U.D.C. 541.124.16:541.12.031

Mechanochemistry of Inorganic Solids

V.V.Boldyrev and E.G.Avvakumov

The chemical consequences of the mechanical treatment of inorganic solids has recently become the subject of detailed studies arising from increasing mechanical loading and the development of a highly effective technology of size reduction. The present review of published data examines the influence of mechanical treatment on the structural and thermodynamic properties of materials, the reactivities of substances, and the rates of physicochemical and chemical processes involving substances subjected to mechanical treatment. The possible mechanisms and characteristic features of mechanochemical processes are discussed, and routes to their practical utilisation are indicated. The bibliography contains 145 references.

CONTENTS

I. Introduction	847
II. The production of new physicochemical properties as a result of dispersion	847
III. Chemical reactions during the mechanical treatment of a substance	850
IV. Mechanism of mechanochemical reactions	852
V. Practical aspects of mechanochemistry.	855

I. INTRODUCTION

In the search for new methods of carrying out processes in chemical technology and the development of methods for the directed control of the reactivity of solids, the study of processes taking place during the mechanical treatment of a substance has become extremely important. The mechanical treatment of solids (either beforehand or at the moment when the reaction is carried out), together with the use of heat, light, ionising radiation, electric fields, etc., provides one method for the physical stimulation of chemical processes, the possibilities of which have recently been extended considerably in connection with the development of highly effective techniques of size reduction.

Mechanochemical processes play a unique role in the chemistry of solids. Chemical reactions involving solids take place chiefly on a surface, and the state of the surface plays an important role in these processes. The action of heat on a solid leads to the excitation of all sites in the crystal lattice, whereas by mechanical treatment it is possible to bring only part of it into the excited state. There is another difference between the processes which take place on heating and on mechanical treatment. In thermal decomposition there is a slow increase in temperature, whereas on mechanical treatment there is a rapid pulse-wise increase in temperature at the points of contact between the friction solids, followed by rapid cooling. A consequence of this may be that in contrast to thermal decomposition, secondary processes may not be able to take place during mechanical treatment, and the primary products formed in the initial stages of the process are quenched. This may be one of the reasons for the specific features of the chemistry of mechanochemical reactions.

A number of reviews and monographs on the mechanochemistry of macromolecular organic substances have recently been published in the Soviet and other literature[1-7]. The aim of the present work is to review the mechanochemistry of inorganic solids. We shall therefore not deal here with problems of mechanochemical treatment of organic materials, and we shall not concern ourselves with special problems, such as the mechanochemical corrosion of metals, the study of which has recently undergone extremely intensive development[8-12].

In the examination of mechanochemical phenomena it is necessary to deal with two aspects, which are difficult to separate from one another. The first is the production of new physicochemical properties by the production of finely dispersed particles with increased energy. The second concerns the chemical changes taking place during the treatment of a substance under the influence of the physical processes taking place.

Since the problems of the state of finely dispersed particles have been fairly fully reviewed[13], most attention in the present review is paid to the second aspect, and also to the discussion of the specific features and nature of mechanochemical reactions.

II. PRODUCTION OF NEW PHYSICOCHEMICAL PROPERTIES AS A RESULT OF DISPERSION

1. Change in Free Energy, Solubility, and Thermal Stability

The process of size reduction can be regarded not only as a process of increasing surface area, but also as a process of increasing free energy (chiefly surface free energy). In this sense it can be said that size reduction is also a chemical process, since a change in free energy leads to a displacement of chemical and phase equilibria. The absence of excess free energy in a solid leads to the production of thermodynamically unstable states. A higher concentration of excess free energy corresponds to a higher content of excess internal energy ΔH and an excess entropy ΔS.

When the entropy change is small (the crystalline state is preserved), the change in free energy can be estimated from the change in excess enthalpy by calorimetric methods[14]. According to published work[15,16], the increase in enthalpy, for example, for oxides on going from the single crystal to the finely divided state is 1–3 kcal mole^{-1}. If the entropy change cannot be neglected, the excess free energy can be measured by measuring the equilibrium position of a chemical reaction in which the activated substance reacts with another substance of known activity.

From the relationship

$$\Delta G = -RT \ln \frac{k_2}{k_1} \quad (1)$$

where ΔG is the change in free energy and k_1 and k_2 the rate constants of the forward and back reactions respectively, it can be seen, for example, that a change in ΔG from 0 to 20 kcal mole^{-1} leads to a change in the ratio of k_2 to k_1 from 1 to 1×10^{15}. An example is provided by the reaction [18]

$$Ni + 4CO \rightleftarrows Ni(CO)_4. \quad (2)$$

The equilibrium position of the reaction is displaced to the right with increase in the surface area of the nickel, for example on going from nickel foil to nickel dust. The change in free energy is 1.38 kcal mole^{-1}; the ratio k_2/k_1 changes accordingly by one order of magnitude.

The free energy of finely dispersed particles can be estimated approximately by means of Thomson's equation

$$\Delta G = \frac{2\sigma V}{r}, \quad (3)$$

where σ is the surface tension, r the particle radius, and V the molar volume. Eqn. (3) is approximate, if only because the value of σ must also change when the particle dimensions become very small.

The fine particles exhibiting increased values of the free energy differ from large particles in other properties. In particular, if the particles are sufficiently small, their dissolution may produce concentrations exceeding those corresponding to the usual equilibrium solubility of the substance. Ostwald, and later Freundlich, obtained equations giving the dependence of the solubility on the dimensions of the particles [19]:

$$\ln \frac{C_r}{C^*} = \frac{2\sigma M}{RT\rho r}, \quad (4)$$

where C_r is the solubility of the particles with radius, r, C^* the equilibrium solubility, ρ the density of the solid, and M the molecular weight.

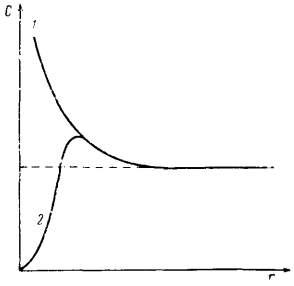


Figure 1. Dependence of solubility on particle size.
1) Freundlich's equation, *2*) Knapp's equation.

The Ostwald–Freundlich equation contains the same assumptions as were made in the derivation of Thomson's equation. For example, it is assumed that the density of the solid and the surface energy are independent of the particle dimensions.

The solubility of finely dispersed particles was examined from another viewpoint by Knapp [20]. He assumed that the particles carry a small surface electric charge, so that the total surface energy is the sum of the surface and electrical energies. On the basis of these assumptions he derived for isolated charged particles the equation

$$C_r = C^* \exp\left(\frac{a}{r} - \frac{b}{r^4}\right), \text{ where } a = \frac{2\sigma M}{RT\rho}, \; b = \frac{QM}{8\pi RT\varepsilon\rho}, \quad (5)$$

Q is the electrical charge of the particle, and ϵ the dielectric constant of the solid. Eqn. (5) gives the curve shown in Fig. 1. The experimental data obtained by Dundon and Mack [21,22] can be regarded as confirming Knapp's conclusions.

A large amount of work has shown that the increase in the surface area of solid particles produced during size reduction leads to an increase in the rates of solid-phase reactions, in particular decomposition [23]. In a number of instances the rates of topochemical reactions pass through a maximum with decrease in the particle dimensions. The reason for this dependence is that with change in the degree of dispersion, the ratio between the rate of formation of the nuclei of the new phase and the rate of their growth changes in such a way that the rate of the process is determined in some instances by nucleous formation, and in other instances by the growth of nuclei [24-26].

2. Kinetics of Size Reduction and the Dissolution of a Finely Divided Substance

Irrespective of the type of apparatus used for size reduction (with the condition that the apparatus is efficient and operates for a sufficiently long time), the change in the particle dimensions on size reduction takes place in three stages [27-30]. The first stage is characterised by a progressive decrease in the particle dimensions with time; the second by the start of aggregation of the particles; and the third by the establishment of equilibrium, in which the particle dimensions remain unchanged with time. The specific surface changes analogously. A characteristic picture of the change in the specific surface and particle dimensions on size reduction is given in Fig. 2.

For the description of the dependence of the particle dimensions on the duration of the size reduction, Schneider [31] proposed the equation

$$\frac{dr}{dt} = -k_0 e^{-\frac{U_B}{U_M}}(r - r_g) + k_r e^{-\frac{U_a}{f\frac{\sigma}{r} + \frac{E}{2}\left(\frac{A}{B + r^4}\right)^2 + U_M}}, \quad (6)$$

where r represents the particle size, r_g the minimal particle size, k_0 the rate constant for the formation of fractures in the lattice, k_r the recrystallisation rate constant, U_B the mean specific energy of fracture, U_M the specific mechanical load, U_a the activation energy of the recrystallisation process, E the modulus of elasticity, and A, B, f, and n constants.

