

*Dedicated to Dr. Robert Mackenzie on the occasion of his 75th birthday*

## **KINETIC ANALYSIS OF THERMAL DECOMPOSITION OF MAGNESITE**

### **Influence of generated defects and their annealing**

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### **Abstract**

The excess enthalpy of magnesite accumulated by vibration grinding at low specific grinding energy consumption is due predominantly to an increase in specific surface area; at higher energy supply, it is caused by changes in the X-ray amorphous phase content, and when the supplied energy exceeds ca 2000 kJ kg<sup>-1</sup> it is a result of the generation of other kinds of defects. The generated defects are relatively stable below 800 K and are the reason for a broad range of distribution of local molar Gibbs energies. Thus, at low temperatures only the 'active' portion of samples is able to decompose. Defects relax above ca 800 K, with rates comparable with the rate of decomposition itself. Accordingly, the efficiency of mechanical activation is impressive only below this temperature.

**Keywords:** decomposition, defect annealing, excess enthalpy, magnesite, mechanical activation

### **Introduction**

The influence of structure defects on heterogeneous and solid-state reactions has been the subject of numerous discussions and intensive experimental research. It is generally supposed that structure defects influence the reactions of solids markedly at temperatures below 500 K, where the annealing of defects is relatively slow. Mechanically activated solids are suitable models for experimental study of this problem. Variation of the conditions of mechanical activation allows the preparation of reactants differing in structure, energy and properties.

The aim of the mechanical treatment of solids is usually to increase their reactivity. This effect is caused by influencing both the kinetic factors of the solid reactant (particle size, shape, specific surface area, etc.) and its thermodynamic parameters, by the creation of different types of structure defects [1]. However, these two groups of parameters can hardly be separated exactly. Similarly, it is a problem to find general relations between the set of experimentally detectable structure and

thermodynamic parameters of a solid [2] and its kinetic behaviour. The root of the problem stems from the fact that it is not yet possible to define unambiguously the state of real solids. Attempts so far concern projects of experiments [3] and computer simulations of two-dimensional solids [4] in order to determine the distribution of their internal energy. On the other hand, there is a problem with reactivity quantification too. Experience with heterogeneous reactions shows that traditional kinetic models do not in general fulfil this purpose because of the complexity of the structure of the reactants and products and of the mechanisms of the processes as well [5]. The aim of the present work was to investigate the mutual relations between (i) the specific grinding energy consumed for mechanical activation, (ii) sample properties (specific surface area, amorphization and excess enthalpy), and (iii) the dissociation reactivity of magnesite as a model substance. To this end, the experimental data have been interpreted by means of a stochastic kinetic model [6], developed especially for studies of this kind.

## Experimental

Investigations were carried out with natural magnesite of calcareous type from the locality of Jelšava, Slovakia. Its chemical composition was 42.33% MgO, 3.58% CaO, 3.72% Fe<sub>2</sub>O<sub>3</sub>, 0.68% SiO<sub>2</sub> and 49.26% loss on ignition. Samples with an initial granularity of 0.1–1.0 mm were ground in a laboratory vibration mill made in the Institute of Geotechnics, Košice. The ball to powder weight ratio was 10:1. Grinding was performed at a preselected number of revolutions,  $n=20.5$  rev./s, and various amplitudes. The number of revolutions was controlled by means of a stroboscope (Medimpex, Budapest). Effective values of the amplitude of the vibration motion of the vial in longitudinal and transverse directions were determined from readings of the piezoelectric sensor (KD 11 and equipment 11 003, VEB RFT Messelektronik, Dresden). The specific mill power was calculated from the experimentally determined frequencies and amplitudes of the vibration motion and known masses of the charge and medium according to the formula

$$P = \frac{m_1}{m_2} n(4\pi na)^2 \quad (1)$$

where  $P$  is the specific mill power,  $m_1$  is the mass of the grinding medium,  $m_2$  is the mass of charge,  $a$  is the amplitude and  $n$  is the frequency of the vibration motion. Samples were activated by grinding for a constant time of 2 h. Through variation of the amplitude of vibration motion from 2.2 to 6.6 mm, the specific grinding energy supplied for the mechanical activation of samples was changed in the range 617.76 to 3983.4 kJ mol<sup>-1</sup>. The reference sample was prepared by grinding 7.5 min at the lowest amplitude, 2.2 mm.

