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# Mechanochemical synthesis of nanoparticles by a dilution method: derivation of kinetic equations

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**A kinetic equation was derived for the mechanochemical preparation of nanosystems by a dilution method; the equation was used to calculate mechanical activation times necessary for the completion of exchange reactions and mass-transfer coefficients in ball milling.**

The kinetics and mechanism of mechanically activated chemical reactions is of considerable current interest.[1,2] Hypotheses regarding the mechanisms range from the oldest scenarios of hot spot theory[3] and defect-enhanced diffusion[4] to the most recent ones of shear-induced mixing, interface roughening and contact melting (including virtual melting).[4–10] While passing from the former approach to the latter ones, the emphasis gradually shifts from inherently thermal processes to coupled thermally and mechanically induced phenomena (so-called $t-P-T$ conditions).[8–10] Various questions also arise in studying the kinetics of mechanically induced phase transformations[11,12] and the synthesis of nanostructured and nanometer-sized systems,[13,14] especially by means of soft mechanochemistry[15] and dilution.[16,17]

Previously,[18] mechanochemical reactions were theoretically studied to estimate the optimum dilution parameter $z^*$ for the preparation of nanosized TlBr and other compound particles in the exchange chemical reactions

$$km\mathrm{A}_h\mathrm{D}_l + hl\mathrm{B}_k\mathrm{C}_m + z\mathrm{A}_k\mathrm{C}_l = (z + hm)\mathrm{A}_k\mathrm{C}_l + lk\mathrm{B}_h\mathrm{D}_m \quad (1)$$

$$\mathrm{KBr} + \mathrm{TlCl} + z\mathrm{KCl} = (z + 1)\mathrm{KCl} + \mathrm{TlBr}, \quad \Delta_r G^\circ = -12.6\ \mathrm{kJ\ mol^{-1}} \quad (1a)$$

Note that exchange reactions in the stoichiometric mixtures of ionic crystal salts in planetary mills proceed at very high rates. For example, the reaction $NaNO_3 + KCl = KNO_3 + NaCl$ in an EI-2×150 ball planetary mill proceeds to completion within the mechanical activation (MA) time $\tau = 15$ min.[9,10,19] In view of this, it was necessary to establish (i) how the dilution of the initial stoichiometric mixture with one of the end reaction products affects the rate of MA exchange reaction and (ii) the mechanism and kinetics of the exchange reaction with dilution by the end product.

It is evident that, with the addition of a large amount of a diluent, the exchange process should not only slow down but also cease completely after the contacts between the initial reagents in the MA mixture are exhausted. However, this is not observed experimentally.[16–18] Therefore, a mass transfer mechanism exists in a mechanochemical reactor; this mechanism can be connected only with mobile milling tools. In this case, the particle size of the end products should change from a subnanometer scale to a micrometer one, which is characteristic of reactions in the stoichiometric mixtures of salts. Hence, an optimal time $\tau$ of MA should exist, which would provide both the completeness of the reaction and obtaining nanoscale particles of the desired reaction product in the diluent matrix.

The mechanism and kinetics of traditional mechanochemical reactions was studied in detail.[8–10,20–23] In this work, published data[9,10,18,21–25] are applied to estimate the kinetics of abrasive-reactive wear of particles under processing. The calculation model

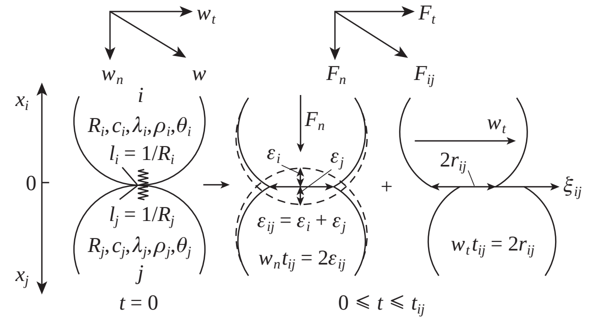


**Figure 1** Kinematics and dynamics of the impact-friction contact of two particles $i$ and $j$ selected arbitrarily from the lined layer in the region $\pi r^2\delta$ of impact action produced by a ball.[8,10,18]

for estimating the characteristics of the impact-friction interaction of two contacting reagent particles is shown in Figure 1.

