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Mechanism and kinetics of mechanochemical processes in comminuting devices
2. Applications of the theory. Experiment

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Abstract

The equations describing the kinetics of contact melting and crystallization of the substances have been deduced on the basis of the obtained distributions of temperature and pressure impulses during impact–friction interaction of the particles treated in comminuting devices. Possible mechanisms of the formation of nanocrystal particles and of chemical reactions during the crystallization of thin films of a melt at high rates of local temperature changes in the near-contact regions have been studied. Various examples are presented that deal with the application of the generalized kinetic equation to the calculations of ab initio rate constants of specific mechanochemical processes in comminuting devices. The obtained theoretical values have been compared with experimental results. © 2000 Elsevier Science S.A. All rights reserved.

1. Introduction

In the previous communication [1], we have reported the calculations of t–P–T conditions in local regions (in some vicinity x of an impact–friction contact) of the particles under treatment and deduced the generalized equations to describe the kinetics and to calculate the rate constants of mechanochemical processes in comminuting devices. In the present paper, we consider the application of results obtained earlier and confirmed experimentally [2–4], both to describe some general mechanisms of activation and chemical transformations of substances (these mechanisms being based on numerical evaluations and deduced from the local character $\Delta x \sim 10^{-6}$ cm and short-time scale $\tau \sim 10^{-8}$ s of the existence of pressure $\sigma \sim 10^{10}$–10^{11} dyn/cm^2 and temperature $\Delta T \sim 10^3$ K impulses), and to calculate numerically the rate constants of activation and mechanochemical reactions in ball planetary mills in the impact regime of their operation.

2. Mechanism of mechanochemical processes

The general questions concerning the effect of local character and short time scale (kinetic factors) on the mechanism of mechanochemical processes and specific character of their course had been discussed qualitatively earlier [5,6]. The quantitative aspect of this problem includes numerical estimates of heat and mass transfer in the local regions of the particles under some given t–P–T conditions aimed at the description of the possibilities and mechanisms of different physicochemical processes, namely, phase transitions and chemical reactions. In the present section, we consider local processes of melting and the subsequent inevitable solidification (crystallization or

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amorphization) of the particles of model substances treated in ball mills and the consequences which are important for mechanochemistry in the general sense.

2.1. The mechanism of activation and formation of nanocrystalline (X-ray amorphous) state

If we demonstrate the possibility of local contact melting [7–10] of the treated particles in comminuting devices (for which the experimental grounds exist [3,4,11]), then the subsequent process of solidification will take place under very unusual conditions (high temperature gradient values and large ratio of the surface of melted region to its volume, or, in other words, when a spot of thin film is solidified between the contacting particles).

2.1.1. Contact melting

The calculations performed in the previous communication [1] show that the impulse of temperature $\Delta T = T - T_0$ in the vicinity of the impact–friction contact of NaCl particles treated with steel balls with the radius of 0.2 cm in a planetary centrifugal mill rotating at the frequency of $\omega = 10 \text{ s}^{-1}$ can be much higher than their melting temperature $\Delta T_m \approx 700 \text{ K}$ where $T_0 \approx 375 \text{ K}$ is a background temperature in operating mill. However, the question concerning contact melting of particles requires special consideration since the time of $\Delta T(x,t)$ existence at a level above ΔT_m is relatively small: $\Delta\tau_m = \tau_m' - \tau_m \approx 8 \times 10^{-9}$ s (see Table 4 in Ref. [1]).

The question concerning the melting rate of crystals under the action of heat flux of different intensity has been poorly discussed in the literature. It is assumed that a crystal cannot be in equilibrium contact with its melt at a temperature above the melting point. In this case, ''the melting rate will be fully controlled by heat transfer; the melting rate will always be higher than the temperature increase rate at equal gradients of temperature'' [12–15].

Starting from this point of view, it has been shown in Ref. [15] that the propagation rate of the melting zone surface m' is determined by a single parameter h:

$$h = (\pi)^{0.5} c_1 \Delta T_m / 2 H_m. \tag{1}$$

Here (see, for example, Ref. [16] for numerical values) $H_m(\text{NaCl}) = 4.8 \times 10^9 \text{ erg/g}$ is latent heat of fusion, $c_1(\text{NaCl}, T = 700 \text{ K}) = 98 \times 10^9 \text{ erg/g K}$ is average heat capacity till the melting point of the solid. The rate of fusion $m'(t,h)$ increases with time and approaches the stationary rate of fusion m_s':

$$m_s' = q/\rho_1(H_m + c_1\Delta T_m) \tag{2}$$

where q is the density of the heat source (flux) at the boundary between the phases (crystal and melt). In Ref. [15], nomograms of the ratio $m'/m_s' = f(t,h) = F[y(t),h]$

have been presented as a function of a dimensionless parameter $y = (t/\tau_m) - 1$ for different h values where τ_m is time required to achieve the melting point of the initial crystal. In the case under consideration, from Ref. [1] (see Table 4) and Eq. (1), it is easy to obtain the required valuable parameters $\tau_m \approx 2.5 \times 10^{-9}$ s; $\tau_m' \approx 1.0 \times 10^{-8}$ s is the time of ceasing fusion ($q = 0$) as determined by the condition $\Delta T(0,\tau_m) = \Delta T(0,\tau_m') = \Delta T_m$; $q(t \geq \tau_m') = 0$; $y = (\tau_m'/\tau_m) - 1 \approx 3$ and $h \approx 1.3$.

Let us define q for the fused zone existing at the impact–friction contact of NaCl particles treated in the mill. The solution of this problem has been presented in Ref. [17]. The laminar flow of the viscous film of a liquid between two parallel plane walls moving at a relative rate of w_t (in our case, $w_t \approx 5400 \text{ cm/s}$, see Table 4 in Ref. [1]) is considered. If the viscosity of the melt is $\mu(\text{NaCl}, T = 1100 \text{ K}) = 0.014 \text{ dyn s/cm}^2$ [16] and the distance between the walls is $2d^*(t)$, the density of heat source $2q$ (in the case of symmetry along the middle plane) will be:

$$q = \mu w_t^2 / d^*. \tag{3}$$

Using Eqs. (2) and (3), a graphic solution $m'/m_s' = f(t)$ [15] and the identity $d^*(t) = m'(t - \tau_m)$, we obtain the required solutions:

$$m' = w_t\left[\mu f(t)/(t - \tau_m)\rho_1(H_m + c_1\Delta T_m)\right]^{0.5}$$

$$d^* = w_t\left[\mu(t - \tau_m)f(t)/\rho_1(H_m + c_1\Delta T_m)\right]^{0.5}$$

$$q = w_t\left[\mu\rho_1(H_m + c_1\Delta T_m)/f(t)(t - \tau_m)\right]^{0.5}. \tag{4}$$

Since $f(t = \tau_m') = f(3, 1.3) \approx 0.55$ [15], it is easy to determine from Eq. (4) also the numerical values of the required parameters for fusion at $t = \tau_m'$ before the reverse process (i.e., crystallization) starts, in the vicinity of the impact–friction contact of NaCl particles under treatment:

$$m'(\tau_m') \approx 33 \text{ cm/s}; \quad d^*(\tau_m') \approx 2.7 \times 10^{-7} \text{ cm};$$

$$q(\tau_m') \approx 1.5 \times 10^{12} \text{ erg/cm}^2 \text{ s}.$$

So, the total thickness of the fused zone and the overall density of the heat source (taking an additional account of the increase in μ for $T \to T_m$) are $2d^* \approx 7 \times 10^{-7}$ cm and $2q \approx 5 \times 10^{12} \text{ erg/cm}^2$ s when the size of NaCl particles in contact is $R \approx 1.63 \times 10^{-4}$ cm (see Ref. [1]). It is important to compare $2q$ with $2q_1 \approx 9 \times 10^{13} \text{ erg/cm}^2$ s [1] for ''dry'' friction between NaCl particles.