The specific surface area of the ground samples was measured with a Gemini 2360 nitrogen gas adsorption instrument (Sylab, Vienna), based on the BET method.

The changes in structural disordering in activated magnesite were investigated by the XRD analysis procedure proposed by Ohlberg and Strickler [7]. The diffraction plane  $/hkl/=/104/$  with the interplanar spacing  $d=0.2742$  nm was measured by using a Dron 2.0 diffractometer with a GUR 5 goniometer (Tekhsnabexport, Moscow) in the following regime:  $\text{CuK}_\alpha$  radiation, stabilized voltage 30 kV and current 20 mA, time constant 1 s, limit of measurement  $10 \text{ imp s}^{-1}$ , rate of detector  $2^\circ \text{min}^{-1}$ , and paper drive  $2.4 \text{ m h}^{-1}$ .

The crystalline phase content,  $K$ , in ground samples was calculated according to the formula

$$K = \frac{B_o I_o}{I_x B_x} 100\% \quad (2)$$

where  $B_o$  and  $B_x$  are the background, and  $I_o$  and  $I_x$  are the integral intensities of X-ray diffracted by a non-activated standard and a mechanically activated sample, respectively. The X-ray amorphous phase content,  $w_A$ , was calculated from the difference

$$w_A = 100 - K \quad (3)$$

The defect state or excess enthalpies  $\Delta H$ , were determined from the difference between the heats released on dissolution of activated samples and a non-activated standard sample of magnesite in 5 M HCl solution. Heats evolved during dissolution were determined by means of an adiabatic microcalorimeter constructed at the Institute of Geotechnics of the Slovak Academy of Sciences. The accuracy of measurements was  $5 \cdot 10^2$  J, and the reproducibility of the results was 3%.

The thermal decomposition was investigated in a dynamic reactor with a static bed in an argon flow. The mass of the magnesite samples was 100 mg and the rate of argon flow was  $0.303 \cdot 10^{-3} \text{ m}^3 \text{ s}^{-1}$ . The decomposition took place at six temperatures in the interval 733–973 K, i.e. well above the dissociation temperature of stable, crystalline magnesite (however, the dissociation equilibrium data are still the subject of discussion). The decomposition yield was determined from the mass losses of the samples as a function of the heating time.

**Table 1** Changes of specific surface area,  $S$ , X-ray amorphous phase,  $w_A$ , and excess enthalpy,  $\Delta H$ , with increasing specific grinding energy consumption,  $A$ , during grinding of magnesite ( $\tau$ -grinding time)

Sample	N	A1	A2	A3
$\tau/\text{min}$	7.50	240.00	240.00	240.00
$A/\text{kJ kg}^{-1}$	19.30	617.76	1582.56	3938.40
$S/\text{m}^2 \text{ g}^{-1}$	0.63	3.58	5.10	6.49
$w_A$	0.04	0.34	0.55	0.62
$\Delta H/\text{kJ kg}^{-1}$	0.00	6.47	9.36	13.57

**Table 2** Yields of decomposition,  $\alpha$ , in dependence on heating time at different temperatures,  $T$ . (Sample N)

Time/ min	$\alpha$ at $T/K$					
	733	793	813	873	923	973
1.00	0.0008	0.0110	0.0130	0.0170	0.0205	0.1786
2.00	0.0018	0.0400	0.0450	0.0934	–	0.3323
2.50	–	–	–	–	0.3271	–
3.00	0.0114	0.0490	0.0521	–	–	0.4766
4.00	0.0149	–	–	–	–	–
5.00	0.0222	0.0550	0.1076	0.1502	0.6586	0.8775
7.50	0.0359	–	–	–	–	–
10.00	0.0543	0.1111	0.1793	0.3481	0.8200	0.9356
15.00	0.0596	–	0.2730	0.5679	0.8850	–
20.00	0.0731	0.2399	0.3456	0.6724	0.9232	0.9813
30.00	0.0830	0.3311	0.4177	0.8764	0.9613	0.9820
60.00	0.1246	0.5452	0.6592	0.8974	0.9634	–
180.00	0.1468	–	–	0.9054	–	–

**Table 3** Yields of decomposition,  $\alpha$ , in dependence on heating time at different temperatures,  $T$ . (Sample A1)