For the temperature impulse $\Delta T(x,t)$ over the averaged distance $x$ and time $t$ in the vicinity of the impact-friction contact of the particles $i$ and $j$ (Figure 1), the equation of thermal conductivity is solved with the heat source of the density $2q_{ij} = \xi_{ij}\underline{\sigma}w_t$ symmetric on the sliding plane[8,10] (Figure 2):

$$\Delta T(x,t) = 2q_{ij}(c_ic_j\lambda_i\lambda_j\rho_i\rho_j)^{-0.25}\{t^{0.5}\,\mathrm{iErfc}[x/2(a_ia_j)^{0.25}t^{0.5}] - (t-t_{ij})^{0.5}\,\mathrm{iErfc}[x/2(a_ia_j)^{0.25}(t-t_{ij})^{0.5}]\} = B\{t^{0.5}\,\mathrm{iErfc}[x/2(a_ia_j)^{0.25}t^{0.5}] - (t-t_{ij})^{0.5}\,\mathrm{iErfc}[x/2(a_ia_j)^{0.25}(t-t_{ij})^{0.5}]\} \quad (2)$$

$$\Delta T_{\max} = \Delta T(x = 0,\ t = t_{ij}) = Bt_{ij}^{0.5}\,\mathrm{iErfc}[0] \quad (2a)$$

$$\Delta T_{\mathrm{m}} = \Delta T(0, t_{\mathrm{m}}) = \Delta T(0, t'_{\mathrm{m}}) = \Delta T(x_{\mathrm{m}}, t_{ij}) \quad (2b)$$

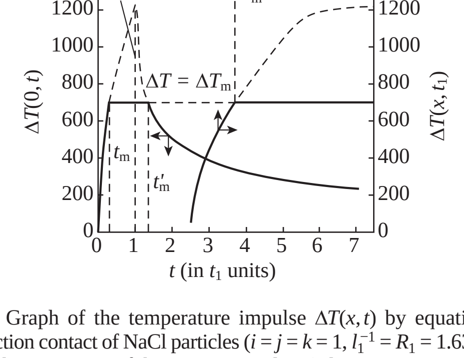


**Figure 2** Graph of the temperature impulse $\Delta T(x,t)$ by equations (2) at impact-friction contact of NaCl particles ($i = j = k = 1$, $l_1^{-1} = R_1 = 1.63\times10^{-4}$ cm, $\xi_1 = 0.8$; taking account of their contact melting) during MA in an EI−2x150 steel planetary ball mill at $\omega = 10\ \mathrm{s^{-1}}$ (or $W_{\mathrm{n}} = |W(\omega)| \approx 840\ \mathrm{cm\ s^{-1}}$).[9,10]

**Table 1** Physical properties of reaction (1a) components and milling tools: Young's modulus $E_i$, Poisson coefficients $\nu_i$, compliances $\theta_i = 4(1-\nu_i^2)/E_i$, and $\underline{\theta} = (\theta_1 + \theta_2 + z\theta_3)/(2+z)$, thermal conductivities $\lambda_i$, capacities $c_i$, temperatures of melting $T_{mi}$, latent heats of melting $Ƕ_{mi}$, viscosities $\mu_i$.[26,27]

