ASSESSMENT OF THE ACTIVATION DEGREE OF SOLIDS IN THE PROCESS OF INTENSIVE GRINDING

KLÁRA TKÁČOVÁ

Mining Institute of the Slovak Academy of Sciences, 043 53 Košice, Solovjevova 45

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The study is concerned with the mechanism of activation of selected carbonates and quartz in the process of intensive grinding. A quantitative relationship was derived between enthalpy increase as a thermodynamic characteristic of the activation degree, and changes in specific surface area and the crystalline phase content. The enthalpy increase of a finely dispersed ground material as compared with an intact crystal corresponds to the energy transformed in the process of mechanical dispergation by a system of destruction processes resulting in a decrease of the degree of arrangement of solid particle structure and in an increase in the specific surface area of the dispersion system.

INTRODUCTION

The effect of mechanical deformation of solids on the course of chemical reactions belongs among the oldest empirically established facts in human history. However, mechanochemistry as an exact scientific field has only been developing in the last decades. Practical application of mechanochemistry is aimed at 'evoking or suppressing such chemical reactions, the course of which is rendered possible or accelerated by mechanical activation' (P. A. Rebinder). Theoretical study of mechanochemistry is concerned with derivation of relationships between the phenomena taking place during mechanical straining of solids, and resulting in their activation. Whereas in the case of plastic materials such as metals the main interest is aimed at changes brought about by forming, with brittle crystalline substances mechanical activation is currently effected by grinding, using e.g. vibration and planetary mills. The mechanical effect on the materials in the mills is so intensive that in addition to the comminution and liberation of heat, the substance undergoes changes in its structural arrangement and even chemical reactions can take place directly in the course of the grinding process.

The general energy transformation occurring in the course of intensive grinding can be expressed as a summary quantity

$$E = E_S + E_{pl} + E_{MCH} + E_A + E_g \qquad (1)$$

where E — input energy at indentor-grist contact,
E_S — the energy transformed to newly formed surfaces,
E_{pl} — the energy transformed a system of destruction processes resulting in a change of the structural arrangement degree,
E_{MCH} — the energy available for endergonic solid phase chemical reactions in the course of grinding,
E_A — the energy transformed to heat during the agglomeration process,
E_g — the energy transformed to heat through elastic vibration excitations.

A part of this energy remains retained in the indentor-grist system. Although its quantity cannot be determined directly, it is possible to determine the

increase in energy content in the grist, which is a source of increased activity of the dispersion system in comparison to the intact crystal.

An activated solid is a thermodynamically and structurally unstable arrangement of its lattice building elements which differs from an ideal or little damaged crystal by a higher enthalpy and free enthalpy content [1]. The enthalpy increment of grinding products is determined experimentally by measuring the reaction heats of suitable reactions using the differential method. Conveniently selected physical or physico-chemical methods allow to follow the changes in dispersity degree, changes in primary and secondary solid phase structure in the course of grinding, and thus to obtain indirect information on energy transformation in the material during the grinding.

Elucidation of the activation mechanism of crystalline substances requires complex research concerned with the relationships between various changes in the solid during the grinding process. The present study was aimed at the derivation of relations between enthalpy increment as a thermodynamic characteristic of activation degree, and the changes in specific surface area and the primary structure of the solid in the course of the intensive grinding process.

MATERIALS AND METHODS

Description of the material and the grinding tests

The experiments were performed with the products of vibration grinding of 3 samples of magnesite and 1 sample of calcite. The characteristics of the materials as introduced into the mill are summarized in Table I. The samples

Table I

Characteristics of initial samples

Sample	Locality	Mean grain diameter D_m [μm]	Content of impurities [%]
Magnesite *V*-1	Bankov	454.00	3.73
Magnesite *V*-2	Bankov	585.26	4.99
Magnesite *V*-3	Miková	864.62	7.05
Calcite	Ostrá	390.00	4.02

were ground in a four-chamber laboratory vibration mill (chamber volume $V = 350$ ml, frequency $f = 233$ Hz, amplitude $A = 3.4$ mm, grinding ball charging $\varphi = 75$ %, grinding balls dia. 30 and 16 mm in a ratio of 1 : 2, sample charge 100 g). The times of grinding were in a geometric succession of from 0.5 to 32 hours.