When both walls are kept at a constant temperature $T(x = 0) = T(x = 2d^*) = T_m$ the temperature of the melt T_m follows the square law (the distance from one wall to another being x, and a maximum being achieved at the medium plane of shift, $x = d^*$) [17]:

$$\Delta T_m^* = T - T_m = \mu w_t^2 x\left[1 - (x/2d^*)\right]/2\lambda d^*. \tag{5}$$

Since the heat conductivity of the melt is $\lambda(\text{NaCl}, T = 1074 \text{ K}) = 2.5 \times 10^5 \text{ erg/cm K s}$ [16], a maximum temperature increase according to Eq. (5) at $x = d^*$ in the middle zone

of the melt is $T_m^*(x = d^*) = \mu w_t^2 / 4\lambda \approx 0.6$ K. This indicates that local heatings are limited from above by the melting point of particles treated in comminuting devices when the possibility of fusion is taken into account (see also Ref. [4]).

Fig. 1 is a graphic representation of the calculation, according to Eq. (10) in Ref. [1], of temperature impulse $\Delta T(x,t)$ at the impact–friction contact of NaCl particles treated in a planetary centrifugal mill, taking account of their melting described above.

2.1.2. Crystallization and amorphization

The dependencies of the thickness of crystallized layer d and overcooling ΔT_c at the boundary between the phases on crystallization time τ_c are described by the following equations [14,18,19]:

$$\tau_c = \rho_1 H_m \left[d^2 + (2\lambda d / \rho_1 H_m A) \right] / 2\lambda \Delta T_s \approx d / A \Delta T_c \tag{6}$$

$$\Delta T_s / \Delta T_c = \left[1 + (2\rho_1 H_m A^2 \Delta T_s \tau_c / \lambda) \right]^{0.5} \approx 1 \tag{7}$$

where $\Delta T_s = T_s - T_m$ (ΔT_s is the substrate temperature). One can see that at the start of crystallization process at small τ_c and d values, their interdependence is expressed in a linear form and $\Delta T_s \approx \Delta T_c$ [19]. The value of crystallization factor is $A \approx 0.1$ cm/K s for rapidly crystallized substances [18,19]. A maximum overcooling which is possible for the existing melt of NaCl is $\Delta T_c^* \approx 170$ K [13]. If this value is taken as ΔT_c for the crystallization in the region near the contacts between NaCl particles treated in a mill, the time of crystallization for a layer with a thickness of $d = 2d^*$ will be (see Eq. (6)), $\tau_c \approx 4 \times 10^{-8}$ s. This assumption can be shown to be correct both by a

graphic representation according to Fig. 1 or by Eq. (10) in Ref. [1]. Even taking account of the released crystallization heat $2q_c = 2d^*\rho_1 H_m / \tau_c \approx 3.5 \times 10^{11}$ erg/cm^2 s $< 2q < 2q_1$, overcooling of the melt in the zone of contacts between NaCl particles by $\Delta T_c = \Delta T_c^* \approx 170$ K is achieved within time interval $\Delta \tau^* \approx 5 \times 10^{-9}$ s which is much less than τ_c. Since crystallization and solidification are generally not identical processes (cf., Refs. [13,20,21]) (this is not important for the compounds similar to NaCl), the obtained very high cooling rate of the fused contact zone of the treated particles is an explanation of widely known process involving amorphization of difficultly crystallized substances during their mechanical treatment [6,22–27].

However, for any compound that undergoes crystallization, it is important to know the size of critical nuclei r_{cr} at which new crystals are formed in the fused zone (see for example, Refs. [13,14,20,21]):

$$r_{cr} = 2\sigma_s T_m / \rho_1 H_m \Delta T_c \tag{8}$$

where $2r_{cr}$ is the diameter of a sphere or a side of a cube of the new phase (a crystal that has just formed), σ_s is the surface tension at the boundary between the melt and the crystal (for NaCl, $\sigma_s = 23$–34 erg/cm^2 [28]). In order to meet the demand $r_{cr} < d^*$, it is necessary that $\Delta T_c > 17$ K. As we have shown above, this ΔT_c can be easily achieved in the fused zone at the impact–friction contact between NaCl particles. It is clear that the size of new formed crystalline nuclei of NaCl on the surface of treated particles will remain in the order 10^{-7} cm (since there is no time and conditions for growth).

So, we have shown that at the impact–friction contact of NaCl particles treated in comminuting devices, the formation of nanocrystal particles with a size of about 10^{-7} cm occurs due to local short-time fusion–crystallization processes ($\sim 10^{-7}$ s). As an experimental confirmation of this result, the data concerning the formation of nanocrystal particles in the layers directly adjacent to the scratches of an indenter in NaCl single crystals [29].

It is known [30] that the properties of nanocrystals can be substantially different from the properties of macrocrystals. Because of this, mechanical activation of the substances in comminuting devices can be considered as a result of the formation of nanocrystal or X-ray amorphous state of the particles under treatment at a submicron level [31]. In more general aspect, this is a result of quenching of non-equilibrium defects and structures (dislocations, twinning and inter-grain boundaries, nanocrystal or nanoamorphous submicron state) during crystallization (solidification) of the melt during rapid cooling (to be more exact, for short time of existence of pressure and temperature impulses). The process of contact fusion at the impact–friction contact of the particles of different types leads to a sharp increase of diffusion coefficients. As a consequence, the crystallization of the melted layer should
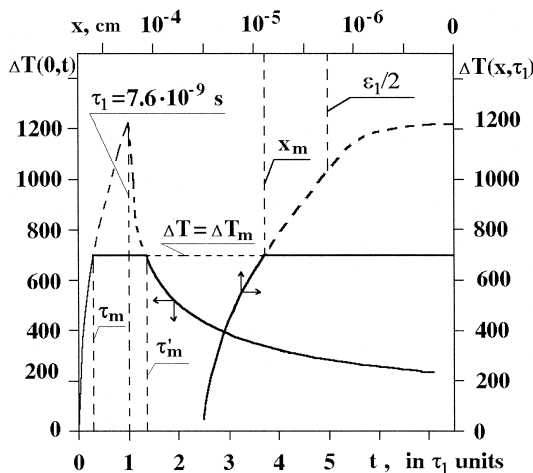

Fig. 1. Graphic section of the temperature impulse (see Table 4 and Eq. (10) in Ref. [1]) at the impact–friction contact of NaCl particles under treatment (taking account of their contact melting).

result also in the formation of nanocrystal products of different mechanochemical reactions, in accordance with thermodynamic and kinetic conditions in the fused zone [11,32–35].