The first term in the right hand side of Eqn. (6) describes the breakdown of the substance, whereas the second term describes the recrystallisation. The quantities appearing in the equation depend on the nature of the substance undergoing size reduction, and in particular on the type of chemical bonding. For ionic compounds the activation energy of recrystallisation is small, whereas for covalent compounds it is much larger (greater energetic interference is required to restore broken

valency bonds). As a consequence, the $dr/dt = \varphi(t)$ curves for ionic compounds pass through a minimum; for covalent compounds the minimum is poorly defined, or completely absent; in the last instance the particle size decreases smoothly with time until the equilibrium value is reached.

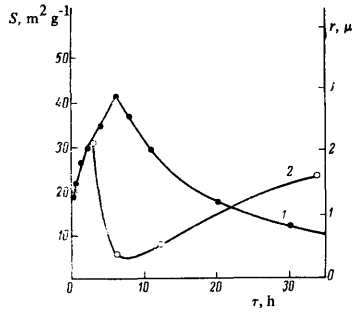


Figure 2. Dependence of specific surface and particle size on duration of size reduction: *1*) specific surface; *2*) particle size.

The specific surface (and the particle size) are influenced to a significant extent by the medium in which the size reduction is carried out. In a study of the mechanical properties of inorganic crystals (galena, calcite, and graphite), Rebinder [32] established that the strength of these crystals is greatly reduced in the presence of surface-active substances. He showed that the changes in the mechanical properties of solids under the influence of surface-active substances results from a decrease in the surface free energy and hence a decrease in the work required to increase the surface area. The decrease in hardness with change in the concentration of surface-active substance takes place in parallel with a change in adsorbability, and is described by an equation analogous to Langmuir's equation

$$\Delta B = \Delta B_\infty \frac{C}{C+\alpha}, \qquad (7)$$

where ΔB is the decrease in hardness, C the concentration of surface-active substance, ΔB_∞ the total decrease in hardness on complete saturation of the absorption layer, and α a constant.

The phenomenon of adsorption decrease in strength under the influence of surface-active substances (the Rebinder effect) provides a basis for the development of methods for controlling the rate of size reduction of solids [33,34]. Despite the fact that with increase in the duration of dispersion the specific surface increases only as far as a certain limit, the breakdown of the crystal lattice continues until the substance is completely converted into the amorphous state [29,30]. Because of the presence of the amorphous state, the solubility increases on size reduction, and the maximal attainable solubility may exceed the normal solubility. Khodakov and Plutsis established that the solubility of quartz in water, after size reduction on a vibro-mill, is given by the equation

$$C = C_\infty(1 - e^{-k\tau}), \qquad (8)$$

where C_∞ is the maximal solubility, τ the duration of size reduction, and k a constant. Eqn. (8) is also applicable to other substances [13,14].

An increase in solubility under the influence of mechanical treatment was also observed for iron oxide [35], copper oxide [16], sodium chloride [16], calcium carbonate [35,36], quartz [29,37,38], bauxite [30], monazite [6], alumina [39], tin(IV) oxide [40], chromite [41], etc.

3. Phase Transformations and Behaviour of Solid Solutions on Size Reduction

Very fine particles with an increased energy content are responsible for the production of metastable states and phases on size reduction. An example is provided by data [42] which show that decrease in particle size is accompanied by an increase in the temperature and enthalpy of solid-phase transformations in quartz, potassium sulphate, and potassium nitrate.

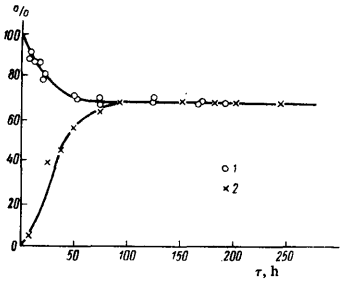


Figure 3. Equilibrium between the two crystalline phases of calcium carbonate under the influence of mechanical treatment [43]. *1*) Aragonite, *2*) calcite.

Under the influence of prolonged size reduction, an equilibrium is established between different modifications of a substance. Thus for example, equilibrium between calcite and aragonite is established after grinding for 80 h in a vibro-mill (Fig. 3) [43]. The high-temperature forms of the substances are also detected during the grinding of zinc sulphide [44], cadmium sulphide and selenide [45,46], barium chromate [47], silicon carbide [47], titanium dioxide [47], silver iodide [48], calcium carbide [49], lead dioxide [50], sulphur [51], selenium [52], quartz [53], nephelite [53], etc.

The establishment of thermodynamic equilibrium between solid phases depends on the rate of diffusion of the components of the mixtures. Since the size reduction of crystals leads to a sharp increase in the number of vacant sites in the lattice [54] and hence to an increase in diffusion and ionic conductivity in ionic crystals, the rate of attainment of thermodynamic equilibrium increases under the influence of size reduction.

The size reduction of a mixture of isomorphous components facilitates solid solution formation. It has been found [55,56] that solid solutions of potassium chloride and bromide can be obtained by grinding them in a mill or by repeated application of pressure to 13 000 atm. If a mixture of two substances is a solid solution of components which mix with difficulty, for example NaCl–TlCl (0.6 mole %) or KCl–AgCl (0.6 mole %), grinding of the solid solution leads to its partial breakdown [57].

III. CHEMICAL REACTIONS DURING THE MECHANICAL TREATMENT OF A SUBSTANCE

1. Decomposition and Preparation of Substances

The possibility of decomposing inorganic substances by grinding was established at an early date. As early as last century it was shown that grinding leads to the decomposition of many solid salts of silver and mercury[58,59]. The mechanochemical decomposition of a large number of inorganic compounds: carbonates, oxalates, nitrates, halates, complexes, etc. has now been studied.

Decomposition to the following extents after grinding for 20 h in a vibro-mill has been reported[60,61]: magnesium carbonate 28.9%, calcium carbonate 13.9%, strontium carbonate 10.8%, barium carbonate 8.4%, sodium carbonate 0.22%, and potassium carbonate 0.16%. Decomposition gives the oxides and oxygen.

Direct mass-spectrometric measurements[62] showed that the average number of monolayers decomposed in the size reduction of crystals of lead, magnesium, and calcium carbonates is 2, 0.37, and 0.09 respectively. The mechanochemical decomposition of calcium carbonate has been studied in detail[43]. The equilibrium thermal dissociation pressure, enthalpy of dissolution, particle size, and specific surface after mechanical activation were determined. The equilibrium pressure of carbon dioxide was used to calculate the values of ΔG, ΔH, and ΔS. Mechanical activation decreases the values of these quantities for thermal decomposition at 625°C: ΔG from 8.1 kcal mole^{-1} to 6.2 kcal mole^{-1}, ΔH from 33.2 kcal mole^{-1} to 14.8 kcal mole^{-1}, and ΔS from 28.0 e.u. to 9.6 e.u.

The decomposition of iron, zinc, and manganese carbonates is analogous. Peters[6] showed that different products may be obtained, depending on the conditions of mechanical treatment. The decomposition of iron carbonate (siderite) in air gives the oxide Fe_2O_3; in the presence of moisture the hydroxide $Fe(OH)_3$ is obtained. When the carbonates are subjected to size reduction in a vacuum, the quantity of carbon dioxide liberated is greater by an order of magnitude than that for decomposition in air. In the size reduction of sulphides (for example cinnabar[63]), decomposition to the metal and sulphur may take place.

A large amount of work has been done on the study of the effect of mechanical action on the decomposition of explosives. The thermal theory of the initiation of explosions by mechanical action has been intensively developed[64]. Criteria by means of which the mechanical sensitivity of explosives might be characterised have not been established, however.

To investigate the characteristic features of mechanochemical decomposition, the properties of the product of the mechanochemical decomposition of silver oxalate were compared with the properties of the product of its thermal decomposition[65]. The results indicated that the activity of "mechanochemical" silver is much less than that of silver obtained by thermal decomposition, but much greater than the activity of photochemical silver.