Determination of dissolution heats

The enthalpy changes of the grinding products were determined on the basis of measuring the heat liberated during the dissolving of 20 mg carbonates in 5 M HCl, or 20 mg quartz in concentrated HF. The dissolution heat was

determined by means of an adiabatic microcalorimeter designed at our institute [2]. The adiabatic calorimeter run is controlled by mutual interaction of three thermistors connected in a Wheatstone bridge and situated in the calorimeter proper and in its adiabatic jacket. The temperature changes in the calorimeter are scanned by a triplet of indicating thermistors fitted in the actual calorimeter. These are connected to the Wheatstone bridge, which has a sensitive mirror galvanometer at its measuring diagonal. The changes in thermistor resistance resulting from thermal processes in the calorimeter are recorded as a function of time. The evaluation is carried out by means of the Joule standard heat which is supplied into the system in the course of measuring. The input of the heating element is in the range of 0 to 14.6 J . min^{-1} in agreement with the control regime. The measuring sensitivity is 5×10^{-2} J. The measuring reproducibility changes with the grain size of samples. In the case of fine-grained samples such as the grinding products in question, $R = \pm 2$ %.

Specific surface determination

Specific surface of the samples was calculated from the data of benzene vapour adsorption isotherms according to the BET theory. The adsorption was measured on a volumetric sorption apparatus constructed at our institute. The sample weight was in the range of 0.1 to 10 g according to specific surface. The determination sensitivity is of the order of 10^{-1} m^2 . g^{-1}, relative reproducibility $R = \pm 2$ to 5 %.

X-ray analytical determination of crystalline phase content

The content of crystalline phase in grinding products was determined by the method of standard addition modified for our purposes. Contrary to the known method (of standard additions) which serves for determining crystalline substances in multicomponent systems, our modified method allows to determine the content of a crystalline substance in mixture with a phase of the same chemical composition, but X-ray-amorphous. It is first necessary to determine the content of the X-ray amorphous phase x_1^0 in the model sample, and to introduce it into the relation

$$I_1 = K \frac{x_1 - x_1^0}{\varrho_1 \sum_{i=1}^{n} x_i \mu_i^*} \qquad (2)$$

where I_1 — total intensity of X-rays diffracted by the component,
K — a constant depending on measuring conditions,
x_1 — the proportion of the substance studied in the model sample,
ϱ_1 — specific gravity,
μ_i^* — mass absorption coefficient,
n — the number of phases in the mixture.

The crystalline proportion of the respective mineral in model mixtures was determined by following the intensity of a selected diffraction line during partial dissolving of the carbonate with dilute acetic acid, or during partial dissolving

of quartz with dilute hydrofluoric acid. The method was based on an assumption that at low solvent concentrations the X-ray-amorphous phase at the subsurface layers of the particles becomes preferentially dissolved. The sample which showed the maximum diffraction line intensity was considered crystalline while the soluble phase was considered X-ray-amorphous.

The analytical function was constructed by means of model mixtures prepared with a 30 % addition of CaF_2 and with a varied ratio of the mineral in question to the filler. In the case of carbonates the filler was quartz, in that of quartz use was made of calcite. Construction of the analytical function was based on the relation

$$x_1 - x_1^0 = K \frac{I_1}{I_p} \tag{3}$$

where $x_1 - x_1^0$ the proportion of crystalline phase in the model mixture,
x_1 — total intensity of X-rays: diffracted by the studied component,
I_p — total intensity of X-rays: diffracted by the standard addition component.

The analytical function constructed in this way allows to read directly the content of crystalline phase x_1 on the basis of values I_1/I_p determined for the individual grinding products. Table II presents a survey of the selected

Table II

Survey of selected diffraction lines and relative reproducibility values R for the minerals in question and the standard addition component

Sample	Diffraction line d/n [nm]		R [%]
Magnesite	(104)	27.42	5.42
Calcite	(104)	30.35	4.44
Quartz	(101)	33.43	2.58
Calcium fluoride	(111)	31.43	2.68

diffraction lines and relative reproducibility values R for the minerals in question.

The measurements were carried out on the Mikrometa II X-ray diffractometer provided with a goniometer. For X-ray detection a GM-counter with integrator and compensation recorder was employed. An X-ray tube with Cu-anode was used. The radiation $K_{\alpha 2}$, K_β was separated from $K_{\alpha 1}$ by a quartz monocrystal monochromator. $U = 26$ KV, $I = 12$ m Amps. The sample — detector distance was 30 cm, the goniometer speed was 1/4 deg . min^{-1}, the recording paper speed 1200 mhr^{-1}. In order to suppress the effect of primary extinction on the integral intensity value, the 0—40 μm grain size region was selected for the measurements. The samples were prepared according to Klugg and Alexander [3].