2.2. On the mechanism of chemical reactions in the fused zone

Now, we shall consider the exchange mechanochemical processes that are permitted thermodynamically in a system of ionic salts, i.e., $NaNO_3 + KCl = KNO_3 + NaCl$. These reactions are known to proceed at a high rate to a completeness in an EI 2×150 ball mill [7,23]. It is evident that these reactions should occur due to the mutual diffusion of ions. Assuming that the reaction mechanism involves the crystallization of the final products from the fused zone of the thickness d^* at the impact–friction contact of particles at the melting point. In the beginning of the process, it is a double eutectic melting point T_{m2} while in course of the reaction these are melting points of triple eutectics T_{m3} which are the lowest melting points in systems under consideration [8–10]. Melting points of the eutectics in the $NaNO_3$–KCl system are close to each other (the difference is some degrees) and only $10°$ lower than the melting point of $T_m(NaNO_3) = 580$ K. Because of this, for the numerical calculations, the contact melting point in the system under consideration will be taken equal to that of the lowest-melting component which is sodium nitrate ($T_m = 580$ K). If the thickness of the fused layer d^* at the contact between particles 1 and 2 under the conditions providing the development of the temperature impulse $\Delta T(x,t)$ is less than the depth of mutual diffusion of the ions $2d_\nabla$ within the time interval of the fused zone existence $\Delta\tau_m$, the reaction rate will be limited by fusion. In the opposite case ($2d_\nabla < d^*$), the reaction rate will be limited by the diffusion of ions.

When performing the theoretical calculation of d^* for the mechanochemical reaction under consideration in an equimolar mixture of $NaNO_3$ (index 1) and KCl (index 2) particles, the parameters accepted for use in the equations from Table 3 of Ref. [1] are as follows [1,16,36,37] (for temperature-dependent parameters, the values corresponding to the melting point of $NaNO_3$ are given): $\omega = 10$ s^{-1}; $R = 0.2$ cm (steel balls); $R_1 \approx R_2 \approx 3 \times 10^{-5}$ cm [7,23,38–40]; $\rho = 7.9$, $\rho_1 = 2.71$ and $\rho_2 = 2.59$ g/cm^3; $\theta = 11.0 \times 10^{-12}$, $\theta_1 = 6.64 \times 10^{-12}$ and $\theta_2 = 15.35 \times \overline{10}^{-12}$ cm^2/dyn ($\nu_1 = 0.196$ and $\nu_2 = 0.274$, $E_1 = 5.79 \times 10^{11}$ and $E_2 = 2.41 \times 10^{11}$ dyn/cm^2); $c_1 = 150 \times 10^5$ and $c_2 = 70 \times 10^5$ erg/g K; $\lambda_1 = 1.2 \times 10^5$ and $\lambda_2 = 7.5 \times 10^5$ erg/cm K s; viscosity $\mu_1 = 0.03$ and $\mu_2 = 0.02$ dyn s/cm^2 [16,41]; heat of fusion $H_{m1} = 1.8 \times 10^9$ and $H_{m2} = 3.5 \times 10^9$ erg/g; $\nabla = 3 \times 10^{-5}$ cm^2/s is the diffusion coefficient of KCl in the $NaNO_3$ melt [41].

Using Table 3 from Ref. [1], we find the approximate values $\tau_m \approx 1.2 \times 10^{-10}$ and $\tau_m' = (\tau_{12} + \tau_m)^2/4\tau_m \approx 4.8 \times 10^{-8}$ s in the equation describing the temperature im-

pulse at the impact–friction contact of KCl and $NaNO_3$ particles $\Delta T(x,t) = \Delta T(0,\tau_m) = \Delta T(0,\tau_m') = \Delta T_m = T_m - T_0 \approx 200$ K. These values determine the time interval $\Delta\tau_m = \tau_m' - \tau_m \approx \tau_m'$ of existence $\Delta T(x,t) > \Delta T_m$, the interaction time $\tau_{12} \approx 4.7 \times 10^{-9}$ s and the rate of particles friction $w_t \approx 5500$ cm/s. Using Eqs. (4) and (6) we determine:

$$h_1 = (\pi)^{0.5} c_1 \Delta T_m / 2 H_{m1} = 1.5 \text{ and}$$

$$d_1^* = w_t \left[\mu_1(\tau_m' - \tau_m) f_1(t,h_1)/\rho_1(H_{m1} + c_1\Delta T_m) \right]^{0.5};$$

$$h_2 = (\pi)^{0.5} c_2 \Delta T_m / 2 H_{m2} = 0.35 \text{ and}$$

$$d_2^* = w_t \left[\mu_2(\tau_m' - \tau_m) f_2(t,h_2)/\rho_2(H_{m2} + c_2\Delta T_m) \right]^{0.5},$$

$$\tau_c = \rho_{12} H_m \left[d^2 + (2\lambda d/\rho_{12} H_m A) \right]/2\lambda\Delta T_s \approx d/A\Delta T_c$$

$$\approx 2.2 \times 10^{-7} \text{ s,}$$

where the values $f(t,h) = f[(\tau_m'/\tau_m) - 1,h] = f(\sim 400, h)$ are $f_1 = f_2 \approx 1$ [15]; $H_m \approx (H_{m1} + H_{m2})/2$; $\lambda \approx (\lambda_1 + \lambda_2)/2$; $A \approx 0.1$ and $\Delta T_c \approx 170$ K are accepted as for NaCl; $d_1^* \approx 2 \times 10^{-6}$ and $d_2^* \approx 1.7 \times 10^{-6}$ cm; τ_c is the time of crystallization of the fused layer with a thickness of $d = d^* = d_1^* + d_2^*$.

So, the overall thickness of the fused zone will be $d^* \approx 3.7 \times 10^{-6}$ cm. The comparison of d^* with the depth of mutual diffusion of ions $2d_\nabla$, where $d_\nabla = (\nabla\Delta\tau_m)^{0.5} \approx 1.2 \times 10^{-6}$ cm is the depth of KCl diffusion into the melt of $NaNO_3$, corresponds to the condition $2d_\nabla/d^* \approx 0.65$. Consequently, the rate of the exchange reaction will be limited by diffusion; the mechanism of the reaction under consideration will involve the crystallization of final products formed in the fused layer. The time of reaction will be a sum of the time intervals required for the formation, development and a complete crystallization of the melt at the contacts of particles: $\Delta\tau_m + \tau_c \approx 2.7 \times 10^{-7}$ s.