The mechanochemical decomposition of alkali metal, alkaline earth metal, and rare earth metal nitrates has been studied[66,67]. The degree of decomposition of the alkali metal nitrates was determined from the yield of nitrate, and that of the alkaline earth metal nitrates and anhydrous lanthanum nitrate from the yield of metal oxide. The decomposition curves have the same form as the specific surface curves, that is the degree of decomposition passes through a maximum, after which an equilibrium state is established (Fig. 4). The existence of this correlation may indicate that the mechanochemical reactions are localised on the surface of the substance subjected to size reduction. The decomposition curves before the maximum are described satisfactorily by the equation

$$\alpha = k\tau^n \qquad (9)$$

where α is the degree of decomposition, τ the time, and k and n constants[68]. For the substances studied, $n = 3$.

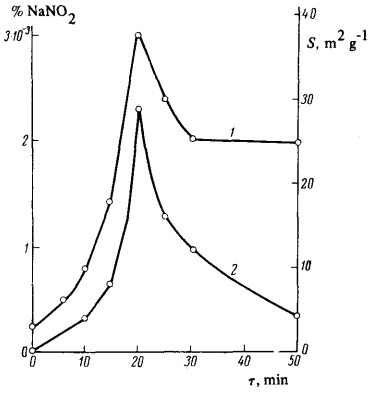


Figure 4. Dependence of the specific surface and yield of the product of the mechanochemical decomposition of nitrate on the duration of size reduction. *1*) Specific surface, *2*) $NaNO_2$ concentration.

With increase in the mechanical energy supplied, the degree of decomposition of the substances increases but the form of the curve is preserved. This can be seen from Fig. 5, which shows curves giving the dependence of the mechanical decomposition of sodium nitrate on the acceleration developed in a centrifugal planetary mill[67]. It follows from published data[66], reproduced in Fig. 6, that in a series of nitrates of the same type, the degree of decomposition increases with decrease in the crystal lattice energy. An analogous dependence is observed for the decomposition of substances under the influence of an explosion[69,70]. The similarity between the decomposition of substances on grinding and decomposition under the influence of an explosion is also shown in the fact that identical decomposition products are formed, for example in the decomposition of copper compounds[69,71].

The rate of mechanochemical decomposition may change in the presence of substances which exhibit redox properties or which act as catalysts. The decomposition of minerals and salts takes place particularly readily in the presence of ammonium salts or their mixtures with one another[72]. The rate of decomposition of substances can be altered by introducing catalysts, such as transition metal oxides. It has been shown[73] that the rates of decomposition of sodium nitrate in the presence of Ni, Fe, Zn, Cu, and Mn oxides show a correlation with the work function of an electron from the oxide.

When a mixture of substances is ground, synthetic and exchange reactions take place between them. The sulphides of Hg, Ag, Mg, Cd, Zn, Sn, Pb, Sb, and Bi are formed in yields of 25–100% when the metals are ground with sulphur, carbides are obtained by grinding with graphite, phosphides by grinding with phosphorus, iodides with iodine, etc.[69,72,74].

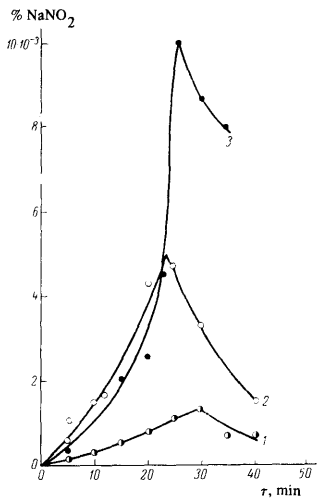


Figure 5. Influence of mechanical load on the degree of mechanochemical decomposition of sodium nitrate. Acceleration:
1) 20g, *2*) 40g, *3*) 60g.

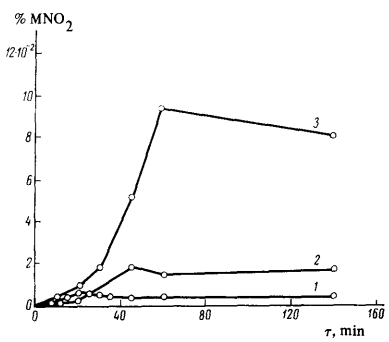


Figure 6. Mechanochemical decomposition of alkali metal nitrates.
1) $NaNO_3$, *2*) KNO_3, *3*) $CsNO_3$.

Oxides are formed when metals are ground in the presence of atmospheric oxygen[4]. The rate of oxidation passes through a maximum, depending on the duration of grinding, and before the maximum it is described by the equation

$$\ln v = k\tau + c \qquad (10)$$

where v is the rate of oxidation, and k and c constants.

Metal carbonyls, in particular Ni, Fe, and Zn carbonyls[75-77], can be obtained by a mechanochemical method. Detailed study of the carbonylation of nickel has established that mechanochemical treatment lowers the activation energy of the formation of nickel carbonyl from 10.2 kcal $mole^{-1}$ to 2.1 kcal $mole^{-1}$ [75]. The rate of formation of nickel carbonyl may be altered by the presence of additives of different types. It has been shown[76,77] that substances such as O_2, $KClO_3$, $K_2Cr_2O_7$, $KMnO_4$, KI_2O_3, Na, Ca, and I_2 decrease the reaction rate, whereas the addition of sulphur and compounds containing sulphur has an activating influence on the formation of carbonyls. It is considered that the catalytic activity of these compounds is due to the formation of the intermediate compound γ-NiS.

Mechanochemical treatment can be used to prepare silicates from silicon dioxide and alkali and alkaline earth metal oxides or carbonates, and to prepare molybdates and tungstates from carbonates and oxides[6]. It has also been possible to carry out preparations which could not be carried out by other methods. Mechanochemical processes have been used to prepare catalysts with high selectivity[78,79], spinels[80], dyes[81], metallates[82], organometallic compounds[83], etc.

A large number of exchange reactions take place on grinding, and these have been used to develop simple methods of qualitative chemical analysis[59,72,84,85].

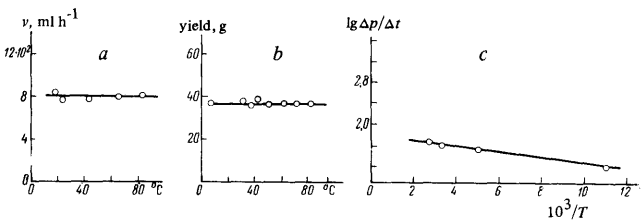


Figure 7. Temperature dependence of the rate of mechanochemical reactions[86-88].
a) $SiC + 2H_2O \rightarrow CH_4 + SiO_2$, *b*) $Sn + 2C_6H_5CH_2Cl \rightarrow (C_6H_5CH_2)_2SnCl_2$, *c*) $2Fe + O_2 \rightarrow Fe_2O_3$.

2. Influence of Temperature on Mechanochemical Reactions

One of the features indicating the specific nature of mechanochemical reactions is the fact that they are independent of temperature. Published data[86-88] on the influence of temperature on the rate of mechanochemical reactions are given in Fig. 7. The reaction rates remain almost unchanged (Fig. 7). Analogous results were obtained in a study of the decomposition of nitrates at room temperature and at the temperature of liquid nitrogen[66].

3. Formation of Free Radicals and Reactions Taking Place on Freshly-formed Surfaces

Measurements made on powders show that in diamagnetic substances after size reduction, paramagnetic centres resulting from the production of free radicals appear in the surface layers to a depth of 20–30 μ.

The regular features of the formation of radicals in the size reduction of quartz and their reaction stability at elevated temperatures have been studied[89-93]. Concentrations of unpaired electrons of the order of 10^{14} to 10^{15} g^{-1} were obtained. With decrease in the size of the particles their concentration increases. According to some authors[94], the paramagnetic centres in quartz are stable at 120°; their concentration decreases linearly in the range 120–360°. According to other data[92], the free radicals produced in quartz are stable as far as 350–400°, so that they can be preserved for a long time at room temperature.

The infrared spectrum of quartz after size reduction[95] showed a peak at 950 cm^{-1} due to the siloxane group SiOH. The production of the peroxo group ≡Si:O:O as a result of the mechanical treatment of quartz has been established[96].

It has been shown[97] that on the surface formed by the size reduction of graphite crystals, the carbon atoms are in two different electronic states—atoms in a bivalent singlet state and atoms forming over-stressed quasi-acetylenic bonds; free radicals containing carbon atoms with broken π- and σ-bonds are also present.