| Object | Knoop hardness | $\rho$/g cm$^{-3}$ | $E$/10$^{-12}$ dyn cm$^{-2}$ | $\nu$ | $\theta$/10$^{12}$ cm$^2$ dyn$^{-1}$ | $\lambda$/10$^{-4}$ erg (cm K s)$^{-1}$ | $c$/10$^{-6}$ erg (g K)$^{-1}$ | $T_m$/K | $Ƕ_m$/10$^{-8}$ erg g$^{-1}$ | $\mu$/dyn s cm$^{-2}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| KBr ($i$ = 1) | 6.45 | 2.750 | 0.201 | 0.283 | 18.31 | $48.1^{317}$ | $4.52^{373}$ | 1003 | 21.85 | 0.0118 |
| TlCl ($i$ = 2) | 12.80 | 7.000 | 0.245 | 0.326 | 14.59 | $10.3^{273}$ | $2.27^{373}$ | 703 | 6.50 | 0.0210 |
| KCl ($i$ = 3) | 8.25 | 1.988 | 0.241 | 0.274 | 15.35 | $49.2^{373}$ | $7.03^{373}$ | 1049 | 35.29 | 0.0115 |
| TlBr ($i$ = 4) | 11.90 | 7.557 | 0.237 | 0.324 | 15.11 | $9.8^{273}$ | $1.88^{293}$ | 773 | 5.77 | 0.0200 |
| AGO-2 steel (no index) | ~300 | 7.860 | 2.232 | 0.285 | 1.647 | 470 | 6.60 | 1812 | 24.70 | — |

Here (Table 1 and Figure 1), $\xi_{ij}$ is the dynamic friction coefficient; $\underline{\sigma} = 2.0\rho^{0.2}(\theta + \underline{\theta})^{-0.8}W_n^{0.4}$ is the mean mechanical stress at the contact point at $\underline{\theta} = (\theta_i + \theta_j)/2$; $W_n$ is the normal component of the relative velocity $W$ of collisions of milling tools;[10,18,24] $w_t = 0.57\rho^{0.3}(\theta + \underline{\theta})^{-1.2}(\theta_i + \theta_j)W_n^{0.6}[(\rho_i l_j^3 + \rho_j l_i^3)/\rho_i\rho_j(l_i + l_j)^3]^{0.5}$ is the relative shear velocity of particles; $t_{ij} = 3.5\rho^{-0.1}(\theta + \underline{\theta})^{0.4}\times$ $\times W_n^{-0.2}[\rho_i\rho_j(l_i + l_j)/(\rho_i l_j^3 + \rho_j l_i^3)]^{0.5}$ is the duration of impact-friction interaction between particles; $B = 2q_{ij}(c_i c_j \lambda_i \lambda_j \rho_i \rho_2)^{-0.25}$; $l_k = 1/R_k$ and $a_k = \lambda_k/c_k\rho_k$ are curvature radii at the contact point and thermal diffusivities of the particles, respectively ($k = i$ or $j$).

The key parameters for calculating the rate of an arbitrary mechanochemical reaction are shown in Figure 3. A dummy degree $\alpha_d(\tau)$ of transformation according to reactions (1) is described by the equations[21]

$$\alpha_d(\tau) = \Psi(z)\Phi^* n(\tau)[V^*(\tau)/V(\tau)]; \quad (3)$$

$$V^*(\tau) = \textstyle\sum_1^n V^*(n) = \sum_1^n g(z)\,d^*(n)\,s_{12}(n); \quad (4)$$

$$V(\tau) = V(0) - \textstyle\sum_1^n V^*(\tau); \quad (5)$$

$$n(\tau) = \zeta\eta\psi\omega_1\tau = f\tau; \quad (6)$$

$$\psi = 2^{-4}[10\pi\rho(\theta + \underline{\theta})W_n^2]^{0.4} = 0.25[\rho(\theta + \underline{\theta})W_n^2]^{0.4}. \quad (7)$$

Here, $\psi(z)$ is the dimensionless function of the dilution parameter $z$ taking into account the necessity of mass transfer in the lining layer for creating new contacts between reagent particles; $\tau$ is the current MA time; $V(0, \tau = \tau')$ is the quasi-equilibrium total volume of particles **1** and **2**; $\Phi^*$ is the fraction of reacted material in volume $V^*$; $V^*(n)$ is the reaction volume or the decrease in the volume $V = V_1 + V_2$ of a pair of particles as a result of a single ($n$th) abrasive-reactive interaction; $g(z)$ is the number of identical abrasive-reactive contacts of the selected pair of particles taking into account the dilution parameter $z$; $d^*(n)$ and $s_{12}(n)$ are the reaction zone thickness and the impact-friction contact area; $n(\tau)$ and $f$ are the number and frequency of impact-friction interactions for particles **1** and **2**; $\zeta(N) \sim N$ is the coefficient of the collective action of the ball load; $\eta(N,R) \sim N(R/L_1)^2$ is the parameter that takes into account the geometric characteristics of MA[18] (as a rule,[8–10] $\zeta\eta \approx 1$); and $\psi$ is the geometric probability for an arbitrarily selected pair of particles **1** and **2** to get into the volume $\pi r^2\delta$.