The proposed mechanism of mechanochemical reaction can be used directly for other types of mechanochemical processes involving contact melting (i.e., mechanodestruction of individual compounds except those decomposing in the solid state below their melting temperature like $Ag_2C_2O_4$ and many other compounds [42,43]). It can be used for the majority of reactions that occur during mechanical alloying of metals [11,23,26,27,34,35] except difficultly fused ones, etc. For example, the mechanism proposed provides an explanation for very low mechanism destruction rate of sodium nitrate in mill [38] and many other compounds because it is identical to their thermal decomposition at their melting point (temperature impulse at the contacts between particles is limited from above by the temperature of contact melting of the particles, as we have shown earlier). Thermal decomposition of sodium nitrate occurs at a noticeable rate only in the fusion at temperatures much above its melting point $T_m = 580$ K [43].

The kinetics of this type of processes occurring in comminuting devices, as well as the kinetics of the processes differing in the mechanisms from the described one (solid state reactions including mechanical alloying of metals) will be considered in detail in Section 3.

3. The use of kinetic equations

In the previous communication [1], we obtained the generalized kinetic equations to describe the transformation degree of mechanochemical processes. The equation for the degree of mechanical activation, without taking account of the changes in particle size, is:

$$\alpha_f(\tau) = \alpha^* \Psi \tau \approx 10 \zeta \eta \psi \omega \Phi^* (V^*/V) \tau = K' \tau. \qquad (9)$$

Here, the geometric probability of the impact treatment of particles for unlined balls (see also below) is

$$\underline{\psi} = \underline{s}/\pi(2R)^2 = 2^{-4}(10\pi)^{0.4}\rho^{0.4}(\theta + \underline{\theta})^{0.4}W^{0.8} \qquad (9a)$$

and the product of dimensionless functions $\zeta \eta$ is

$$\zeta(N)\eta(N, R/l_m) \approx N^2(R/l_m)^2 \sim N^2 R^2. \qquad (9b)$$

For the traditional conditions of mechanical treatment ($N > 50$ is number of balls, $R/l_m \sim 0.04$ is the ratio of ball radius to the linear dimensions of the mill drum) $\zeta \eta$ can be accepted in theoretical estimates to be equal to 1, i.e., $\zeta \eta \approx 1$ [1]. The equations for the transformation degree of mechanical activation and mechanochemical reactions taking account of the changes in the particle size are:

$$K\tau^2 = \alpha \text{ for } p = 0 \qquad (10)$$

$$K\tau^2 = \ln(1 - \alpha) \text{ for } p = 1 \qquad (11)$$

$$K\tau^2 = \alpha/(1 - \alpha) \text{ for } p = 2 \qquad (12)$$

with the same rate constant of mechanochemical processes

$$K \approx 2^{-11} \times 10(10\pi)^{0.8} \zeta \eta \omega W^{1.6} \rho^{0.8}(\theta + \underline{\theta})^{-1.2}$$
$$\times (\theta_1 + \theta_2)^2 \rho_{12} D' d^* \Phi^* \qquad (13)$$

where the numerical factor is $2^{-11} \times 10(10\pi)^{0.8} = 0.077$.

Let us transform Eq. (13) to the form which can be used to estimate K numerically. One can see from Tables 3 and 4 in Ref. [1], and from Fig. 1 that $\Delta T(x, \tau_{12})$ is relatively constant at the depth x of the treated particles till the distance $x = x^* = \varepsilon_{12}/2$. For example, in the case of NaCl treatment, temperature impulse $\Delta T(x, \tau_{12})$ at the impact–friction contact of particles can exceed their melting point ΔT_m till the distance $x_m > \varepsilon_1/2$. Consequently, at some approximation, one can accept $d^*(\sigma, \Delta T) = 2x^* \approx \varepsilon_{12}$, i.e., the thickness of the reaction zone is equal to the total impact deformation of the particles 1 and 2 under consideration. Then, using the result obtained for $\underline{\varepsilon}_{12}$ in Ref. [1], we shall obtain the rate constant (13):

$$K \approx 2^{-14} \times 10(10\pi)^{1.2} \zeta \eta \omega W^{2.4} \rho^{1.2}(\theta + \underline{\theta})^{-2.8}$$
$$\times (\theta_1 + \theta_2)^4 \rho_{12} R_{12} D' \Phi^*. \qquad (14)$$

Here $R_{12} = 2R_1 R_2/(R_1 + R_2)$, $\rho_{12} = 2\rho_1 \rho_2/(\rho_1 + \rho_2)$ are, respectively, the mean radius and density of the particles 1 and 2 under treatment; $2^{-14} \times 10(10\pi)^{1.2} = 0.0382$.

A dimensionless parameter $\Phi^*(U, \sigma, \Delta T)$ is completely determined by the mechanism of the chemical reaction under the conditions providing the realization of σ and ΔT impulses in the region of impact–friction contact of the particles 1 and 2. According to the definition [1], $\Phi^*[U, \sigma(x,t), \Delta T(x,t)] = n^*[\sigma(x,t), \Delta T(x,t)]/n_0$ where n^* is the number of reacted molecules and n_0 is the total number of molecules (atoms) in the volume under consideration V^* in which the pressure $\sigma(x,t)$ and temperature $\Delta T(x,t)$ impulses are realized. The rate of the chemical reaction leading to the final products is $d^2 n/dx dt = n_0 K_r[U, \sigma(x,t), \Delta T(x,t)]$ where K_r is the reaction rate constant. It seems impossible to integrate the equation in this form; so, as a first approximation, for the conditions under which the chemical reaction occurs at the contact of the particles 1 and 2, the mean impulses can be accepted to be $\sigma(x,t) = \langle \sigma \rangle$ and $\Delta T(x,t) = 0.5[\Delta T(0, \tau_{12}) + \Delta T(0.5\varepsilon_{12}, 0)]$ within the time interval τ_{12} [1]. This means that we accept $\tau_{rpc} = \tau_{12}$. In this case, it follows that

$$\Phi^* = \tau_{12} K_r = \tau_{12} K_0 \exp[-(U - \chi_{12}\langle \sigma \rangle)$$
$$/k(T_0 + \Delta T)] \qquad (15)$$

where K_0 is pre-exponential factor, $\chi_{12} \sim 10^{-23}$ cm^3 (the structural factor [44]) and $k = 1.38 \times 10^{-23}$ J/K (the Boltzmann factor) are constants, $T_0 \approx 375$ K is the background temperature in the mill. Now we can present a more specific equation for K taking account of $\underline{\tau}_{12}$ value (see Table 3 in Ref. [1]):

$$K \approx 2^{-16}(\pi/2)^{0.25}(10\pi)^{2.6} \zeta \eta \omega W^{2.2} \rho^{1.1}(\theta + \underline{\theta})^{-2.4}$$
$$\times (\theta_1 + \theta_2)^4 \rho_{12}^{1.5} R_{12}^2 D' K_r. \qquad (16)$$

Here the numerical factor is $2^{-16}(\pi/2)^{0.25}(10\pi)^{2.6} = 0.1334$.

For the dependence of K_r on the conditions of mechanical treatment, we shall take into account only the most important parameters, i.e., density ρ and the impact relative velocity W of ball (the frequency of mill rotation, since $W = \omega l' = 84\omega$ cm/s, [1]) at evident assumptions concerning the known function $K_r = K_0 \exp[-(U - \chi_{12}\langle \sigma \rangle)/k(T_0 + \Delta T)]$.