Time/ min	$\alpha$ at $T/K$					
	733	793	813	873	923	973
1.0	0.0040	0.0144	0.0145	0.0190	0.0400	0.0908
2.0	0.0095	0.0166	0.0200	0.0710	0.2041	0.3578
2.5	–	–	–	–	–	–
3.0	0.0101	0.0350	0.0395	0.1500	0.4080	0.6224
4.0	0.0105	0.0413	–	0.2650	–	–
5.0	0.0220	0.0481	0.1256	0.3844	0.5790	0.7871
7.5	0.0351	0.0994	–	0.5650	–	–
10.0	0.0535	0.1425	0.3060	0.6792	0.7706	0.8914
15.0	0.0600	–	–	0.7736	–	–
20.0	0.0750	0.2724	0.5567	0.8644	0.8764	0.9600
30.0	0.0850	0.3814	0.6968	0.8788	–	0.9800
60.0	0.1792	0.6105	0.8170	0.8983	0.9267	–
90.0	–	0.7305	–	–	–	–

Determined values of specific surface area ( $S$ ), mass fraction of amorphous phase ( $w_A$ ) and excess enthalpy ( $\Delta H$ ), as functions of the parameters of activation,

**Table 4** Yields of decomposition,  $\alpha$ , in dependence on heating time at different temperatures,  $T$ . (Sample A2)

Time/ min	$\alpha$ at $T/K$					
	733	793	813	873	923	973
1.0	0.0028	0.0079	0.0140	0.0190	0.0438	0.0947
2.0	0.0144	0.0207	0.0200	0.0715	0.2252	0.4139
3.0	0.0159	0.0389	0.4000	0.1965	0.6235	0.6568
4.0	0.0177	–	–	0.3050	–	–
5.0	0.0232	0.0622	0.1578	0.4167	0.6911	0.8030
7.5	0.0375	–	–	–	–	–
10.0	0.0569	0.1683	0.3362	0.7252	0.7977	0.9105
15.0	0.0645	–	–	–	–	–
20.0	0.0816	0.2737	0.5694	0.8666	0.8954	0.9612
30.0	0.1200	0.3904	0.7608	0.8972	0.9044	0.9800
60.0	0.2020	0.6272	0.8406	0.9253	0.9300	–
90.0	0.2622	0.7421	0.8456	–	–	–

**Table 5** Yields of decomposition,  $\alpha$ , in dependence on heating time at different temperatures,  $T$ . (Sample A3)

Time/ min	$\alpha$ at $T/K$					
	733	793	813	873	923	973
1.0	0.00955	0.0090	0.0150	0.0197	0.0482	0.1520
2.0	0.01020	0.0260	0.0231	0.0737	0.1315	0.4694
2.5	–	–	–	0.1381	0.5467	–
3.0	0.02011	0.0500	0.0459	0.2120	0.6250	0.7050
4.0	0.02052	–	0.0933	0.3560	0.7600	–
5.0	0.02500	0.0914	0.1611	0.5026	0.8192	0.8837
7.5	0.04340	–	0.2410	0.6450	–	–
10.0	0.05910	0.2420	0.3390	0.7436	0.8840	0.9337
15.0	0.08932	–	0.5147	0.7800	0.9149	–
20.0	0.12040	0.4462	0.6766	0.8610	0.9660	0.9650
30.0	0.17240	0.7093	0.7622	0.8910	0.9665	0.9827
60.0	0.28780	0.7231	0.8547	0.9335	–	–
90.0	0.39300	0.7897	0.8547	0.9628	0.9700	–
180.0	0.39350	–	–	0.9650	–	–

are shown in Table 1. Tables 2–5 give the determined yields of decomposition of activated samples (A1, A2 and A3) and the reference sample (*N*) for various heating times at different temperatures.

## Data processing

The dependences of the yields,  $\alpha$ , of dissociation on time,  $t$ , were described by the stochastic (relaxation) kinetic model [6]:

$$\alpha(t) = \beta \int_0^{\infty} E(r)F(r, t)dr \quad (4)$$

where  $\beta$  is the 'pseudo-equilibrium constant',  $r$  are the rate constants,  $E(r)$  is the distribution function of the rate constants and  $F(r, t)$  is a relaxation function, used as  $[1 - \exp(-rt)]$ , expressing the time dependence of the yield of the differential fraction of the sample,  $E(r)dr$ , reacting with rate constant  $r$ . For the distribution function of reactivities, the lognormal distribution was used, i.e. the concrete form of (1) is given by

$$\alpha(t) = \beta \int_0^{\infty} \left\{ \frac{1}{r\sigma\sqrt{2\pi}} \exp\left[-\frac{(\ln r/\bar{r})^2}{2\sigma^2}\right] \right\} [1 - \exp(-rt)]dr \quad (5)$$

where  $\bar{r}$  denotes the mean value of the rate constants and  $\sigma$  is their standard deviation. Thus,  $\sigma$  is here a dimensionless quantity.