The EPR spectrum of zinc oxide subjected to mechanical treatment has been studied. The spectrum of the original zinc oxide showed two weak signals with $g = 2.006$ and $g = 1.956$, of approximately equal intensity. After the specimen had been ground in a mortar, the EPR spectrum, in place of the singlet with $g = 2.006$, showed a strong unsymmetrical triplet superimposed on a weaker spectrum, from which two components could be seen; with decrease in temperature to −196° these components increased by a factor of 4, whereas the amplitude of the triplet remained almost unchanged. The singlet with $g = 1.956$ decreased by a factor of several times after the substances had been ground. The EPR spectrum produced on grinding remains unchanged when the specimen is exposed to air, on evacuation of 10^{-3} mmHg, on treatment with solvents, or when iodine and quinone are adsorbed on its surface, but it gradually disappears when the specimen is heated above 100° in a vacuum or in air.

The EPR spectra of silicon, germanium, silicon carbides, diamond, the oxides of magnesium, calcium, strontium, and zinc, calcium and zinc sulphides, quartz, and α-alumina have been studied[88,90]. It has been stated[93] that the spectra obtained after mechanical treatment show a similarity to the spectra obtained after the irradiation of substances with fast neutrons. This is observed particularly clearly for magnesium and silicon oxides, for which both mechanical treatment and irradiation with neutrons lead to the formation of an F-centre with identical g-factor for the single signal.

As a consequence of the formation of active centres on the surface, reactions which do not take place under ordinary conditions become possible. An increase in pH and the bonding of atmospheric nitrogen as nitrate and ammonia has been observed on size reduction of sodium chloride. The change in the concentration of hydroxide ions was found to be proportional to the square of the surface area. The authors cited consider that the binding of nitrogen as the compounds on sodium chloride particles produced by the evaporation of sea water is an extremely important source for the accumulation of nitrogen compounds in the atmosphere.

The influence of the mechanical breakdown of crystals (NaCl and $BaSO_4$) on the polymerisation of vinyl monomers has been studied[100]. It has been shown that the initiation of the formation of polymers is brought about by the electron emission arising on breakdown of the crystals (mechano-electrons) and not by static defects in the solid phase (vacancies, colour centres, etc.), obtained by preliminary irradiation of the salts.

IV. MECHANISM OF MECHANOCHEMICAL REACTIONS

1. Physical Phenomena on Grinding

In early work on the mechanochemical reactions of solids[72,101], the chief role was assigned to particles of moisture adsorbed on the surface. It was assumed that there is no fundamental difference between reactions taking place in concentrated solutions and reactions taking place on grinding. It was established[102], however, that there is no relationship between the rate of reaction on grinding and the solubility of a salt. Moreover, it was established that in a number of instances, water decreases the reaction rate. It was found that a more important role in mechanochemical reactions is played by physical processes taking place on contact between solids in friction. The following phenomena are related to these processes.

Liberation of heat. When solids slide together, the greater part of the work done against the forces of friction is liberated in the form of heat. At locally restricted points on the surface, the temperature reaches an extremely high value. Bowden and Tabor[103] showed theoretically and experimentally that in sliding friction the temperature at the points of contact increases as far as the melting point, but never rises above it. For refractory substances, an instantaneous local increase in temperature to 1000°C may be achieved in the surface layer. The main bulk of the substance at this moment remains cold. The duration of existence of these temperature spikes on an area of 10^{-3}–10^{-5} cm is of the order of 10^{-4} s.

Production of high pressures. At the points of contact of friction solids, the production of a high temperature is accompanied by a simultaneous short-lived increase in pressure. The magnitude of this pressure has been estimated[104]. A series of substances for which the pressures (bar) of the phase changes were known were taken: PbO 5500, MnF_2 9500, Sb_2O_3 10 800, SiO_2 13 500, BeF_2 17 500, B_2O_3 18 500, and $BaAsO_4$ 30 000. The substances were ground in a mill, after which the ground products, for all the above substances except $BaAsO_4$, were found to contain the modifications existing at high pressures. On the basis of these data it was concluded that on contact between the solids in the mill, pressures of up to 15 000 bar were developed.

Production of electric charges. On friction between solids, electric charges are produced. The reasons for the production of electric charges on surfaces are varied. According to one view[105], solid dielectrics, because of the presence of structural defects, carry on their surface a charge which is compensated by ions adsorbed from the air. On friction, the compensation of the intrinsic charges is destroyed, and electrification results.

It has been shown[106] that the charges produced on contact between semiconductors and metals are linearly dependent on the difference in the work functions of an electron from the solids in contact.

When the surface of a crystal carries a charge, a space charge with sign opposite to the sign of the charge on the surface is produced in the volume of the crystal in order to preserve its electrical neutrality; this space charge undergoes oscillations (like the oscillation of the charge between the plates of condensers[107]). In large crystals the amplitude of the oscillations of the space charge is small, and the magnitude of the varying potential difference produced on breakdown of the crystal is correspondingly small. As the size of the crystal decreases, the potential difference increases, but for very small crystal dimensions it decreases again. The potential produced on the surface of ionic crystals under the influence of shock or deformation shows a correlation with the plasticity of the crystal[108]. The softer the crystal, the higher the potential, and vice versa.

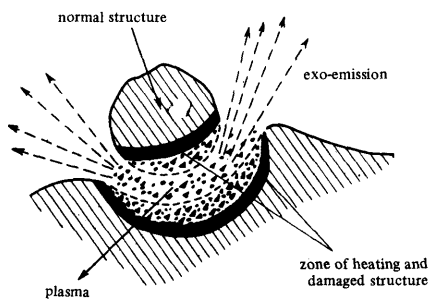


Figure 8. "Magma-plasma" model of mechanochemical processes[4].

Exo-emission and mechano-emission of electrons. In solids at the moment of mechanical treatment and afterwards, mechano-emission and exo-emission of electrons takes place. The electrons of the exo-emission, which is quenched extremely slowly after mechanical treatment, have an energy not greater than 1 eV, [109] whereas the mechano-emission electrons (mechano-electrons) have energies of tens of keV. [110] Exo-electronic emission results from heating, irradiation, chemosorption, etc., that is it is similar to thermal emission with its over-the-barrier removal of electrons. The mechano-electrons obtain their high energy by acceleration in the field of a "micro-condenser", the plates of which are the separated surfaces of the fracture. The electrons tunnel through the barrier, as a consequence of the high electric field.

Triboluminescence. When solids are subjected to size reduction and shock, extremely intense luminescence is produced. Most workers consider that the triboluminescence is associated with electric charges produced between the broken particles[111]. In triboluminescence accompanying the breakdown of ionic crystals in air, the nitrogen spectrum observed is the same as that for an electric discharge.

With allowance for the physical phenomena associated with size reduction, Thiessen and coworkers[4] put forward a "magma-plasma" model of mechanochemical processes (Fig. 8). According to this model, the energy liberated on shock or grinding, as a consequence of the low thermal conductivity of solids, leads not only to a local increase in temperature and sublimation of the substance, but also to the production of a state of the substance in which it exists in the form of ions and electrons (plasma). It was noted above that in the decomposition of substances under the influence of an explosion and on grinding, identical products are obtained. On this basis it may be stated that when a substance is ground, characteristic "micro-explosions" take place on contact between the solids in friction. These results also provide evidence in support of the "magma-plasma" model.

The production of the above phenomena on mechanical treatment brings mechanochemical reactions closer to plasma reactions, and if the treatment is carried out in aqueous medium, conditions are created for hydrothermal reactions.

2. Comparison with Reactions Taking Place Under the Influence of Heat, Light, and Radiation. Mechanochemical Equilibrium

It can be seen from the foregoing that mechanochemical reactions show almost no temperature dependence, whereas the latter is a characteristic feature of reactions taking place under the influence of heat. Another characteristic feature of mechanochemical reactions is that the reactions may take place by a thermodynamically unfavourable route. An example is provided by the decomposition of the alkali metal bromates, which can take place by two reactions:

$$MBrO_3 \rightarrow MBr + {}^3/_2O_2 \ . \qquad (11)$$

$$MBrO_3 \rightarrow {}^1/_2M_2O + {}^1/_2Br_2 + {}^5/_4O_2 \ . \qquad (12)$$

The free energy (T = 298°K) for reaction (11) is negative, and that for reaction (12) is positive. Mechanochemical decomposition, however, takes place almost entirely according to Eqn. (12)[112]. Data for other reactions taking place by a thermodynamically unfavourable route have been published[113].

