] have pointed out serious deficiencies in these methods due to the formation of "pseudoequilibria". Though the reaction is thermodynamically favoured in one way, an hypothetical equilibrium can be reached because the system is changing so slowly that we cannot detect any net reaction. In other words, kinetic factors can mislead the results obtained for the equilibrium constant.

Results obtained for the enthalpy and activation energy for the thermal decomposition of $CaCO_3$ ground for short periods of time can be explained in terms of the polymorphic transitions of calcite into aragonite and vice versa, produced by grinding in the samples studied in this paper[8]. This means that there is probably an elimination of the microstrains created during grinding, since there is a rearrangement in the crystal structure as a result of the phase transformations. This explanation conforms with the results of several authors[24, 25] who have studied the effect of grinding on the calcite → aragonite phase transformation. They find a decrease in the microstrains of the ground samples as the phase transformation progresses. As regards the alterations produced after prolonged grinding (see Tables 1 and 2), they are probably due to a progressive deterioration of the crystal lattice of the two polymorphs.

As mentioned above, the activation energy of these salts is approximately equal to the enthalpy of decomposition. Therefore, the activated complex will lie close to the products when the potential energy of the thermal decomposition reaction is plotted as a function of the reaction coordinate. This means that the activated complex structure may be similar to that of the reaction products. According to these considerations, Shannon[26] has suggested a model for the activated complex to explain the frequency factors of the thermal decomposition of $MgCO_3$ and $CaCO_3$ — 2.2×10^{10} and 1.3×10^{11} sec^{-1}, respectively — obtained by Britton et al.[27]. Although the values reported by these authors are higher than those included in Table 1, it seems probable that, as pointed out in ref. 27, these results are influenced

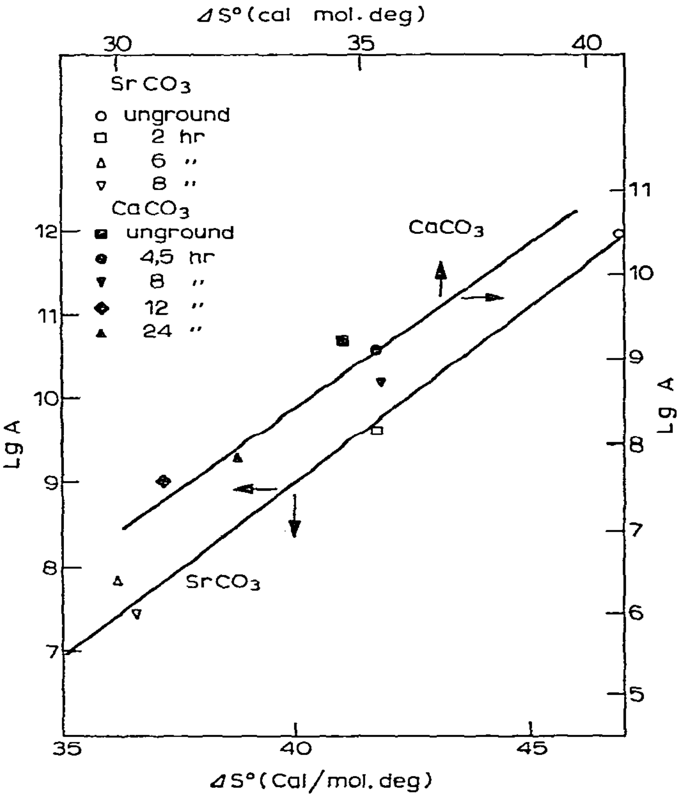

Fig. 6. Relation between frequency factor and entropy of thermal decomposition reaction of $CaCO_3$ and $SrCO_3$.

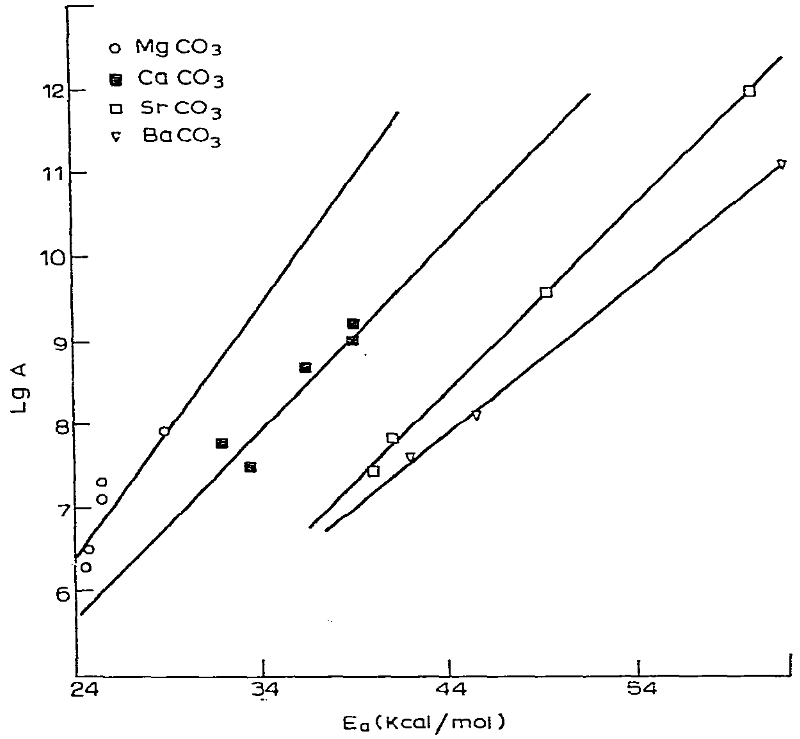

Fig. 7. Relation between activation energy and frequency factor of thermal decomposition reaction of alkaline-earth carbonates, ground for different periods of time.