The processing of data consisted of the following steps: a) the expression of the  $\alpha(t)$  data by model (5) and the primary determination of its constants ( $\beta$ ,  $\bar{r}$  and  $\sigma$  denoted by the index 1) by the Simplex method, b) representing the constants ( $\beta$ ,  $\bar{r}$  and  $\sigma$ ) as functions of temperature ( $T$ ) and specific grinding energy consumption ( $A$ ), c) smoothing the dependences of the constants on temperature by finding suitable regressions and their representation as a function of  $A$ , d) the regression relation  $\ln r(A, T)$  and tabulated values of smoothed  $\beta$  and  $\sigma$ , together with (5), represent the mathematical model of the process studied and form the basis of conclusions on the prevailing mechanisms of the action of grinding energy and temperature on the dissociation process.

The dependence of reactivities ( $Ra_1 = \ln \bar{r}_1$ ) on temperature (smoothing of their scatter) could be expressed by a quadratic relation (Fig. 1). This smoothed  $Ra$  value exhibits a linear dependence on the specific grinding energy consumption (Fig. 2):

$$Ra_2 = pA + q \quad (6)$$

The constants ( $p$ ,  $q$ ) in Eq. (6) thus depend on temperature according to a quadratic relation:

$$p = d_1 + e_1T + f_1T^2 \quad (7)$$

$$q = d_2 + e_2T + f_2T^2 \quad (8)$$

Determining the parameters of (6), (7) and (8) by optimization (Simplex method) and combining them, we get

$$Ra_2 = -78.6583 + 0.0133A + 0.1565T - 2.877 \cdot 10^{-5}AT - 7.9236 \cdot 10^{-5}T^2 + 1.5606 \cdot 10^{-8}AT^2 \quad (9)$$

All parameters of (5) obtained by smoothing their scatter by regression relations are denoted by the index 2. Typical dependences of coefficients  $\beta_1$  and  $\sigma_1$  on temperature are shown in Fig. 3. The  $\beta_2$ - $T$  dependences could be described by a regression function of the form

$$\beta_2(T) = (aT - b)^c \quad (10)$$

(solid line in Fig. 3) and values of the coefficients ( $a, b, c$ ) determined again by optimization. The smoothed values  $\beta_2$  display a dependence on  $A$  according to Fig. 4. Values of  $\sigma_1$  below 0.01 are not significant and are practically equal to zero. In consequence, the  $\sigma_2$  values could be expressed, in spite of their scatter, by

$$\sigma_2 = \exp(-a_1T - b_1) \quad (11)$$

Thus, relations (5), (9), (10) and (11), together with the determined values of the coefficients of (10) and (11), represent the mathematical model of the process studied in the whole field of experimental  $t$ ,  $A$  and  $T$  values with coefficients having a phenomenological meaning. The smoothed values  $Ra_2$ ,  $\beta_2$  and  $\sigma_2$  are listed in Table 7.

The applied processing of data respects the trends of primarily determined coefficients ( $Ra_1$ ,  $\beta_1$  and  $\sigma_1$ ) and smooths their scatter. It can be supposed that the obtained mathematical model

$$\alpha = \alpha(t, A, T) \quad (12)$$

with smoothed coefficients, given in Table 7 affords more correct results than individual experiments. This may hold in spite of the understandable fact that the sums squared of deviations of  $\alpha$ ,  $\Sigma(\Delta\alpha_2)^2$  (Table 7), are higher than those obtained with primarily determined parameters  $\Sigma(\Delta\alpha_1)^2$  (Table 6). The basis of this acceptable assumption, stemming from the physical essence of the process studied, is that partial derivations of  $\beta$ ,  $\sigma$  and  $\bar{r}$  relative to  $T$  and  $A$  should not show any, or only a single local extreme.

## Discussion

The kinetic model used is a stochastic one; it is based on two suppositions:

1. The solid reactant is composed of mass elements with different local Gibbs energies, forming a statistical set. Thus, the local driving forces of its reaction will also be distributed in a certain range.

2. Cross-sections for various types of diffusion, diffusion paths and even values of diffusion coefficients are also statistical quantities.