The tribochemical decomposition of a number of inorganic substances has been studied[64], and a correspondence between the start of the thermal decomposition and the ability to undergo mechanochemical decomposition was not observed. Thus for example, the temperature of the start of decomposition of ammonium chromate is 110°, but it does not decompose on grinding, whereas mercury(I) chromate, for which the temperature of the start of thermal decomposition is 500°, decomposes readily on grinding. A large number of studies[114,115] have shown that the mechanochemical splitting of molecules gives products which have nothing in common with the products of thermal decomposition, and reactions which take place in the opposite direction on heating are possible[6].

In a study of the reaction of copper with water under the influence of mechanochemical activation, it was found that after grinding for 5–6 d, more than 2% of metallic copper reacts with water with the liberation of hydrogen[12]. The equilibrium constants for the reaction of copper with water in the range 298–3000°K are given in Table 1. Calculation shows that even at 3000°K the partial pressure of hydrogen should not exceed 10^{-2} mmHg. The experimental data show that the pressure exceeds the calculated

value by a factor of 1000. It was concluded that the local-heating theory cannot explain the displacement of hydrogen by copper.

Peters[6] showed that the reactions taking place on mechanical treatment are reversible. For example, treatment of zinc oxide in the presence of carbon dioxide leads to the formation of zinc carbonate, whereas dissociation of zinc carbonate takes place on treatment in a vacuum. In recent years, many systems in which mechanochemical reactions take place in both directions have been detected[116]. If the rates of the forward and reverse reactions on mechanical treatment are equal, there is no overall macroscopic change in the system.

Table 1. Thermodynamic calculation of equilibrium constants[12].

Reaction	ΔG, kcal mole^{-1}	k_r, °K			
		298°	1000°	2000°	3000°
$Cu + H_2O_{gas} \rightarrow CuO + H_2$	+24.2	10^{-18}	10^{-17}	10^{-5}	10^{-4}
$2Cu + H_2O_{gas} \rightarrow Cu_2O + H_2$	+19.6	10^{-15}	10^{-5}	10^{-5}	10^{-3}

For purely thermal action, we speak of chemical equilibrium. In contrast to chemical equilibrium, the steady state produced on mechanical treatment is described as mechanochemical equilibrium.

Quantitative data on mechanochemical equilibrium in the system $CdC + CO_2 \rightleftharpoons CdCO_3$ have been obtained[116]. The dependence of the reaction rate on the carbon dioxide pressure and the composition of the solid phase are shown in Fig. 9. A positive value of the ordinate denotes the forward reaction, and a negative value the back reaction. For different compositions of the solid phase, the reaction rate becomes equal to zero at different CO_2 pressures. This steady state can be reached from two directions. Fig. 9 shows that mechanochemical equilibrium differs from chemical equilibrium. The position of chemical equilibrium does not depend on the concentration of carbonate in the solid phase. According to Gibbs' phase rule, in the carbonate system $MCO_3 + MO + CO_2$, each temperature corresponds to a definite CO_2 pressure. Thus the equilibrium pressure for the $CdCO_3 + CdO + CO_2$ system is $p_{CO_2} = 133 \times 10^{-6}$ mmHg at 298°K, whereas for the carbonate subjected to preliminary mechanical treatment $p_{CO_2} = 1.7$ mmHg at 298°K. It can be seen from Fig. 9 that on mechanical treatment the pressure corresponding to mechanochemical equilibrium depends markedly on the composition of the material undergoing size reduction. With change in the concentration of $CdCO_3$ from 50 mole % to 90 mole % the equilibrium pressure of CO_2 increases by approximately two orders of magnitude. For pure cadmium carbonate at mechanochemical equilibrium the CO_2 pressure is $p_{CO_2} =$ 660 mmHg at 298°K.

The next difference between mechanochemical and chemical equilibrium is that its maintenance requires the irreversible introduction of mechanical energy into the system. In this respect, mechanochemical processes are similar to photochemical and radiochemical processes.

As shown above, radical formation is possible when inorganic solids are ground. The first stage in a mechanochemical reaction may therefore be bond rupture and the formation of free radicals, the second stage being the reaction of the free radicals. Thus in some instances the overall picture of mechanochemical transformations shows features in common with radiochemical reactions[117].

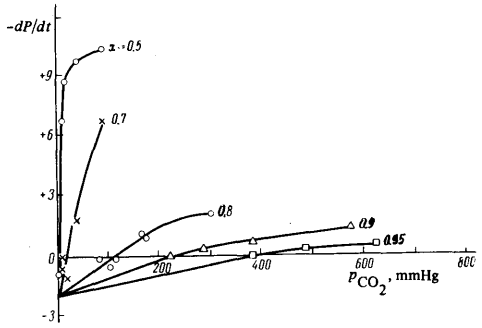


Figure 9. Dependence of the rate of reaction in the $CdO + CO_2 \rightarrow CdCO_3$ system on the pressure of CO_2 and the composition of the solid phase[116] (x is the mole fraction of $CdCO_3$).

The mechanochemical decomposition of alkali and alkaline earth metal nitrates, and the decomposition of sodium nitrate in the presence of heterophase (metal oxides) and homophase (added by cocrystallisation) additives have been studied[66] in order to compare the results with thermal, radiochemical, and photochemical decomposition. The results showed that, as in radiation decomposition, a correlation is observed in mechanochemical decomposition between the degree of decomposition and the free volume. The correlation is less distinct, however, than that for radiation decomposition. A correlation between the degree of mechanochemical decomposition and the order of the thermal stabilities of these compounds is not observed, however. An analogous picture is observed when the action of homophase and heterophase additives is compared.

3. Characteristic Kinetic Features of Mechanochemical Reactions. The Role of Non-equilibrium States

Since the decomposition of molecules on mechanical treatment takes place chiefly in the surface layers and the layers next to the surface, the rate of the mechanochemical decomposition of molecules is determined in the initial stages of size reduction by the rate of increase in the surface area, which depends on the nature of the substance undergoing size reduction and also on the type of size-reducing apparatus. After the particle radius during size reduction has decreased to the thickness of the surface layer, a constant maximal rate of decomposition is established. As a consequence of the recrystallisation which takes place on size reduction, however, a decrease in the rate of mechanochemical decomposition may take place after the maximum rate has been reached. If during size reduction conditions are created for the reverse reaction (for example through the difficulty of removing reaction products from molecularly compact aggregates), a state of mechanochemical equilibrium is established.

To explain the nature of the process of bond rupture in mechanically stressed molecules, Zhurkov[118] suggested that under the influence of stress, the F-energy [dissociation energy? (Ed. of Translation)] of the bond Q decreases by an amount of energy ϵF, and the rate constant for bond rupture k increases according to the equation

$$k = k_0 \exp\left(-\frac{Q - \epsilon F}{RT}\right) \quad (13)$$

where k_0 is a constant, with order of magnitude close to that of the vibrational frequency ($\sim 10^{13}$ s^{-1}).

It was shown above that the rate of mechanochemical processes either is weakly dependent on temperature or is characterised by a negative temperature coefficient[119], so that Eqn. (13) is not applicable in all instances.

To explain the nature of mechanochemical processes, Butyagin[120] introduced the concept of non-equilibrium states of bonds in molecules. This makes it possible to explain why small energies are sufficient to bring about mechanochemical decomposition (this differs from the "magma-plasma" model, according to which mechanochemical decomposition takes place as a consequence of the liberation of large amounts of energy on contact between colliding particles).

On mechanical treatment the energy of deformation of a bond is converted into thermal energy and redistributed between other bonds. This excess energy, the magnitude of which is much smaller than the bond strength, may be sufficient for the rupture of bonds present in a non-equilibrium state. On the basis of this assumption, Butyagin obtained an equation for the rate constant of the mechanochemical reaction, of the following form

$$k = A \exp\left(-\frac{E_M^*}{\Delta E_M}\right) \quad (14)$$

where A is a coefficient which takes account of the rate of redistribution of the mechanical energy in the system, E_M^* is the minimal mechanical energy required for bond rupture, and ΔE_M the average level of the excess energy.