EXPERIMENTAL RESULTS

The quantitative relationship between the heat of dissolution ΔH, the specific surface value S_A and the crystalline phase content x_1 in the grinding

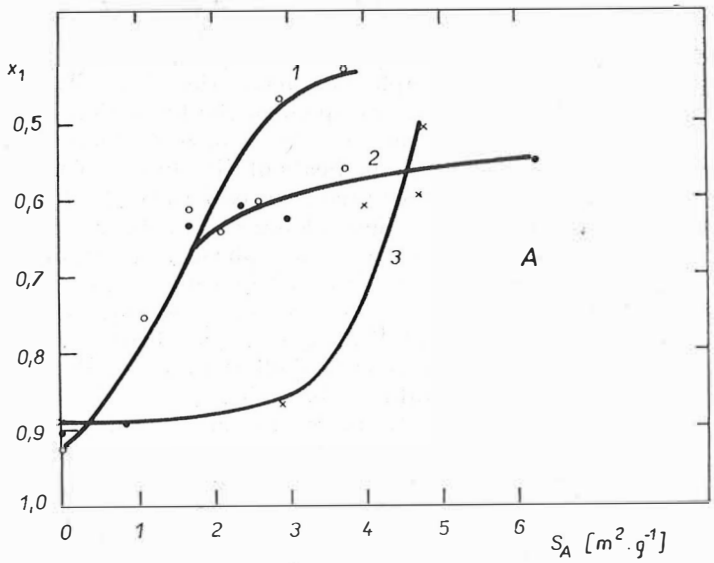

Fig. 1A. The content of crystalline phase in $MgCO_3$ (x_1) *vs. specific surface area* S_A *of three magnesite samples after grinding; Curve 1: V — 1, Curve 2: V — 2, Curve 3: V — 3.*

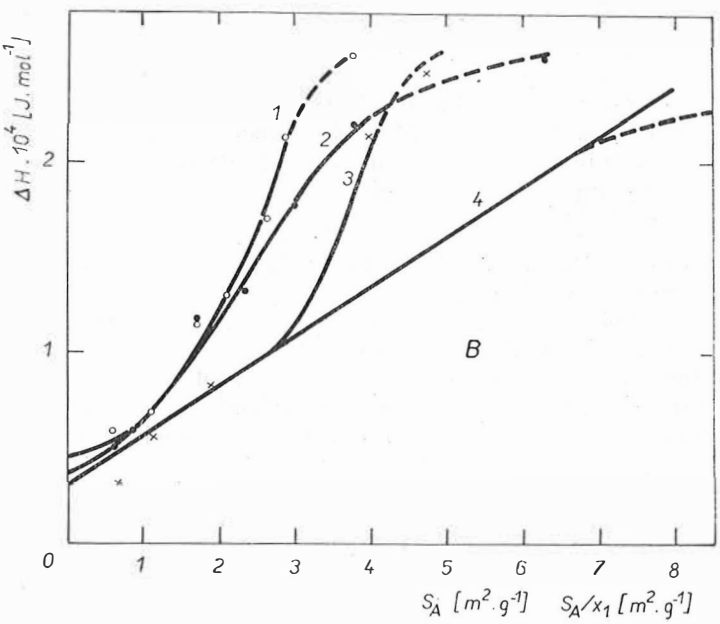

Fig. 1B. Heats of dissolution ΔH *vs. specific surface area* S_A *and ratio* S_A/x_1 *for the products of grinding three magnesite samples; Curve 1:* $\Delta H = f(S_A)$, *V — 1, Curve 2:* $\Delta H = f(S_A)$, *v — 2, Curve 3:* $\Delta H = f(S_A)$, *v — 3, Curve 4:* $\Delta H = f(S_A/x_1)$, ○ — *V — 1,* ● — *V — 2 + V — 3.*