Thus the meaning of the parameters of the model is phenomenological, i.e. they can not be directly related to physical quantities of the solid sample or to those of the process studied, as they depend on all quantities mentioned above. Nevertheless, the dependences of the parameters ( $\beta$ ,  $\sigma$  and  $\bar{r}$  or  $Ra$ ) on conveniently changed parameters of the reactant (e.g. grinding energy consumption, annealing temperature, etc.) or conditions of reaction (e.g. temperature, pressure, composition of atmosphere) can surely contribute to disclosure of the substance of these influences. Thus, the decrease in the slope of  $Ra$  with temperature (Fig. 1) indicates a change in the mechanism of the decomposition process from chemical to diffusion and/or heat transfer control of decomposition at higher temperatures. A short calculation of the dependence of  $Ra$  on  $1/T$  shows that the Arrhenius relation holds up to 923 K. The activation energy of decomposition decreases in this temperature range with increasing excess enthalpy. At the accumulation of excess enthalpy amounting to  $\Delta H = 13.57 \text{ kJ kg}^{-1}$  (sample A3), the activation energy of decomposition decreases to half the value determined for the non-activated sample  $N$ .

The dependence of  $Ra$  on the specific grinding work consumption (Figs 2 and 6) shows that defect generation in the sample proceeds proportionally to the grinding energy supply even at the highest experimental value A3 (Table 1). The decrease in the slope of the straight lines in the above Figures show that mechanical activation

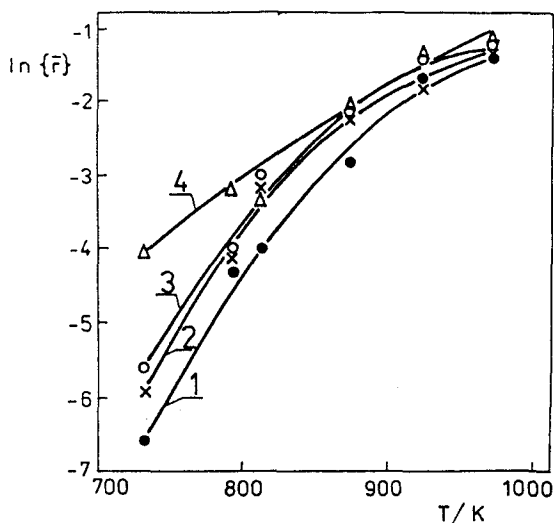


Fig. 1 Dependence of reactivities  $Ra_1 = \ln \bar{r}_1$  on temperature,  $T$ , for the non activated sample (1) and samples activated at specific grinding energy consumption  $A$  in  $\text{kJ kg}^{-1}$ : 617.76 (2), 1582 (3) and 3938.40 (4)



becomes inefficient at high temperatures of reactions. This is caused by the fading out of generated defects during heating of the sample [8]. This effect is simultaneously impressively confirmed by the temperature dependence of the standard deviation (Fig. 3, Table 7). High values of sigma below ca 800 K indicate that the sam-

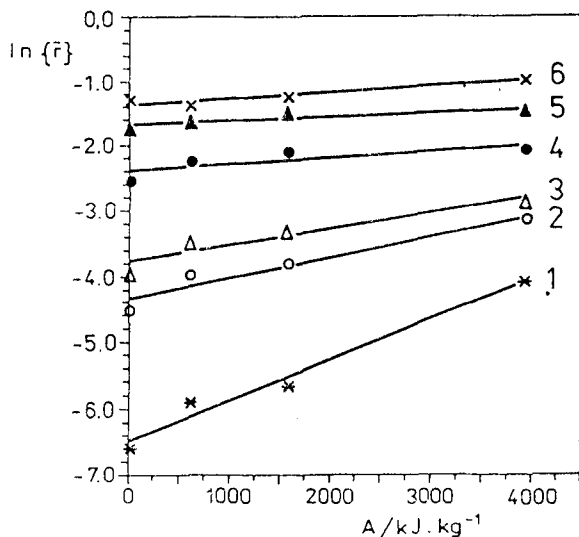


Fig. 2 Dependence of reactivity  $Ra = \ln \bar{r}$  on specific grinding energy consumption,  $A$ , for samples decomposed at temperatures  $T$  in K: 733 (1), 793 (2), 813 (3), 873 (4) 923 (5) and 973 (6)