It is assumed that on mechanical treatment of a substance, the rate of absorption of the mechanical energy supplied is to a first approximation proportional to the intensity of its introduction I, and the rate of relaxation of the stresses is proportional to the average level of the excess energy ΔE_M. In the steady state the rates of the two processes are equal, that is

$$\gamma I - k_r \Delta E_M = 0 \quad (15)$$

where γ is a dimensionless coefficient which takes account of the efficiency of absorption of the mechanical energy, and k_r the rate constant for the relaxation of the stresses. With allowance for Eqn. (15), Eqn. (14) becomes

$$k = A \exp\left(-\frac{k_r E_M^*}{\gamma I}\right). \quad (16)$$

If the dependence of the rate constant of a mechanochemical reaction on the quantity of mechanical energy introduced is determined, the values of A, E_M, and k_r can be calculated from Eqn. (16). Experimental data on the mechanochemical decomposition of polymethyl methacrylate and quartz, treated by means of Eqn. (16), give values of A 10^{-3}–10^{3}, $E_M^* \sim 10$–10^2 kcal, $\gamma \sim 1$–10^{-3}, and $k_r \sim 10^{-1}$–10^{-4} s^{-1}. It can be seen that E_M^* is much smaller than the bond energy Q, and A differs from k_0 by several orders of magnitude.

Analogous concepts were used by Bartenev and Razumovskaya[121] to develop the concept of the phonon breakdown of brittle solids. They consider that in the breakdown of solids it is necessary to examine not the thermal vibrations of the atoms but the propagation, interaction, and generation of phonons. The stages in the breakdown of a solid (the first is the formation of defects, and the second the growth of micro-cracks from these defects) can be regarded as independent processes only in the initial period. As the defects develop, the energy liberated on rupture leads to an increase in the density of phonons of definite frequencies (non-equilibrium phonons). This energy source influences both the development of the actual defect generating the phonons, and also the development of neighbouring defects.

There is thus a fundamental difference between the rupture of bonds in a solid and the rupture of bonds between isolated atoms in a molecule. The change to the phonon concept makes it possible, as the authors cited assert, to introduce for each structure a characteristic spectrum, which can be obtained experimentally, and also to use the achievement of the modern quantum theory of solids to develop a theory of breakdown processes.

V. PRACTICAL ASPECTS OF MECHANOCHEMISTRY

It follows from the foregoing that mechanochemical phenomena touch on a wide range of problems of practical interest. The utilisation of mechanochemical processes is proceeding along the following lines.

Intensification of dissolution and leaching processes. The conversion of sparingly soluble substances into a soluble state, usually carried out by heating with concentrated acids or alkali, or by fusion with active components (sodium carbonate, alkali, hydrogen sulphate, etc.) can be accelerated by mechanochemical treatment of the components to be dissolved. An increase in solubility under the influence of mechanochemical treatment is observed for many inorganic substances of practical importance. Data on the increase in solubility under the influence of mechanochemical activation for various substances are given in Table 2.

Increase in the rate of decomposition and synthesis. The problem of increasing the rates of chemical reactions is extremely important, particularly for solid-phase reactions. The reaction product formed at the contact between the granules has a blocking influence on solid-phase reactions. When the reaction is carried out under conditions of intensive mechanical treatment, the reaction product is removed and the surface is renewed, with a consequent significant increase in reaction rate. Moreover, the preliminary mechanochemical treatment of substances not only can provide a means of preparing substances to increase the rate of a reaction, for example with heating, but also can provide an independent and the only possible method of decomposing or preparing substances. Examples of processes which it has been possible to carry out by means of mechanical activation are the preparation of rongalite[126], phosphors[82], metallates[81], organometallic compounds[83], complex compounds[4], catalysts[75,76,127], etc.

Activation of catalysts. On mechanical treatment, the activity of catalysts changes not only as a result of a change in the surface but also as a result of the fact that some of the kinetic energy of the solids in friction is

transferred to the surface. The stresses created in the surface layers are sufficient for breakdown of the structure and rearrangement of the atoms and molecules to form less ordered structures exhibiting a higher potential energy than the ordered crystal structure.

Table 2. Increase in the solubility of inorganic substances under the influence of mechanochemical activation.

Substance	Solvent	Duration of grinding in mill, h	Duration of dissolution, h	Quantity transferred to solution, % of original	Refs.
α-Al_2O_3 (fused)	3*N* NaOH	0	1 (70°)	0	39
		50		8	
		100		14	
		150		22	
		200		28	
SiO_2	H_2O	0	1200	0	28
		0.033		0.10	
		0.066		0.14	
		0.132		0.18	
		0.264		0.27	
SnO_2	18% HCl	12	0.5 (60—80°)	6.9	40
		25		21.2	
		47		29.8	
		72		43.7	
		152		70.0	
		210		80.2	
		300		100	
SnO_2	10% NaOH	12	0.5 (60—80°)	8.7	
		25		25.0	
		47		28.0	
		72		40.4	
		152		63.5	
		210		78.0	
		300		100	
Bauxite (Al_2O_3—48%, Fe_2O_3—22%, SiO_2—7.4%, TiO_2—2.4%)	30% NaOH	0	0.5	3	122
		0.5		22	
		1.0		48	
		2.0		66	
		3.0		72	
		5.0		82	
		7.0		90	
		10.2		100	
Bauxite (Al_2O_3—58%, Fe_2O_3—26%, SiO_2—1%, TiO_2—2%)	30% NaOH	0	2	0.15	23
		20		75	
Kaolin (Al_2O_3—43%, SiO_2—54.2%, K_2O—1.65%)	1 *N* HCl	0	1 (100°)	10	123
		400		20	
		600		40	
		1000		50	
Wolframite (Fe, Mn)WO_4	30% HCl	0	1	32	124
		10		48	
		20		67	
		60		73	
		120		80	
		360		84	
Olive titanomagnetite (Fe_3O_4—27%, $FeTiO_3$—15%)	15*N* H_2SO_4	0	—	34 0	125
		5		60 10	
		30		90 30	
		100		95 60	
		200		95 90	

Study of the catalytic activity of nickel oxide [128] and zinc oxide [129] established that the catalytic activity increases with increase in the degree of subdivision. It was shown that the catalytic activity changes in step with the breakdown of the crystal lattice.

The dependence of the catalytic activity of α-Fe_2O_3 on the duration of mechanical treatment passes through a maximum. According to Schrader [130], the activity of α-Fe_2O_3 at the maximum (grinding for 16 h) in the oxidation of carbon monoxide to carbon dioxide is greater than the activity of the original catalyst by a factor of 5. Analogous data were obtained for catalysts such as copper oxide [131], magnesium oxide [132], alumina [133], etc. [134-137].

The influence of mechanical treatment on the temperature of reduction of oxides has been studied [138]. After treatment for 20 h, the temperature of the start of reduction was decreased by 80 deg for Fe_2O_3, 75 deg for Fe_3O_4, 50 deg for NiO, and 40 deg for CuO.

Mechanical treatment also alters considerably the properties of complex catalysts. It has been shown [139] that prolonged grinding of an aluminosilicate catalyst alters its acidic properties, leading to a decrease in the catalytic activity of the catalyst in the depolymerisation of paraldehyde in benzene solution. Annealing of a catalyst treated in this way leads to the restoration of its activity. Infrared spectroscopic data indicate that water molecules, bonded to the surface by hydrogen bonds, appear on the catalyst surface during size reduction.

The use of mechanochemical treatment for the preparation of new catalysts also appears promising. This method has been used, for example, to prepare a mixed vanadium—molybdenum—aluminium catalyst, used for the oxidation of acrolein, with increased activity and selectivity [75], iron and zinc ferrites [77], etc.

Preparation of substances with new properties. Mechanochemical treatment can be used to solve problems in the modification and improvement of the properties of such substances as adsorbents, zeolites, binding agents, etc. The ability of kaolin to form zeolites on grinding has been studied [140]. It has been established [142] that on dispersion, aluminosilicates are converted into minerals of the kaolinite group. The mechanochemical technology of the production of binding agents from industrial wastes is being developed [143].

Separation of elements with similar properties and the components of complex mixtures. A procedure has been proposed [29] for the extraction of titanium from titanium magnetic ores by mechanical treatment followed by thermal treatment and dissolution in hydrochloric acid. After these operations, TiO_2 passes into solution, and iron(II) oxide is converted into insoluble iron(III) oxide.

A method for separating pyrite and haematite by grinding a mixture of these minerals in the presence of ammonium nitrate has been proposed [72]. On grinding, pyrite is converted into acid-soluble iron sulphate, and haematite remains in the insoluble residue. This operation can be used to separate other substances, for example lead from iron, etc.

Elements with similar properties can also be separated by making use of differences in the rates of their mechanochemical decomposition.

Improvement of existing technological processes. Mechanochemical reactions take place in chemical technology during the size reduction of substances and their mixtures at ordinary temperatures. Little attention has been paid to these reactions until now. For example, before flotation, pyrite is subjected to size reduction in the presence of moisture and atmospheric oxygen. Size reduction is accompanied by the formation of water-soluble oxidation products (sulphates, sulphides, hydroxides, oxides, etc.), and these are lost on flotation [144]. Analogous losses take place in the processing of other mineral products.