products was studied on three magnesite samples in which various initial grain sizes and other initial sample characteristics (Tab. I) were used to achieve different distribution of energy spent in the formation of new surfaces and in the destruction of structure in the course of long-term vibration grinding (Fig. 1(A), Fig. 1(B) shows the heats of dissolution of three magnesite grinding products vs. specific surface area (curves *1* through 3). A comparison of Figs. 1A and 1B shows that the dependence of dissolution heat on specific surface area changes in terms of crystalline phase content in the grinding products. In the first stages of grinding when the energy supplied to the material is spent for the formation of new surfaces only, the relationship $\Delta H = f(S_A)$ is linear (for V-1 and V-2 up to $S_A = 1\ m^2\ g^{-1}$, for V-3 up to $S_A = 3\ m^2\ g^{-1}$). With increasing mechanical effect intensity during prolonged grinding the content of the crystalline phase decreases and the heats of dissolution increase exponentially with increasing specific surface. This course does not include the values ΔH obtained by dissolution of the products of the longest time of grinding (32 hours). When plotting the dissolution heat values in terms of the ration of increasing specific surface and decreasing crystalline phase content S_A/x_1 one obtains a straight line (No. 4 in Fig. 1) on which all the values of the grinding products of the three magnesite samples are placed. The general form of this straight line is

$$\Delta H - \Delta H_0 = k \frac{S_A}{x_1} \tag{4}$$

where ΔH — the heat of dissolution of the fine-dispersed sample,
ΔH_0 — the intercept cut by the straight line on axis y, corresponding to the heat of dissolution of intact crystal,
S_A — the specific surface of finely dispersed sample,
x_1 — crystalline phase content in finely dispersed sample,
k — the slope of the straight line, can be regarded as a material constant.

When expressing the heats of dissolution in [J g^{-1}] k has the dimension of specific surface energy [J m^{-2}].

Equation (4) holds for magnesite grinding products obtained by grinding for periods $t \leqq 16$ hours. With the longest time of grinding of 32 hours, when the conditions become complicated as a result of increasing intensities of agglomeration and mechanochemical decarbonization [4], there appears a slight deviation from the rectilinear course, as indicated by the dashed

Table III

The values of constants ΔH_0, k and scattering δ calculated for the values measured on the minerals in question according to relationship (4)

Mineral	H_0 [J . mol^{-1}]	H_0 [J . g^{-1}]	k [J . m^{-2}]	δ [%]
Magnesite	2971.96	35.246	33.94	0.239
Calcite	22348.70	2234.870	14.957	0.158
Quartz	64305.80	1070.24	273.280	2.064

Table IV

Fine-grained quartz samples selected for verifying wider validity of relationship (4).

Quartz	Locality	Treatment	Notice
SQ series *SQ*-2 *SQ*-3 *SQ*-4 *SQ*-5 *SQ*-7	 Slovinky Smolník Nižná Slaná Rožňava-Maria Baňa Velká Krač	 Grinding in agate ball mill, separation of 5/μm fraction by sedimentation	 Measured for the purpose of determining the homogeneity of mining dust
DS series *D* 112-S *D* 113-S *D* 114-S *D* 115-S *D* 116-S *D* 117-S	Hochenbocke	Grinding in disintegrator at variable speed	Samples groundat the Ore Dressing Research Institute of the Academy of Sciences, GDR. Measured at the Mining Institute of the SAS.