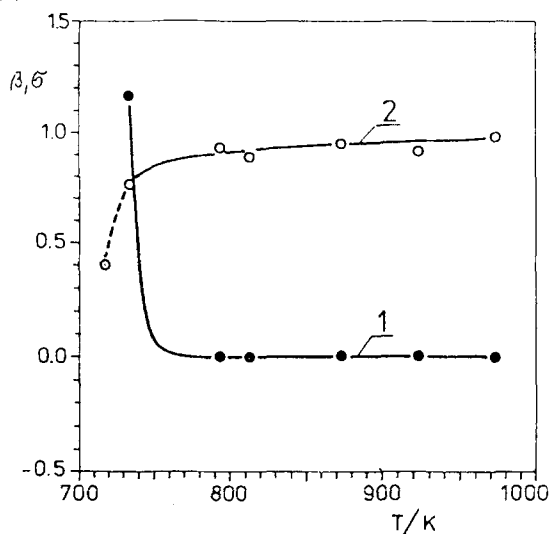


Fig. 3 Typical dependencies of  $\beta_2$  (1) and  $\sigma_2$  (2) values on temperature  $T$  (Sample A2). Solid line computed from equations (10) and (11),  $\odot$  - additionally determined value

**Table 6** Computed values of the constants of Eq. (5)

Sample	T/K	$\ln(\bar{r}_1)$	$\sigma_1$	$\beta_1$	$\Sigma(\Delta\alpha_1)^2$
N A=19.30/ kJ kg <sup>-1</sup>	733	-6.6325	2.6867	0.42819	1.0537e-03
	793	-4.2880	1.6535e-03	0.97336	8.5041e-04
	813	-4.0125	0.6061	0.99977	1.1603e-03
	873	-2.8453	1.8378e-05	0.94307	2.5975e-02
	923	-1.6973	4.1858e-05	0.96245	2.7684e-02
A1 A=617.76/ kJ kg <sup>-1</sup>	973	-1.3495	3.7079e-06	0.99977	3.5206e-02
	733	-5.9071	1.2672	0.75199	5.6136e-04
	793	-4.1237	8.8145e-06	0.96414	2.0736e-03
	813	-3.1826	3.2829e-05	0.92153	1.4129e-02
	873	-2.2641	7.2391e-06	0.94185	4.2918e-02
A2 A=1582.56/ kJ kg <sup>-1</sup>	923	-1.7688	1.5600e-05	0.92608	1.9284e-02
	973	-1.3076	2.7927e-05	0.97904	3.3155e-02
	733	-5.6541	1.1659	0.76425	1.6484e-04
	793	-4.0192	4.2713e-05	0.93385	9.2538e-03
	813	-3.0100	4.3008e-05	0.88901	1.9804e-02
A3 A=3938.4/ kJ kg <sup>-1</sup>	873	-2.2411	4.5587e-05	0.95381	3.5567e-02
	923	-1.4281	1.6330e-05	0.91464	6.6241e-02
	973	-1.2183	1.6485e-05	0.97973	3.4193e-02
	733	-4.0282	7.6207e-05	0.43540	3.4912e-02
	793	-3.1481	2.5846e-05	0.80831	2.6994e-02
A3 A=3938.4/ kJ kg <sup>-1</sup>	813	-2.9703	3.6546e-06	0.90502	3.6975e-02
	873	-2.1335	4.0849e-05	0.95462	6.1954e-02
	923	-1.3077	2.6919e-06	0.97262	1.4642e-01
	973	-1.0548	1.9748e-05	0.98667	2.9885e-02

ple is made up to mass elements with local molar Gibbs energies varying in a broad range [9]. At higher temperatures, unification of local Gibbs energies proceeds by the annealing of defects (of both the reactant and the product) and thus the scatter of the reactivities approximates to zero.

Values of beta less than unity (Fig. 3, Table 7) may have two different meanings:

1. A fraction of the solid reacts orders of magnitude more slowly than the rest. This is a frequently occurring case in solid-state reactions, which is observed when the reactant is composed of both highly activated and well-crystalline portions or when mixing inhomogeneities of the sample are present in solid-state reactions. Thus, when  $\alpha-t$  dependences are measured only in the region of high reaction rates, the  $\beta$  values obtained suggest that equilibrium has been reached.