The actual ($\alpha$) and dummy ($\alpha_d$) degrees of transformation are related as $d\alpha(\tau) = (1-\alpha)^\kappa d\alpha_d(\tau)$, where the parameter $\kappa$ takes into account the influence of the final products on the reaction kinetics, and at $\kappa = 1$, which gives $-\ln[1 - \alpha(\tau)] = \alpha_d(\tau)$.[8–10]

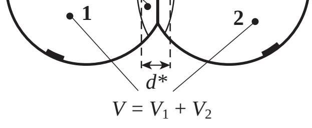


**Figure 3** Impact-friction contact of two particles **1** and **2** (in calculating the kinetics of mechanochemical reactions), where $V$ and $V^* = s_{12}d^*$ are the volumes of particles near the contact area, $s_{12}$ is the contact area and $d^*$ is the thickness. Blackened regions point to similar abrasive-reactive interaction of particles **1** and **2** with the surroundings.[8,10]

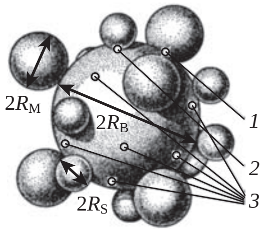


**Figure 4** Schematic image of the areas (○) of the impact-friction contacts for nanoscale abrasive-reactive wear in the system exchange mechanochemical reactions: (*1*) particle in the position close-packing (B, diameter $2R_B$ = $= 2.5\times10^{-4}$ cm) – particle in the position octahedral voids ($2R_M = 2\times0.414R_B$ = $= 0.828\times10^{-4}$ cm); (*2*) particle B – particle in the position tetrahedral voids ($2R_S = 2\times0.225R_B = 0.45\times10^{-4}$ cm); (*3*) particle B – particle B.[18]

Let us estimate $\sum_1^n V^*(n)$. If $\varsigma(n = 1) = V^*(n = 1)/V(0) = 3g(z)\times$ $\times d^*(n = 1)s_{12}(n = 1)/4\pi(R_1^3 + R_2^3)$, then $\varsigma(n) = V^*(n)/V(n-1)$ for the subsequent interactions. It was found[21] that $\varsigma = \varsigma(1) = \varsigma(2) = ... =$ $= \varsigma(n)$. As $V^*(n)/V(n-1)$ is constant for all $n = f\tau$, one can write:

$$\textstyle\sum_1^n V^*(n) = \varsigma V(0)\,[1 + (1-\varsigma) + (1-\varsigma)^2 + ... + (1-\varsigma)^n] =$$
$$= V(0)[1 - (1-\varsigma)^n]; \quad (8)$$

$$V^*(\tau)/V(\tau) = [1 - (1-\varsigma)^n]/(1-\varsigma)^n. \quad (9)$$

The final equations for calculating the degree $\alpha(\tau,z)$ of the completion of reaction (1a) are

$$\varsigma = \varsigma(z) = V^*(n = 1)/V(0) =$$
$$= 3g(z)d^*(n = 1)s_{12}(n = 1)/4\pi(R_1^3 + R_2^3); \quad (10)$$

$$-\ln[1 - \alpha(\tau,z)] = \alpha_d(\tau,z) = \Psi(z)\Phi^* f\tau[1 - (1-\varsigma)^{f\tau}]/(1-\varsigma)^{f\tau}. \quad (11)$$