(1) If $\Delta T \gg T_0$, $U \gg \chi_{12}\langle \sigma \rangle$; it follows that (see Ref. [1])

$$K_r \approx K_{r0} \exp[-(U/k\Delta T)] = K_{r0} \exp(-\beta/\omega^{0.9}\rho^{0.45}) \qquad (17)$$

$$\beta \approx 2.0(\theta + \underline{\theta})^{1.8}[\xi_{12}(\theta_1 + \theta_2)(l')^{0.9}]^{-1}$$
$$\times (c_1 c_2 \lambda_1 \lambda_2 \rho_1 \rho_2 \rho_{12}/R_{12}^2)^{0.25}(U/k). \qquad (17a)$$

Here the constant $2.0 \approx 3(\pi/2)^{1.625}/2^{1.5}(10\pi)^{0.2} iErfc[0]$;

(2) If $\Delta T \gg T_0$, $U \ll \chi_{12}\langle\underline{\sigma}\rangle$; it follows from Ref. [1] that

$$K_r \approx K_{r0} \exp\left[\left(\chi_{12}\langle\underline{\sigma}\rangle/k\Delta T\right)\right] = K_{r0} \exp\left(\beta'/\omega^{0.5}\rho^{0.25}\right) \quad (18)$$

$$\beta' \approx 3.3\left[(\theta+\underline{\theta})/\xi_{12}(\theta_1+\theta_2)(l')^{0.5}\right]$$
$$\times\left(c_1 c_2 \lambda_1 \lambda_2 \rho_1 \rho_2 \rho_{12}/R_{12}^2\right)^{0.25}(\chi_{12}/k) \quad (18a)$$

the constant being $3.3 \approx 2^{0.5}(\pi/2)^{0.625}/iErfc[0]$.

The activation energy U [41–43] of thermal solid-phase processes controlled by diffusion and chemical transformations are usually (with some exceptions) much higher than $\chi_{12}\langle\sigma\rangle$ [44]. Because of this we recommend to accept according to Eqs. (9b), (16) and (17):

$$K \sim R^2 N^2 \Theta^{1.6}\rho^{1.1}\omega^{3.2}\exp\left(-\beta/\omega^{0.9}\rho^{0.45}\right) \quad (19)$$

where $(\theta+\underline{\theta})^{-2.4}(\theta_1+\theta_2)^4 = \Theta^{1.6}$ depicts the dependence of K on the mechanical properties (compliancies) of the material of both the balls (θ, or $\underline{\theta} = (\theta_1+\theta_2)/2$ for lined balls) and the particles under treatment (θ_1, θ_2).

Let us consider specific cases of application of Eqs. (9)–(19) to various mechanochemical processes occurring in comminuting devices.

3.1. Mechanical activation of substances

Let us assume that the mechanism of mechanical activation (cf., Ref. [45]) of NaCl particles involves their contact melting followed by hardening which is accompanied by the formation of non-equilibrium defects (dislocations, twinning boundaries, nanocrystal blocks, etc., up to amorphization). Time interval within which $\Delta T \geq \Delta T_m$ for NaCl particles is $\tau_{pc} = \Delta\tau_m = \tau'_m - \tau_m \approx 8 \times 10^{-9}$ s (see Figs. 1 and 2). The possibility of NaCl particles melting under these conditions and the determination of the thickness of fused layer $d^* \approx 7 \times 10^{-7}$ cm were presented above. Returning to Eq. (9) for the conditions under which NaCl particles are treated in mill EI 2×150 at $\zeta\eta \approx 1$, $R = 0.2$ cm, $\omega = 10$ s^{-1}, we shall also use Eq. (9a) or Table 4 in Ref. [1] to find $\Psi = \underline{\Psi} = \underline{\psi}\omega \approx 53 \times 10^{-3}$ s^{-1} and $1/\underline{\Psi} \approx 20$ s. This means that in reality the NaCl particles of the size $R_1 \approx 1.6 \times 10^{-4}$ cm [1] are subjected to the impact action of the balls about once every 20 s (it is easy to note that $\Psi \sim \psi\omega \sim \omega^{1.8}$; for example, for $\omega = 5$ s^{-1} one could obtain $\underline{\Psi} \approx 16 \times 10^{-3}$ s^{-1} and $1/\underline{\Psi} \approx 60$ s). The coefficient providing the transition to real time of treatment will be $\tau_{pc}/\tau = \tau_{pc}\underline{\Psi} = \Delta\tau_m\underline{\Psi} \approx 4.2 \times 10^{-10}$ (see Fig. 2). To estimate K' in Eq. (9) assuming $\zeta\eta \approx 1$, one should take into account that $\Phi^* \equiv 1$ as an identity since the accepted mechanism of NaCl particle activation is based on the process involving fusion and quenching. Let us determine (using Table 4 in Ref. [1]) the ratio $V^*/V = 3d^* s_1/8\pi R_1^3 \approx 2.5 \times 10^{-5}$; so, at the frequency $\omega = 10$ s^{-1} the rate constant will be $K' \approx 1.3 \times 10^{-5}$ s^{-1}. Because of this, for
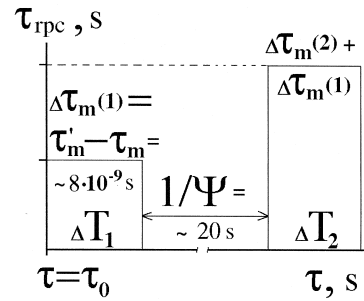

Fig. 2. An illustration to the dependence of real time (τ_{rpc}) of the physicochemical process at the contact between particles 1 and 2 on the current time (τ) of the treatment in the mill drum, for melting of NaCl particles as an example: τ_0 — the time within which the first temperature impulse arises, $1/\Psi$ (~ 20 s, for $\omega = 10$ s^{-1}) the period of the following ΔT_i pulses.

complete fusion and quenching (activation) of all NaCl particles in a mill ($\alpha_f = 1$) the time of their treatment will be, according to Eq. (9): $\tau = 1/K' \approx 7.5 \times 10^4$ s or ~ 21 h.

Now, we shall assume that for the same mechanism of NaCl activation ($\Phi^* \equiv 1$) the size of particles under treatment changes. In this case, the activation kinetics will be described by Eq. (10) with the constant (13). For the process under consideration, according to Eq. (13), the following relation will be obtained (see the values in Ref. [1]):

$$K \approx 0.3\zeta\eta\omega W^{1.6}\rho^{0.8}(\theta+\theta_1)^{-1.2}\theta_1^2\rho_1 D'd^*$$
$$\approx 3.8 \times 10^{-12}\zeta\eta D'\omega^{2.6}, \text{ in s}^{-2}.$$

The slope of the straight lines describing the growth of the specific surface of ionic compounds is $D' \approx 10^2$ cm^2/g s [23,38–40,45–51]. Taking $\zeta\eta \approx 1$, as it was assumed above, we obtain $K(\omega = 10$ s$^{-1}) \approx 1.5 \times 10^{-7}$ s^{-2}. According to Eq. (10), the corresponding time of activation (τ) necessary for complete remelting ($\alpha = 1$) of NaCl particles will be $\tau(\omega = 10$ s$^{-1}) = (1/K)^{0.5} \approx 2600$ s or only ~ 0.7 h. One can see that a substantial difference is observed at the poles. It is only experiment that can indicate which Eq. (9) or Eq. (13) is of priority when applied to the activation in comminuting devices. A similar approach can be used also for a series of mechanochemical reactions when the reaction rate is determined by the contact melting of particles.