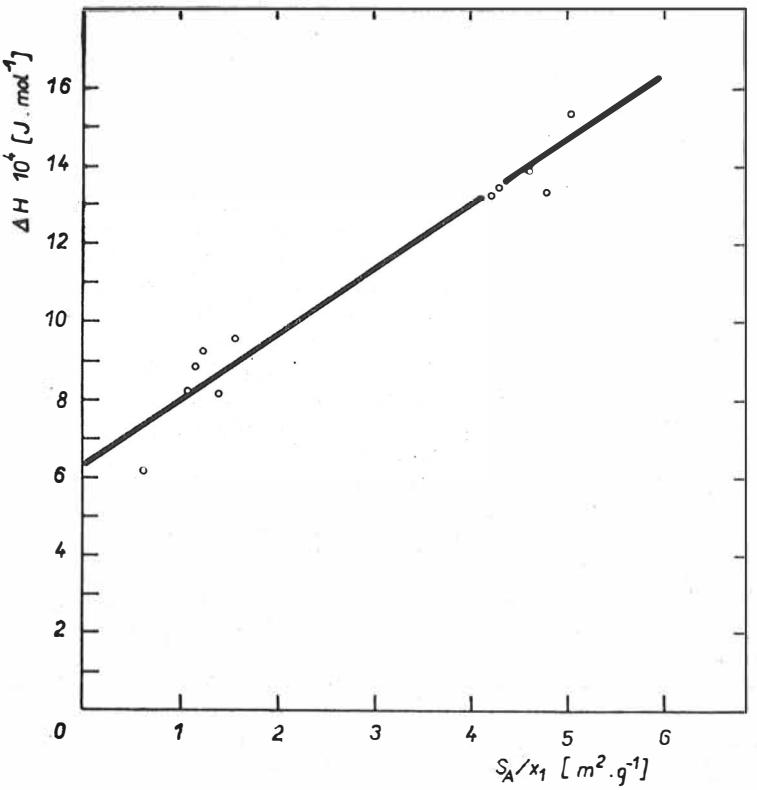

Fig. 2. The heats of dissolution ΔH vs. the ratio S_A/x_1 for quartz samples; ○ — Series SQ, ● — Series DS.

line in Fig. 1. In the case of calcite where decarbonization proceeds at a lower intensity as compared to magnesite, relationship (4) holds within the entire 32-hour grinding interval. The values of constants ΔH_0, k and scattering δ which were calculated by the least square method, are listed in Table III for the minerals in question.

The significance of the slope as a material constant was verified on quartz samples differing genetically [5] as well as in their treatment (Table IV). As shown in Figs. 2 and Table III, equation (4) holds for these different quartz samples with a scattering of 2.064 %.

DISCUSSION

When dissolution of a solid phase takes place as a result of a chemical reaction between the solid and a liquid medium, the heat of dissolution can be divided into three main components,

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 \qquad (5)$$

where ΔH_1 is the heat of transformation of the substance being dissolved into the state in which it is found in solution,

ΔH_2 is the thermal effect of the chemical reaction between the solid and the liquid medium,

ΔH_3 is the heat of solvation.

Dissolution of the carbonates in hydrochloric acid and that of quartz in hydrofluoric acid are exothermic reactions. Similarly, heats of solvation have a negative sign and together with the reaction heat supply the energy necessary for the destruction of the solid lattice ΔH_1. The sign and quantity of the heat of dissolution will therefore depend on ΔH_1.

The results of our experiments have shown that in the case of the products of grinding of carbonates or in that of finely dispersed quartz samples, the heats of dissolution increase linearly with increasing specific surface and decreasing crystalline phase content. This linear relationship which holds within a wide range of dissolution heats, allows to determine the heat of dissolution of an intact sample by graphic extrapolation, or by calculation using the least square method. The ΔH_0 values obtained in this way are characteristic for a given mineral. By determining ΔH_0 from relation (4) one avoids the inaccuracy involved in experimental determination of this value by measuring the heats of dissolution of relatively coarse-grained standard samples as recommended in literature [1].

The increase in enthalpy of a fine-grained material as compared to the intact sample $\Delta H - \Delta H_0$ can be explicitly ascribed, as shown in the discussion above, to the decrease of the ΔH_1 value in relationship (5). This increase therefore corresponds to the energy transformed in the course of mechanical dispergation by a system of destruction processes resulting in a loss of structural arrangement of the solid particles, and in an increase in specific surface area of the dispersion system.

Determination of specific enthalpy increase on the basis of the difference in the heats of dissolution of two samples of diverse dispersity degrees is made use of in calorimetric determination of the specific surface energy of solids [1], [6]. As follows from the relationship between dissolution heats and speci-

fic surface (curves *1* through *3* in Fig. 1) the method permits to obtain adequate results only in those specific surface regions where no changes in structural arrangement of the respective mineral arise. Determination of specific surface energy as the slope of the linear relationship between enthalpy increase, and the ratio of the specific surface area and crystalline phase content found in the present study is a more laborious but more precise method of calorimetric determination of the specific surface energy of solids.

The methodical significance of relation (4) derived in the present study for the investigation of energy changes in materials in the course of their grinding as well as for material characterization of solids, requires verification of its validity on a wider assortment of model minerals while varying broadly the way and intensity of their mechanical stressing in the course of grinding. This will be the subject of our continuing research program.