Table 7 Smoothed values of the constants of Eq. (5)

Sample	T/K	$\ln(\bar{r}_2)$	$\sigma_2$	$\beta_2$	$\Sigma(\Delta\alpha_2)^2$
N A=19.30/ kJ kg <sup>-1</sup>	733	-6.5709	2.6786	0.5239	4.6693e-03
	793	-5.2220	0.5962	0.8794	2.5931e-02
	813	-3.9468	0.1422	0.9005	8.8895e-03
	873	-2.5427	1.5727e-02	0.9430	7.2938e-03
	923	-1.7420	2.5105e-03	0.9671	2.8152e-02
A1' A=617.76/ kJ kg <sup>-1</sup>	973	-1.2770	1.0075e-04	0.9859	3.7117e-02
	733	-5.8865	1.2672	0.7519	5.7453e-04
	793	-3.9700	5.9077e-05	0.9351	6.4386e-03
	813	-3.4485	2.1262e-06	0.9423	3.2826e-02
	873	-2.2354	9.9123e-11	0.9563	4.5523e-02
A2 A=1582.56/ kJ kg <sup>-1</sup>	923	-1.6275	2.4358e-14	0.9641	4.0593e-02
	973	-1.3859	1.0000e-14	0.9702	3.7682e-02
	733	-5.6664	1.1659	0.7645	1.7404e-04
	793	-3.8078	7.6931e-05	0.9044	1.0107e-02
	813	-3.2986	3.1087e-06	0.9181	3.9804e-02
A3 A=3938.4/ kJ kg <sup>-1</sup>	873	-2.1021	2.0512e-10	0.9456	4.2974e-02
	923	-1.4843	6.7329e-14	0.9612	7.3764e-02
	973	-1.2114	1.0000e-14	0.9733	3.4184e-02
	733	-4.0648	7.5310e-05	0.4353	3.6378e-03
	793	-3.1582	2.3948e-05	0.8423	3.0958e-02
A3 A=3938.4/ kJ kg <sup>-1</sup>	813	-2.8755	1.6346e-05	0.8731	3.9301e-02
	873	-2.0856	5.1979e-06	0.9366	6.3445e-02
	923	-1.4944	2.0007e-06	0.9731	1.6994e-01
	973	-0.9639	7.7008e-07	0.9999	3.7024e-02

2. The situation is as above, but only the CO<sub>2</sub> tension of the 'active' part of the sample exceeds the CO<sub>2</sub> partial pressure of the environment, i.e. the inactive portion can not react at all under the given conditions.

In the case of our system, probably both of these effects influence the  $\beta$  values [9]. However, it is not clear what the reason is for the decrease in  $\beta$  at high grinding energy ( $A$ ) values, and especially at the lowest temperatures of decomposition (Fig. 4). This seems of course to be in contradiction with the observed rise in excess enthalpy. An explanation could perhaps be provided by the suggested idea of the 'oscillatory instability' of mechanochemical equilibrium [10].

A comparison of the dependence of the increase in reactivity  $\Delta Ra = Ra_{A_i} - Ra_N$  and that of other excess quantities ( $\Delta Y = Y_{A_i} - Y_N$ ), where  $Y$  denotes  $S$ ,  $w_A$  and  $\Delta H$ , respectively, on the grinding energy consumption ( $A$ ) (Fig. 6) reveals that the reac-

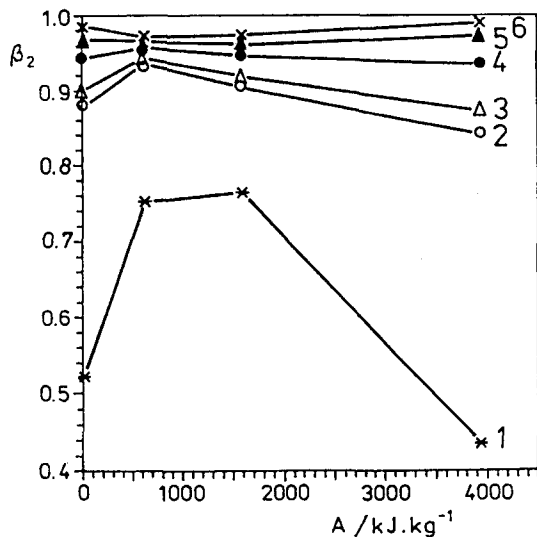


Fig. 4 Dependence of smoothed values of  $\beta_2$  on specific grinding energy consumption,  $A$ , for samples decomposed at temperatures  $T$  in K: 733 (1), 793 (2), 813 (3), 873 (4), 923 (5) and 973 (6)