Mechanochemical methods of activating a substance in order to increase solubility, separate substances, etc. are also promising in that they make it possible to reduce the consumption of water, a shortage of which has recently been noted. Certain preparations which are usually carried out in aqueous or organic media can be carried out in the solid phase. The reduction of, for example, metals from their sulphides [145] and oxides, etc., can be carried out in this way.

In conclusion it may be noted that despite the fact that the theoretical interpretation of mechanochemical phenomena, because of the complexity of the processes taking place and the restricted nature of the methods for studying them, is extremely far from complete, mechanochemistry has already progressed beyond the trial stage and is providing a means of solving fundamental problems facing chemistry, such as the development of methods for decomposing and preparing substances, and methods for the directed control of chemical reactions.

REFERENCES

1. A. A. Berlin, Uspekhi Khim., 27, 94 (1958).
2. N. K. Baramboim, Uspekhi Khim., 28, 877 (1959).
3. N. K. Baramboim, "Mekhanochimiya Polimerov" (The Mechanochemistry of Polymers), Izd. Khimiya, 1963.
4. P. Thiessen, G. Mayer, and K. Heinicke, Grundlagen der Tribochemie, Berlin, 1967.
5. A. K. Simionescu and K. Oprea, "Mekhanokhimiya Vysokomolekulyarnykh Soedinenii" (Mechanochemistry of Macromolecular Compounds), Izd. Mir, Moscow, 1970.
6. K. Peters, "Trudy Evropeiskogo Soveshchaniya po Izmel'chaniyu" (Proceedings of the European Conference on Size Reduction), Moscow, 1966, p. 80.
7. K. Kubo, J. Chem. Soc. Japan, 71, 1301 (1968).
8. E. M. Gutman, Fiz.-Khim. Mekh. Materialov, 3, 264 (1967).
9. E. M. Gutman, Fiz.-Khim. Mekh. Materialov, 3, 550 (1967).
10. E. M. Gutman, Fiz. i Khim. Obrabotki Materialov, 5, 143 (1969).
11. E. M. Gutman, Poroshkovaya Metallurgiya, No. 4, 80 (1970).
12. G. Heinicke and H. Harenz, Schmierstoffe und Schmiertechnik, 4, 30 (1968).
13. G. S. Khodakov, Uspekhi Khim., 32, 860 (1963) [Russ. Chem. Rev., No. 7 (1963)].
14. G. Jimbo, J. Chem. Soc. Japan, 71, 1309 (1968).
15. W. F. Giauque, J. Am. Chem. Soc., 71, 3192 (1949).
16. G. Naeser, W. Scholz, and A. Fiedler, Kolloid. Ztschr., 188, 147 (1963).
17. V. A. Kireev, Izv. Sektora Fiz.-Khim. Anal. Inst. Obshch. Neorg. Khim. Akad. Nauk SSSR, 19, 136 (1949).
18. A. Mittasch, Ztschr. Phys. Chem., 40, 11 (1902).
19. H. Freundlich, "Kapillarchemie", Leipzig, 1920, ctp. 143.
20. L. F. Knapp, Trans. Faraday Soc., 17, 457 (1922).
21. M. L. Dundon and E. Mack, J. Am. Chem. Soc., 45, 2479 (1923).
22. M. L. Dundon, J. Am. Chem. Soc., 45, 2658 (1923).
23. V. V. Boldyrev, "Metody Izucheniya Kinetiki Reaktsii Termicheskogo Razlozheniya Tverdykh Veshchestv" (Methods for Studying the Kinetics of the Thermal Decomposition of Solids), Izd. Tomsk. Univ., 1958.
24. O. M. Todes, Zhur. Fiz. Khim., 14, 1224 (1940).
25. G. A. Razumov, B. N. Brounshtein, and A. A. Kale, "Trudy Gosudarstvennogo Instituta Prikladnoi Khimii" (Proceedings of the State Institute of Applied Chemistry), 1963, p. 170.
26. V. V. Boldyrev and V. I. Eroshkin, Zhur. Vses. Khim. Obshch. im. D. I. Mendeleeva, 6, 704 (1964).
27. R. Schrader and G. Jacob, Chem. Technik, 18, 414 (1966).
28. H. Takahashi and K. Tsutsumi, Bull. Chem. Soc. Japan, 40, 542 (1967).
29. G. S. Khodakov and Z. P. Plutsis, Dokl. Akad. Nauk SSSR, 123, 725 (1958).
30. E. von Szantho, "Trudy VIII Mezhdunarodnogo Kongressa po Obogashcheniyu Poleznykh Iskopaemykh" (Proceedings of the Eighth International Congress on the Concentration of Minerals), Leningrad, 1968.
31. U. Schneider, Aufbereit. Techn., 9, 567 (1968).
32. P. A. Rebinder, Zhur. Tekh. Fiz., 2, 726 (1932).
33. G. S. Khodakov and P. A. Rebinder, Dokl. Akad. Nauk SSSR, 127, 1070 (1959); 131, 1366 (1960).
34. G. S. Khodakov and P. A. Rebinder, Koll. Zhur., 22, 365 (1960); 23, 482 (1961).
35. A. G. Smekal and J. A. Hedvall, Proc. of Inter. Sympos. on Reactivity of Solids, Goteburg, 1952, ctp. 131.
36. F. Puchegger, Naturwiss., 39, 428 (1952).
37. R. Schrader and W. Dusdort, Kristall und Technik, 1, 59 (1966).
38. R. Schrader, Vortrag auf der Deutschen Vereinigung für Kristallografie in Leipzig, 1966.
39. T. Shirasaki and Y. Ochiai, J. Chem. Soc. Japan, 71, 1363 (1968).
40. R. Paudert, S. Liebscher, and W. Trinks, Chem. Techn., 19, 356 (1967).
41. R. Schrader, "Trudy II Vsesoyuznogo Soveshchaniya po Mekhanokhimii i Mekhanoemissii" (Proceedings of the Second All Union Conference on Mechanochemistry and Mechano-emission), Izd. ILIM, Frunze, 1971.
42. M. Natarajan, A. R. Das, J. C. Ahluwalia, and C. N. R. Rao, Trans. Faraday Soc., 65, 3081 (1969).
43. R. Schrader and B. Hoffman, Ztschr. anorg. allgem. Chem., 369, 41 (1969).
44. M. A. Short and E. G. Steward, Ztschr. Phys. Chem., 13, 298 (1957).
45. E. Zielinski, Roczn. Chem., 27, 207 (1953).
46. K. Hashimoto and Y. Toda, J. Chem. Soc. Japan, 71, 1402 (1968).
47. W. Kaufmann, Chem. Ztg., 81, 43 (1957).
48. N. H. Kolmeijer and J. V. A. van Hengel, Ztschr. Krist., 88, 317 (1934).
49. M. A. Bredig, J. Phys. Chem., 46, 801 (1943).
50. G. L. Clark and R. J. Rowan, J. Am. Chem. Soc., 63, 1302 (1941).
51. J. Hume and J. Colvin, Phil. Mag., 8, 589 (1929).
52. P. P. Vaimarn, Zap. Gorn. Inst., Coll., 4, 139 (1913).
53. G. M. Gusev and A. V. Nikolaev, Dokl. Akad. Nauk SSSR, 182, 343 (1968).
54. F. Seitz, Phys. Rev., 80, 239 (1950).
55. L. Vegard and T. Hauge, Ztschr. Phys., 42, 1 (1927).
56. F. M. Acampora, A. S. Tompa, and N. O. Smith, J. Chem. Phys., 24, 1104 (1956).
57. F. D. Klement and R. I. Gindina, "Issledovaniya po Lyuminestsentsii, Trudy Instituta Fizika i Astronomii Akademii Nauk Estonskoi SSR" (Studies on Luminescence, Proceedings of the Institute of Physics and Astromomy of the Academy of Sciences of the Estonian SSR), 1956.