3.2. Reactions controlled by diffusion

Now let us consider the kinetics of the exchange mechanochemical reactions in a system of ionic salts, e.g., $NaNO_3 + KCl = KNO_3 + NaCl$ (kinetic curves $\alpha(\tau)$ for this reaction were obtained by means of X-ray studies [7,23]). It has been shown above that the rate of this exchange reaction is limited by mutual diffusion of ions in the fused layer near the contact. So, in Eq. (13) we have (see Section 2.2) $d^*\Phi^* = 2d_{\overline{V}} \approx 2.4 \times 10^{-6}$ cm. Using the

relation (13) it is easy to obtain the calculated value of the rate constant for the mechanochemical reaction under consideration from Eqs. (10)–(12):

$$K \approx 0.15 \zeta \eta \omega W^{1.6} \rho^{0.8} (\theta + \underline{\theta})^{-1.2} (\theta_1 + \theta_2)^2 \rho_{12} D' d_{\overline{V}}$$

$$\approx 2.2 \times 10^{-6}, \text{ in s}^{-2}.$$

Here $\zeta \eta \approx 1$, $\omega = 10 \text{ s}^{-1}$, $D' \approx 10^2 \text{ cm}^2/\text{g s}$ similarly to the above case for NaCl particles remelting.

Fig. 3 presents the results of the treatment of kinetic curves in the coordinates determined by Eqs. (11) and (12) for a series of mechanochemical reactions performed in ball planetary centrifugal mills. One can see that the experimental points well agree with the straight lines in the coordinates of Eq. (11) within the whole range of α changes. The relation (12) describes the observed kinetic dependence for small α. For $\alpha > 0.5$, substantial and increasing deviations are observed. It can be concluded that the degree of ''screening'' of a mechanochemical transformation by the solid products of the reaction is proportional to the volume of the transformed substance. Therefore, unlike Ref. [23], it is necessary to process the kinetic data in the coordinates of Eq. (11). For the reaction considered, an experimental value of the rate constant in the coordinates of Eq. (11) is $K_{1a} \approx 8.3 \times 10^{-5} \text{ s}^{-2}$ which is about 40 times higher than the calculated value. This difference will be discussed below when considering the dependence of K on the conditions of mechanical treatment which allows, in particular, to estimate the numerical value of $\zeta \eta$ factor using experimental data.

An example of mechanochemical processes controlled by diffusion in the solid state is a reaction of the type

$$BaCO_3 + WO_3 = BaWO_4 + CO_2 \quad [6,23,40,47,48,51–54].$$

Kinetic curves $\alpha(\tau)$ for this reaction were obtained by measuring the pressure of gaseous CO_2 formed [23,47]. Thermal mechanism of this reaction involves the diffusion of tungsten into decomposing carbonate, the reaction rate being determined by the diffusion coefficient of tungsten (cm^2/s) [47,48]:

$$\nabla = \nabla_0 \exp(-U/kT) = 13.6 \exp(-2.8 \times 10^{-19} \text{ J}/kT).$$

In order to estimate the rate constant of this mechanochemical process, we shall use Eq. (14). To determine the key value Φ^*, it is necessary to calculate the depth $d_{\overline{V}}$ of tungsten diffusion under the conditions of σ and ΔT impulse development at the impact–friction contact of particles. It is also necessary to compare the depth with the value of total deformation of the particles $\varepsilon_{12} \approx 9 \times 10^{-7}$ cm which has been determined for a related system (see Table 3 in Ref. [1]). When deducing the relation to describe the depth of atoms diffusion $d_{\overline{V}}(\tau_{12}) = [\nabla(\tau_{12})\tau_{12}]^{0.5}$ during the time $\underline{\tau}_{12} \approx 10^{-9}$ s of particle interaction we shall follow an approach used when deducing Eq. (15). We shall also use the parameters calculated for a related reaction (see Table 3 in Ref. [1]):

$$\nabla(\tau_{12}) \approx \nabla_0 \exp\{-(U - \chi_w \langle \underline{\sigma} \rangle)/k[T_0 + 0.5\Delta T(0,\tau_{12})$$
$$+ 0.5\Delta T(\varepsilon_{12}/2, \tau_{12})]\}.$$

Here $\chi_w \approx 1.6 \times 10^{-23} \text{ cm}^3$ [55], $\langle \sigma \rangle \approx 4.8 \times 10^{10}$ dyn/cm^2, $T_0 \approx 375$ K, $\Delta T(0,\underline{\tau}_{12}) \approx 1300$ K, $\Delta T(\varepsilon_{12}/2, \tau_{12}) \approx 1100$ K. For $\chi_w \langle \sigma \rangle \approx 0.8 \times 10^{-19}$ J, we obtain: $\overline{\nabla}(\underline{\tau}_{12}) \approx 9 \times 10^{-4} \text{ cm}^2/\text{s}$, so the depth of diffusion will be $d_{\overline{V}}(\underline{\tau}_{12}) = [\nabla(\underline{\tau}_{12})\underline{\tau}_{12}]^{0.5} \approx 9.6 \times 10^{-7}$ cm. This value is practically identical to ε_{12}, so $\Phi^* \equiv 1$. The constant of the mechanochemical reaction under consideration will be estimated using Eq. (14):

$$K \approx 0.038 \zeta \eta \omega W^{2.4} \rho^{1.2} (\theta + \underline{\theta})^{-2.8} (\theta_1 + \theta_2)^4 \rho_{12} R_{12} D'$$

$$\approx 0.6 \times 10^{-6}, \text{ in s}^{-2}.$$

Here $\omega = 11 \text{ s}^{-1}$, $\rho_{12} = 2.65 \text{ g/cm}^3$, $R_{12} \approx 10^{-5}$ cm, $D' \approx 10^3 \text{ cm}^2/\text{g s}$ [47], $\zeta \eta \approx 1$, other parameters are listed in Ref. [1]. The rate constant determined experimentally in the coordinates of Eq. (11), see Fig. 3, is $K_{2a} \approx 2.1 \times 10^{-5} \text{ s}^{-2}$ which exceeds the calculated value by a factor of 35. It is easy to note that when the frequency ω of mill rotation is decreased, due to the decrease of temperature pulse at the contacts of particles, the synthesis of barium tungstate should be transferred into the region controlled by the kinetics, this region being determined by the carbonate decomposition rate (see below).