It follows from equations (6), (7) at $\theta + \underline{\theta} = 0.172\times10^{-10}$ cm$^2$ dyn$^{-1}$ and $\zeta(N = 400)\eta(N, R = 0.2$ cm, $L_1 = 3.1$ cm$) \approx 1$ that[8,10,18,21] $n(\tau,\psi, \omega_1 = 29$ s$^{-1}$, $W_n = 900$ cm s$^{-1}) = \zeta\eta\psi\omega_1\tau \approx 0.25[\rho(\theta +$ $+ \underline{\theta})W_n^2]^{0.4}\omega_1\tau = f\tau$ and $f = 0.189$ s$^{-1}$. The numbers $g(z = z^*)$ of abrasive-reactive contacts between reagent particles are known[18] (Figure 4): $g(z_1^*) = 18$ is the number of contacts of reagent 2 (TlCl) particles ($R_2 = R_B$) with reagent 1 (KBr) particles situated in six octahedral, adjacent to $R_2$ particles, ($R_1 = R_M$) and 12 tetrahedral ($R_1 = R_S$) voids adjacent to reagent 2 particles; and $g(z_2^*) = 3$ is the number of contacts in chains of alternating reagent 1 and 2 particles in the close packing framework ($R_1 = R_2 =$ $= R_B$). The role played by the $\Psi(z)$ function is therefore reduced to taking into account mass transfer in a mechanochemical reactor to create new contacts between reagent particles. Clearly,[18] the creation of new contacts by mass transfer is related to the degree of dilution $z$ and takes an additional MA time; that is, $\Psi(z) < 1$. These conditions are satisfied at $z = z^*$ by the equations

$$\Psi(z_1^*) = N_{2B}(z_1^*)/N_{3B}(z_1^*) = 1/14.8 = 0.0675; \quad (12)$$

$$\Psi(z_2^*) = g(z_2^*)/g(R_{1B}, R_{2B} \rightarrow R_{3B}, R_{3M}, R_{3S}) =$$
$$= 3/(20 + 12 + 24) = 0.0536 \quad (13)$$

As the mechanism of reactions between salts involves the contact melting (cm) of particles **1** and **2** at temperature $T_{cm} \leqslant T_{m2}$ [not higher than $T_{m2} \approx 700$ K of reagent 2 (TlCl) with the lowest melting point (Table 1)], the $\Phi^*$ function can be calculated.[9,10,19,22,23] It follows that it remains to determine the key parameter $\varsigma$ in equations (10) and (11), for instance, from the condition $\alpha(\tau = \tau^*) = 0.99$, and find the MA time $\tau^*$ that corresponds to the occurrence of selected model reaction (1a) by 99%.

The area $s_{12}(n = 1)$ of the abrasive-reaction contact in (10) at $R_{12} = R_1R_2/(R_1 + R_2)$ is:[8,10] $s_{12}(n = 1) = 3.1R_{12}^2\rho^{0.4}(\theta + \underline{\theta})^{-1.6}\times(\theta_1 + \theta_2)^2W_n^{0.8}$. Calculations for $s_{12}(n = 1)$ in (10) give $s_{12}(n = 1, z_1^*) = 3.1\times10^{-10}$ cm$^2$ and $s_{12}(n = 1, z_2^*) = 11.7\times10^{-10}$ cm$^2$, see Online Supplementary Materials.

The values of $d^*(n = 1) = d_1 + d_2 = 2d_{12}$, where $d_{12}$ is the thickness of the zone of contact melting of particles **1** and **2** counted from the initial relative shear (viscous flow) surface during their impact-friction interaction (Figure 3), will be calculated using (2), (2a), (2b), Figure 2 and Table 1.[9,10,19,22,23] The equation for calculating the melting zone thickness is[9,10,28]

$$d^*(n = 1) = 2w_t[(t'_m - t_m)\mu\iota(y,h)/\rho(\text{Ƀ}_m + c\Delta T_m)]^{0.5} \text{ or}$$
$$d^*(n = 1, z) = 2w_t(z)\{[t'_m(z) - t_m(z)]\mu_{12}\iota(y,h)/\rho_{12}(\text{Ƀ}_{m12} + c_{12}\Delta T_{m2})\}^{0.5}. \quad (14)$$

Calculations for $d^*(n = 1)$ in (10) give $d^*(n = 1, z_1^*) \approx 1.6\times10^{-6}$ cm and $d^*(n = 1, z_2^*) \approx 2.2\times10^{-6}$ cm, see Online Supplementary Materials..