by the diffusion of CO_2 resulting from the reaction and heat transfer phenomena through the sample. Thus, it is not evident that the frequency factors reported by Britton et al. are representative of the interface reaction.

The frequency factors in Table 1 have been obtained using 10^{14} molecules cm^{-2} for N (number of molecules per unit area of interface). The values lie in the range of 10^8–10^{12} sec^{-1}, depending on the nature of the salt. These data fall within the region of those calculated by Cordes[28] for monomolecular surface reaction, by means of absolute reaction rate theory.

In general, an increase in the frequency factor and the activation energy takes place across the series $MgCO_3 \rightarrow BaCO_3$. This fact can be explained taking into account that, as the bond energy of the salt increases, the mobility of carbonate ion decreases with regard to the reaction products and the activated complex, increasing in this way the reaction and activation entropies. This hypothesis is in agreement with the correlation found between the frequency factors and entropies of decomposition of the different samples of $CaCO_3$ and $SrCO_3$, salts in which it has been possible to determine the latter parameter (see Fig. 6).

On the other hand, a compensation effect is observed between the enthalpy and entropy of decomposition and also between the activation energy and frequency factor in each carbonate (see Figs. 7 and 8). We interpret these correlations as being due to the fact that the reaction in each set of samples gives the same activated

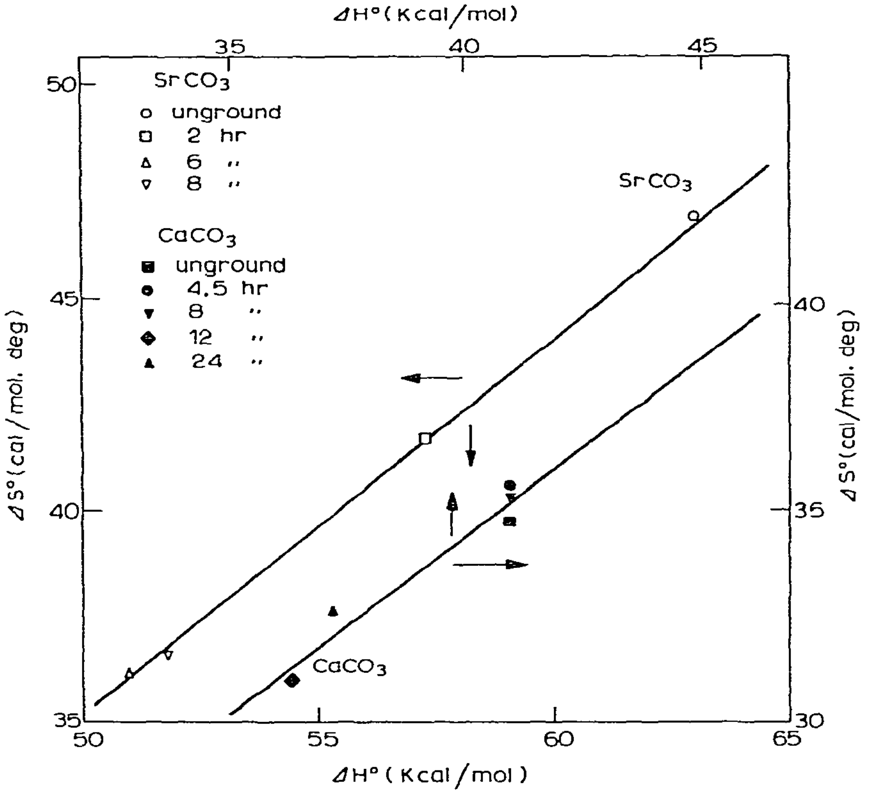

Fig. 8. Relation between enthalpy and entropy of the thermal decomposition reactions of $CaCO_3$ and $SrCO_3$.

complex, the thermodynamic constants of which depend on the nature of the cation. In this way, the decrease in the frequency factor, as the grinding of the salt continues, ought to be related to an increase in the carbonate ion entropy.

The results discussed in this paper clearly show that the thermal decomposition of alkaline-earth carbonates is affected in different ways by mechanical processes such as grinding. The changes observed in reactivity must be attributed to an increase in the degree of lattice distortion induced by grinding. However, to explain the results more accurately, it is necessary to have a quantitative knowledge of the mechanically produced lattice disorder. This research based on X-ray diffraction and electron microscopy studies is now in progress in our laboratory.

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