3.3. Reactions controlled by the kinetics

As an example of mechanochemical reaction controlled by kinetic stage, decomposition of silver oxalate can be used. Kinetic curves $\alpha(\tau)$ for thermal [42] and mechano-
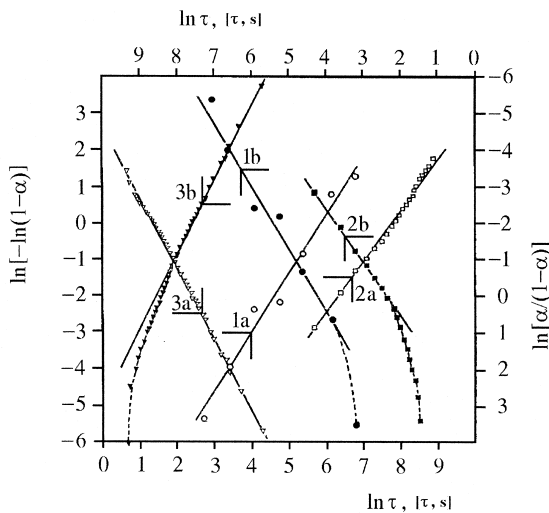

Fig. 3. Experimental kinetic curves processed in the logarithmic coordinates of Eqs. (11) and (12): the straight lines (a) correspond to Eq. (11), (b) to Eq. (12); 1 is related to the reaction $NaNO_3 + KCl = KNO_3 + NaCl$ in a planetary centrifugal mill EI 2×150 [7,23], $\omega = 10 \text{ s}^{-1}$; 2 and 3 are related to the reactions $BaCO_3 + WO_3 = BaWO_4 + CO_2$ [23,47] and $Ag_2C_2O_4 = 2Ag + CO_2$ [46] in a planetary centrifugal mill KhK 871, $\omega = 11$ and 9 s^{-1}, respectively.

chemical [46] decomposition of silver oxalate according to the scheme $Ag_2C_2O_4 = 2Ag + 2CO_2$ were obtained also by measuring the pressure of gaseous CO_2 formed. The rate constants K_r and K of silver oxalate mechanodestruction under the conditions of pressure and temperature impulses realized at the impact–friction contact of the particles under treatment can be estimated by using Eqs. (15) and (16). The rate constant of thermal decomposition of $Ag_2C_2O_4$ is $K_r = 6.6 \times 10^9 \exp(-1.5 \times 10^{-19} \, J/kT)$ in s^{-1} [42,46]. Because of this, when calculating the kinetic parameters and the rate constant K of silver oxalate mechanodestruction according to Eq. (16), it has been accepted [46] that $\omega = 9 \, s^{-1}$, $\rho = 15.6$ (balls made of WCo8 alloy) and $\rho_1 = 5.0 \, g/cm^3$, $R \approx 0.2 \, cm$ and $R_1 \approx 1.0 \times 10^{-5} \, cm$, $\theta \approx 1.1 \times 10^{-12}$ and $\theta_1 \approx 8.4 \times 10^{-12}$ cm^2/dyn, $c_1 \approx 58 \times 10^5 \, erg/g \, K$, $\lambda_1 \approx 2.3 \times 10^5 \, erg/cm$ $K \, s$, $D' \approx 170 \, cm^2/g \, s$ [46], $\chi \approx 3 \times 10^{-23} \, cm^3$ [46,56], $\zeta\eta \approx 1$. Using Table 4 in Ref. [1] we obtain $\langle\sigma\rangle \approx 2.7 \times 10^{10} \, dyn/cm^2$, $\varepsilon_1 \approx 3.7 \times 10^{-7} \, cm$, $\tau_1 \approx 6.2 \times 10^{-10} \, s$, $[T_0 + 0.5\Delta T(0,\underline{\tau_1}) + 0.5\Delta T(\underline{\varepsilon_1}/2,\underline{\tau_1})] \approx 870$ K, $\chi\langle\sigma\rangle \approx 0.8 \times 10^{-19}$ J, and the calculation procedure described above when deducing Eq. (15), we obtain $K_r \approx 2 \times 10^7$ s^{-1} for mechanodestruction of silver oxalate. This gives (see Eq. (16)):

$$K \approx 2.1\zeta\eta\omega W^{2.2}\rho^{1.1}(\theta + \theta_1)^{-2.4}\theta_1^4\rho_1^{1.5}R_1^2D'K_r$$

$$\approx 4 \times 10^{-9}, \text{ in } s^{-2}.$$

The experimental value is $K_{3a} \approx 3.5 \times 10^{-8} \, s^{-2}$ (see Fig. 3 and Ref. [46]) which is about 10 times higher than the calculated value.

3.4. The effect of the conditions of mechanical treatment on the kinetics

In order to establish the dependence of K on the conditions of mechanical treatment, see Eq. (19), a complex investigation of the kinetics of the mechanochemical reactions type $BaCO_3 + WO_3 = BaWO_4 + CO_2$ has been performed [57,58]. This reaction was chosen as a model one (when studying the dependence on $\Theta \sim \theta_1 \sim 1/E_1$, we used the differences in Young's modulus (E) of the alkaline earths carbonates [55]). The parameters to be used in Eq. (19) were as follows: ω (balls made of WCo8, $R = 0.2$ cm, $N = 228$) — 5.0, 7.1, 8.2, 8.8, 9.0, 9.7, 11.0, 12.4 and 15.3, in s^{-1}; ρ ($R \approx 0.2$ cm, $N = 228$, $\omega = 12.4$ s^{-1}) — 4.0 (corundum), 7.9 (steel) and 15.6 (WCo8 alloy), in g/cm^3; R (for steel balls, $N = 137$, $\omega = 12.4$ s^{-1}) — 0.075, 0.11, 0.15, 0.20, 0.25 and 0.4, in cm; $\theta_1 \sim 1/E_1$ (WCo8 alloy, $R = 0.2$ cm, $N = 228$, $\omega = 12.4$ s^{-1}) — 1.07 ($MgCO_3$), 1.37 ($CaCO_3$), 1.75 ($SrCO_3$) and 2.03 ($BaCO_3$), in $Mbar^{-1}$ [55] ($10^{-12} \, cm^2/dyn$); N (steel, $R = 0.2$ cm, $\omega = 12.4 \, s^{-1}$) — 68, 137, 228, 262 and 467. Experimentally determined rate constants of the studied reactions, depending on treatment conditions should be-

come straight lines in the following coordinates (see Eq. (19)):

$$K - R^2; \; K - N^2; \; K - \theta_1^{1.6};$$

$$\lg K - \left[(1.1\lg\rho - (\lg e/\rho^{0.45}))\right];$$

$$\lg K - \left[(3.2\lg\omega - (\lg e/\omega^{0.9}))\right].$$

Fig. 4 shows a result of this treatment which is in satisfactory agreement with the above considerations and assumptions.