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POSÚDENIE STUPŇA AKTIVÁCIE TUHÝCH LÁTOK V PROCESE INTENZÍVNEHO MLETIA

Klára Tkáčová

Banícky ústav SAV, Košice

Skúmal sa mechanizmus aktivácie vybraných karbonátova kremeňa (tab. I) v procese intenzívneho mletia. Odvodil sa vztah medzi prírastkom entalpie, ako termodynamickou charakteristikou stupňa aktivácie meliva a zmenami merného povrchu, resp. obsahu kryštalickej fázy (obr. 1 a 2). Medzi uvedenými veličinami jestvuje v dostatočne širokom rozmedzí rozpúšťacích tepiel lineárny vztah

$$\Delta H - \Delta H_0 = k \, . \, S_A/x_1 ,$$

$\Delta H - \Delta H_0$ — prírastok entalpie stanovený na základe rozdielu rozpúšťacích tepiel jemnodisperznej aktivovanej látky a intaktného kryštálu,
S_A — merný povrch,
x_1 — obsah kryštalickej fázy v melive,
k — smernica priamky.

Tento lineárny vztah umožňuje určenie rozpúšťacieho tepla intaktnej vzorky ΔH_0 grafickou extrapoláciou resp. metódou najmenších štvorcov (tab. III).

V práci sa diskutuje interpretácia smernice priamky k ako mernej povrchovej energie tuhej fázy.

Obr. 1A. Závislosť obsahu kryštalickej fázy $MgCO_3$ x_1 *od merného povrchu* S_A *produktov mletia troch vzoriek magnezitu; krivka 1: V — 1, krivka 2: V — 2, krivka 3: V — 3.*
Obr. 1B. Závislosť hodnôt rozpúšťacích tepiel ΔH *od merného povrchu* S_A *a od pomeru* S_A/x_1 *pre produkty mletia troch vzoriek magnezitu; krivka 1:* $\Delta H = f(S_A)$, $V — 1$, *krivka 2:* $\Delta H = f(S_A)$, $v — 2$, *krivka 3:* $\Delta H = f(S_A)$ $V — 3$, *krivka 3:* $\Delta H = f(S_A/x_1)$, ○ $V — 1$, ● $V — 2$, + $V — 3$.
Obr. 2. Závislosť hodnôt rozpúšťacích tepiel ΔH *od pomeru* S_A/x_1 *pre vzorky kremeňa;* ○ *— série SQ,* ⊗ *— série DS.*

ОЦЕНКА СТЕПЕНИ АКТИВАЦИИ ТВЕРДЫХ ВЕЩЕСТВ В ПРОЦЕССЕ ИНТЕНСИВНОГО ИЗМЕЛЬЧЕНИЯ

Клара Ткачова

Металлургический институт САН, Кошице

Исследовали механизм активации подобранных карбонатов и кварца (табл. I) в процессе интенсивного измельчения. Было выведено отношение между приращением энтальпии в виде термодинамической характеристики степени активации измельчаемого продукта и изменениями удельной поверхности, и содержанием кристаллической фазы (рис. 1 и 2). Между приводимыми величинами имеется в достаточно широких пределах теплот растворения линейное отношение

$$\Delta H - \Delta H_0 = \kappa \,.\, S_A/x_1,$$

где $\Delta H - \Delta H_0$ — приращение энтальпии, установленный на основании разности теплот растворения тонкодисперсного активированного вещества и интактного кристалла,

S_A — удельная поверхность,

x_1 — содержание кристаллической фазы в измельчаемом продукте,

κ — угловой коэффициент прямой.

На основании приведенного линейного отношения можно проводить определение теплоты растворения интактного образца ΔH_0 путем графической экстраполации, или методом наименьших квадратов (табл. III).

В приводимой работе рассматривается интерпретация углового коэффициента прямой κ в качестве удельной энергии поверхности твердой фазы.

Рис. 1А. Зависимость содержания кристаллической фазы $MgCO_3$ x_1 *от удельной поверхности* S_A *продуктов измельчения трех образцов магнезита; кривая 1 — V — 1, кривая 2 — V — 2, кривая 3 — V — 3.*

Рис. 1Б. Зависимость величин теплот растворения ΔH *от удельной поверхности* S_A *и от отношения* S_A/x_1 *для продуктов измельчения трех образцов магнезита; кривая 1 —* $\Delta H = f(S_A)$ *V — 1, кривая 2 —* $\Delta H = f(S_A)$ *V — 2, кривая 3 —* $\Delta H = f(S_A)$ *V — 3, кривая 4 —* $\Delta H = f(S_A/x_1)$*; ⊙ — V — 1, ● — V — 2, + — V — 3.*

Рис. 2. Зависимость величин теплот растворения ΔH *от отношения* S_A/x *- для образцов кварца; ⊙ — серия SQ, ● — серия DS.*