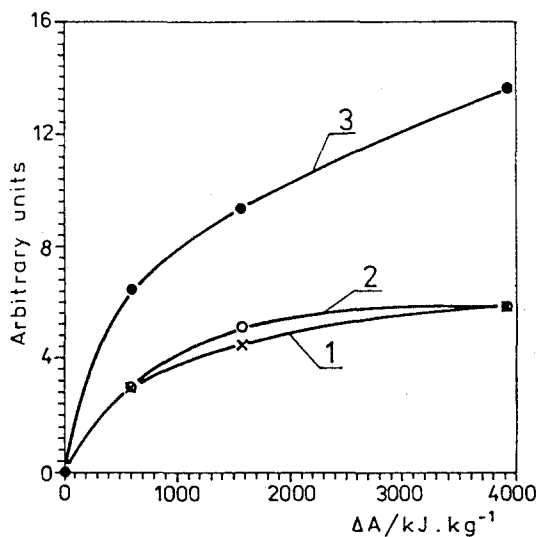


Fig. 5 Dependence of excess parameters  $S$  (1)  $w_A$  (2) and  $\Delta H$  (3) on excess grinding energy consumption ( $\Delta A$ )

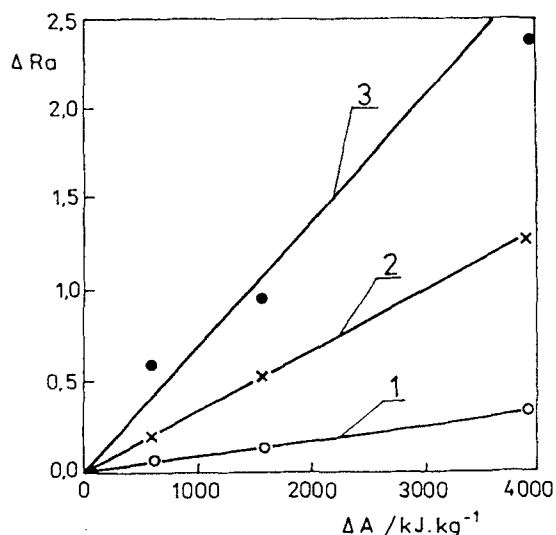


Fig. 6 Dependence of reactivity increase ( $\Delta Ra$ ) on excess energy consumption ( $\Delta A$ ) for samples decomposed at temperatures  $T$  in K: 973 (1), 793 (2) and 733 (3)

tivity still rises after  $w_A$  and  $S$  have just stopped increasing when  $A$  exceeds  $2000 \text{ kJ kg}^{-1}$ . Thus, in this region, only the excess enthalpy is in direct relation to  $A$  (Fig. 5). Here, the following question arises: what type of defects accumulate enthalpy when the specific surface and amorphized fraction are not changing? This question could be answered only by investigation of the fine structure of the particles. In the cases investigated so far, amorphization contributed to the excess enthalpy in similar materials by 70 to 98%. A reduction of the crystallite size, e.g. in periclase, contributed to the excess enthalpy with only secondary importance, by percentages nearly an order lower [11].

## Conclusions

This approach showed that the kinetic model used fulfils its intended goals in any respect. The vibration milling of magnesite with grinding energy consumption up to  $3938 \text{ kJ kg}^{-1}$  does not lead to mechanochemical equilibrium.

At a grinding energy consumption exceeding  $2000 \text{ kJ kg}^{-1}$ , the specific surface and X-ray amorphous phase content change only negligibly, while the excess enthalpy continues to accumulate for other kinds of defects.

The defects with the highest activity anneal up to 800 K. Above this temperature, the remaining defects relax with rates comparable with that of the decomposition. Thus, the efficiency of mechanical activation is impressive only below this limit.

Below 800 K, only the activated fraction of the sample decomposes in consequence of its higher equilibrium pressure of  $\text{CO}_2$ .

Up to 920 K, the decomposition proceeds under chemical control. The activation energy drops markedly with accumulated enthalpy.

Two novel problems arose from the investigation presented:

(1) What types of defects accumulate enthalpy at higher values of specific grinding energy ( $A > \text{ca } 2000 \text{ kJ kg}^{-1}$ )?

(2) What is the reason for the decrease in beta at the lowest temperature (733 K) and the highest supply of specific grinding energy ( $A = 3938 \text{ kJ kg}^{-1}$ )?

These question could be answered only by special investigation of the changes in the structure of samples during mechanical activation.

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