Using the slopes of the straight lines (1) and (2) $\Delta K(N,R)/\Delta(N^2)\Delta(R^2) \approx 3.5 \times 10^{-12} \, s \, cm^{-2}$ (see Fig. 4) one can determine the value $\zeta\eta \approx 3.5 \times 10^{-12}N^2R^2/K(N=1,R) \approx 15$ where $N = 137$ and $R = 0.2$ cm correspond to the identical conditions of the experiment (identical K) when studying the dependence of K on the number and size of balls and $K(N=1,R=0.2) \approx 1.8 \times 10^{-10}$ s^{-2}. Using the slopes of the straight lines (3) and (5) we obtain the values $\lg K(\omega=1,\rho=15.6) \approx -17.8$, $\lg K(\rho=1,\omega=12.4) \approx -6.65$ and $\beta \approx \omega^{0.9}\rho^{0.45}[\lg K(\omega=1) - \lg K(\rho=1) + 3.2\lg\omega - 1.1\lg\rho]/(\rho^{0.45} - \omega^{0.9})\lg e \approx 110$, where $\rho = 15.6 \, g/cm^3$ and $\omega = 12.4 \, s^{-1}$ correspond to identical K when studying the dependence of K on the ball density and on the mill rotation frequency. It seems interesting to compare the experimental value of β with the theoretical one according to Eq. (17a) ($l' = 84$) for a related mechanochemical synthesis of calcium silicate (for parameters, see Ref. [1]), the units being in $g^{0.45} cm^{1.35} s^{-0.9}$:

$$\beta \approx 0.036(\theta + \underline{\theta})^{1.8}\left[\xi_{12}(\theta_1 + \theta_2)\right]^{-1}$$

$$\times\left[\left(c_1c_2\lambda_1\lambda_2\rho_1\rho_2\rho_{12}/R_{12}^2\right)\right]^{0.25}(U/k) \approx 10^3.$$

If the selected relation $K_r = K_{r0}\exp(-\beta/\omega^{0.9}\rho^{0.45})$ is correct, the two values should be close to each other. In
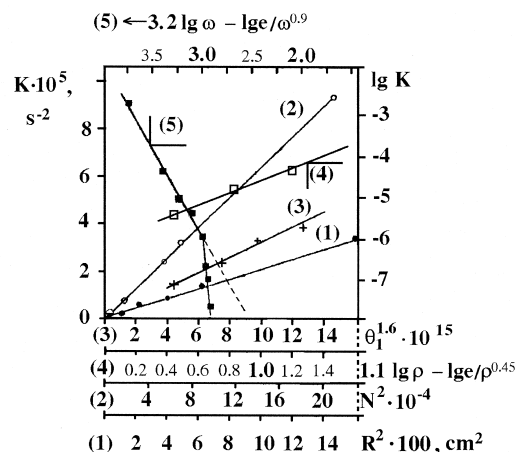

Fig. 4. Experimental values of the rate constants K (in s^{-2}) for $BaWO_4$ mechanochemical synthesis compared to the theoretical dependence of K on the conditions of mechanical treatment in a mill, (see also text and Refs. [57,58]): $(1,\bullet) \rightarrow K - R^2$; $(2,\bigcirc) \rightarrow K - N^2$; $(3,+) \rightarrow K - \theta_1^{1.6}$ $(\theta_1, cm^2/dyn)$; $(4,\square) \rightarrow \lg K - [(1.1\lg\rho - (\lg e/\rho 0.45)]$, ρ in g/cm^3; $(5,\blacksquare) \rightarrow \lg K - [(3.2\lg\omega - (\lg e/\omega^{0.9})]$, ω in s^{-1}.

the case under consideration, the two values agree at an accuracy within an order of magnitude. For the reaction under consideration, the condition $U \gg \chi_{12}\langle\underline{\sigma}\rangle$ is generally fulfilled.

It is important to note that for low rotational frequencies, the diffusion regime of mechanochemical synthesis of barium tungstate is changed for the kinetic regime (see the fracture at the curve (5) in Fig. 4 which is predicted by the calculations described above in Section 3.2): at a definite critical small ω the synthesis reaction passes into kinetically controlled region [58].

When the experimental data do not agree with Eq. (19) the dependence of K_r can be corrected. For example, having assumed a linear dependence on ω as a correct one, in order to linearize the experimental data according to the relation (19), one should select another type of the dependence on the ball density in the exponent $(-\beta/\omega\rho^\kappa)$ where κ is a number, or to analyze the possibility of applying the conditions $U \ll \chi_{12}\langle\underline{\sigma}\rangle$ (see Eq. (18a)).

3.5. Summary

The final results of the comparison between the experimental and calculated rate constants of the mechanochemical reactions in planetary centrifugal mills taking account of the value $\zeta\eta \approx 15$ determined experimentally will be listed below. For the reaction $NaNO_3 + KCl = KNO_3 + NaCl$, $K_{1a} = 8.3 \times 10^{-5}$ s^{-2}, calculated value, $K \approx 3 \times 10^{-5}$ s^{-2}; for the synthesis of barium tungstate, $K_{2a} = 21 \times 10^{-6}$ s^{-2}, calculated value, $K \approx 9 \times 10^{-6}$ s^{-2}; for mechanical destruction of silver oxalate, $K_{3a} = 3.5 \times 10^{-8}$ s^{-2}, calculated value, $K \approx 6 \times 10^{-8}$ s^{-2}. So, one can see that the theory providing the calculation of the kinetics of mechanochemical reactions (controlled by diffusion and by the kinetics) is in quantitative agreement with the kinetic parameters determined experimentally within an order of magnitude.

From the other hand, the kinetic concept presented above provides a satisfactory description of the dependence of mechanochemical process rate on the conditions of treatment in different ball mills (dimensions and frequencies of rotation of the mills, density, number and size of balls, mechanical properties of balls and particles under treatment).

4. Conclusions

On the basis of the obtained theoretical results, it can be stated that the effect of short-time contact fusion of particles treated in various comminuting devices can play the key role in the mechanism of activation and chemical reactions for wide range of mechanochemical processes. This role involves several aspects, i.e., the very fact of contact fusion transforms the solid-phase process into another qualitative level, judging from the mass transfer coefficients. Spatial and time characteristics of the exis-

tence of the fused zone are so that the quenching of non-equilibrium defects and intermediate products of chemical reactions occurs; solidification of the fused zone near the contact results in the formation of ''nanocrystal or nanoamorphous state''. The calculation models considered above and the kinetic equations obtained on their basis allow to perform quantitative ab initio estimates of rate constants for any specific processes of mechanical activation and chemical transformations of substances in comminuting devices operating in the impact regime.

5. List of symbols [2]

m' and m'_s	The rate and stationary rate of melting
h and $f(y,h)$	Dimensionless parameters of melting
H_m	Latent heat of melting
μ	Viscosity of the melting zone
τ_c and A	Time and constant of the crystallization process
r_{cr} and σ_s	Linear dimension of the new phase formed and the crystal–melt surface tension
∇	Diffusion coefficient (diffusivity)
k, χ and K_{r0}	The Boltzmann, structural and pre-exponential factors
n, n_0, n^*	The current, total, reacted number of molecules (atoms)
K_r	The reaction rate constant in the volume V^*
κ and β	constants

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