The high-rate (~$10^5$ K s$^{-1}$) quenching-crystallization of melts results in the formation of the final reaction products, and the size of newly formed phases cannot exceed the value of $d^*$.[9,10] For this reason, the abrasive-reactive wear of contacting reagent 1 and 2 particles always yields nanoscale product particles in MA reaction (1a), and the presence of diluent 3 ensures the retention of the size of desired product 4. Next, one can assume that the mechanism of reaction (1a) in an AGO-2 mill[18] is identical to that of the reaction $KCl + NaNO_3 = KNO_3 + NaCl$ in a similar EI-2x150 mill.[9,19] The rate of this reaction is limited by the depth of the inter-diffusion of the reagents in the molten zone. The degree of its completion in volume $V^*$ was found[9,10] to be $\Phi^* \approx 0.65$. Assuming the same $\Phi^*$ for reaction (1a), we can use (11) to calculate the kinetic curves $\alpha(\tau, z^*)$ and (10) to calculate $\varsigma(z^*)$, and, as a consequence, the MA time $\tau = \tau^*(z^*)$ at $\alpha(\tau^*, z^*) = 0.99$ for the occurrence of model reaction (1a) by 99% (Figure 5):

$$\varsigma(z_1^*) = 3g(z_1^*)\,d^*(z_1^*)\,s_{12}(z_1^*)/4\pi(R_{MS}^3 + R_B^3) = 0.000697; \quad (15)$$
$$\varsigma(z_2^*) = 3g(z_2^*)\,d^*(z_2^*)\,s_{12}(z_2^*)/8\pi R_B^3 = 0.000155; \quad (16)$$
$$-\ln[1 - \alpha(\tau, z^*)] = \Psi(z^*)\Phi^* f\tau[1 - (1 - \varsigma)^{f\tau}]/(1 - \varsigma)^{f\tau}; \quad (17)$$
$$\Psi(z^*)\Phi^* f\tau^*[1 - (1 - \varsigma)^{f\tau^*}] = 4.60\,(1 - \varsigma)^{f\tau^*}. \quad (18)$$

The dependence of the degree $\alpha(\tau, z^*)$ of completion of reaction (1a) on the number of abrasive-reactive contacts $f\tau$ or MA duration $\tau$ in an AGO-2 planetary mill calculated by equation (17) is shown in Figure 5. Using equations (12), (13), (15) and (16), the following solutions to equation (18) has been obtained for the time $\tau^*$ of the occurrence of reaction (1a) by 99% after the establishment of mechanochemical quasi-equilibrium with respect to particle sizes in an AGO-2 mill at $f = 0.189$ s$^{-1}$: $f\tau^*(z_1^*) = 363$ and $\tau^*(z_1^*) = 1920$ s = 32 min; $f\tau^*(z_2^*) = 900$ and $\tau^*(z_2^*) = 4760$ s = 79 min. The theoretical $\tau^*$ time values determined in this work do not exceed 2 h; they are in agreement with but also augment the experimental values.[18]

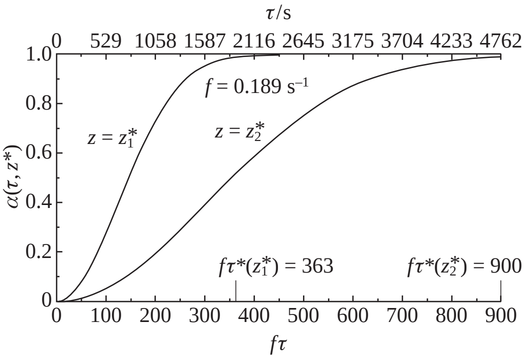


**Figure 5** Kinetic curves of reaction (1a) in an AGO-2 ball planetary mill calculated by equation (17).

*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.03.018.

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