58. M. Carey Lea, Am. J. Sci., 46, 241 (1893).
59. F. M. Flavitskii, Zhur. Russ. Fiz.-Khim. Obshch., 34, 8 (1902).
60. H. Grohn, R. Paudert, and H. J. Bisinger, Ztschr. Chem., 2, 88 (1962).
61. J. C. Jamieson and J. R. Goldsmith, Am. mineralogist, 45, 818 (1960).
62. F. P. Bowden, P. G. Fox, and J. Soria-Ruiz, Nature, 220, 778 (1968).
63. G. M. Gusev, V. M. Klyarovskii, and V. I. Molchanov, "Geologiya i Geofizika" (Geology and Geophysics), 1969, p. 109.
64. G. T. Afanas'ev and V. K. Bobolev, "Initsiirovanie Tverdykh Vzryvchatykh Veshchestv Udarom" (The Initiation of Explosives by Shock), Izd. Nauka, Moscow, 1968.
65. V. V. Sviridov and G. A. Branitskii, "Geterogennye Khimicheskie Reaktsii" (Heterogeneous Chemical Reactions), Minsk, 1961.
66. V. V. Boldyrev, E. G. Avvakumov, I. V. Shmidt, and L. I. Strugova, in Ref. 41.
67. E. G. Avvakumov, V. V. Boldyrev, L. I. Strugova, and I. V. Shmidt, Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim., No. 9, Part 4, 130 (1971).
68. S. Roginskii and E. Shul'ts, Ukrain. Khim. Zhur., 3, 177 (1928).
69. A. N. Dremin and O. N. Breusov, Uspekhi Khim., 37, 898 (1968) [Russ. Chem. Rev., No. 5 (1968)].
70. V. V. Boldyrev, E. E. Zarko, and A. A. Deribas, Khim. Vysokikh Energii, 1, 177 (1967).
71. L. Lecuir and H. Bilde, C. r., 251, 477 (1950).
72. P. I. Isakov, "Kachestvennyi Analiz Rud i Mineralov Metodom Rastiraniya Poroshkov" (The Qualitative Analysis of Ores and Minerals by the Grinding of Powders), Gosgeoltekhizdat, Moscow, 1955.
73. V. V. Boldyrev, E. G. Avvakumov, and G. M. Gusev, Dokl. Akad. Nauk SSSR, 184, 119 (1969).
74. E. Montignie, Bull. Soc. Chim. France, 747 (1947).
75. G. Heinicke, N. Bock, and H. Harenz, Ztschr. anorg. allg. Chem., 372, 162 (1970).
76. G. Heinicke and H. Harenz, Ztschr. anorg. allg. Chem., 324, 185 (1963).
77. G. Heinicke, H. Harenz, and K. Sigrist, Ztschr. anorg. allg. Chem., 352, 168 (1967).
78. T. Shirasaki, Y. Ochiai, and K. Muranaka, J. Chem. Soc. Japan, 71, 1368 (1968).
79. Y. Morita, M. Saito, Y. Takemura, and K. Yamamoto, J. Chem. Soc. Japan, 71, 1453 (1968).
80. R. Kiriyama, Y. Tamai, and F. Kanamura, Nippon Kagaki Zasshi, 88, 618 (1967).
81. H. Takahashi, Dechema-Monographien, 57, 475 (1968).
82. T. Kubo, M. Kato, Y. Mitarai, I. Takahashi, and K. Ohkura, J. Chem. Soc. Japan, 66, 318, 403 (1963).
83. H. Grohn and R. Paudert, Ztschr, für Chemie, 3, 89 (1963).
84. P. I. Voskresenskii, "Analiticheskie Reaktsii Mezhdu Tverdymi Veshchestvami i Polevoi Khimicheskii Analiz" (Analytical Reactions Between Solids and Chemical Analysis in the Field), Moscow, 1963.
85. K. Peters and S. Pajakoff, Mikrochemica et ichnanalytica Acta, 449 (1964).
86. P. A. Thiessen, Ztschr. für Chemie, 5, 162 (1965).
87. H. Grohn and R. Paudert, Ztschr. für Chemie, 3, 89 (1963).
88. R. Rasch, Ber. Deut. Keram. Ges., 40, 635 (1963).
89. G. G. Heinicke, R. Riedel, and H. Harenz, Ztschr. Phys. Chem., 227, 62 (1964).
90. P. Yu. Butyagin, A. A. Berlin, A. E. Kolmanson, and L. A. Blyumenfel'd, Vysokomol. Soed., 1, 865 (1959).
91. M. Voland, R. Schrader, and H. Scheider, Ztschr. anorg. allgem. Chem., 365, 317 (1969).
92. A. E. R. Ots, A. Ya. Pae, and L. E. Wibs, in Ref. 41.
93. J. Arends, A. J. Dekker, and W. G. Perdok, Phys. stat. Solidi, 3, 2275 (1963).
94. G. K. Walkers and T. L. Estle, J. Appl. Phys., 32, 1854 (1961).
95. R. Soda, Bull. Chem. Soc. Japan, 34, 1491 (1961).
96. R. Schrader, G. Glock, and K. Koehnke, Ztschr. für Chem., 4, 156 (1969).
97. V. F. Kiselev, N. N. Lezhnev, and O. V. Nikitin, in Ref. 41.
98. V. V. Golubev and V. V. Evdokimov, Zhur. Fiz. Khim., 38, 477 (1964) [Russ. J. Phys. Chem., No. 2 (1964)].
99. H. M. Papee and G. L. Petriconi, Nature, 195, 4847, 1183 (1962).
100. L. D. Uzhinova, N. P. Plate, and V. V. Golubev, in Ref. 41.
101. E. Montignie, C. r., 192, 416 (1931).
102. V. V. Boldyrev and Yu. E. Eremeeva, Uch. Zap. Tomsk. Gos. Univ., No. 29, 27 (1959).
103. F. P. Bowden and D. Tabor, "Friction and Lubrication of Solids" (Translated into Russian), Mashgiz, Moscow, 1968.
104. F. Dachille and R. Roy, Nature, 186, 34 (1960).
105. M. I. Kornfel'd, Fiz. Tverd. Tela, 11, 1611 (1969).
106. M. M. Bredov and N. B. Kshemyanskaya, Zhur. Tekh. Fiz., 27, 921 (1957).
107. K. M. Khalilov, Ya. M. Palagoshvili, A. I. Agaev, and V. M. Zuev, Fiz. Tverd. Tela, 10, 2987 (1968).
108. A. A. Urusovskaya, G. F. Dobrzhanskii, N. A. Sizova, V. G. Govorkov, and Yu. P. Martynov, Kristallografiya, 13, 1032 (1968).
109. "Collected Papers on Exo-electronic Emission" (Translated into Russian), Inostr. Lit., Moscow, 1962.
110. A. M. Polyakov, in Ref. 41.
111. L. M. Belyaev, Yu. P. Martynov, and V. V. Nabatov, "Fizika Shchelochnogaloidnykh Kristallov" (The Physics of Alkali Halide Crystals), Rigs, 1965.
112. E. G. Awwakumow, V. V. Boldyrew, H. Harenz, G. Heinicke, and L. J. Strugowa, III Symp. für Triebochemie, Berlin, 1971. p. 14.
113. G. Heinicke, Wissenschaft Fortschritt, 14, 163 (1964).
114. K. Bischof, Intern. Chem. Engr., 3, 80 (1963).
115. V. A. Zakrevskii, V. V. Baptizmanskii, and E. V. Tomashevskii, in Ref. 41.
116. G. Heinicke and K. Sigrist, Monatsber. Dtsch. Acad. Wiss., Berlin, 11, 44 (1969).
117. I. V. Kolbanev and P. Yu. Butyagin, in Ref. 41.
118. S. N. Zhurkov, Vestnik Akad. Nauk SS[illegible], No. 11, 78 (1957).
119. N. K. Baramboim, Zhur. Fiz. Khim., 32, 1248 (1958).
120. P. Yu. Butyagin, Vysokomol. Soed., 9, 136 (1967).
121. G. M. Bartenev and I. V. Razumovskaya, Fiz.-Khim. Mekh. Materialov, 5, 60 (1969).
122. R. Schrader, H. Rump, and R. Kressner, Chem. Ing. Technik, 39, 843 (1967).
123. S. J. Gregg, T. W. Parker, and M. J. Stephens, Appl. Chem., 4, 666 (1954).
124. R. Schrader, Ztschr. für. Chemie, 7, 434 (1967).
125. E. V. Szantho, I. Gerlach, and E. Gock, Chem. Ing. Technik, 41, 849 (1969).
126. I. Kunin and M. A. Vlasov, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 4, 638 (1961).
127. A. Krause, Roczn. Chem., 29, 201 (1955).

128. Y. Sadahiro and K. Shimizu, J. Chem. Soc. Japan, 71, 1374 (1968).
129. H. Takahashi and K. Tsutsumi, J. Chem. Soc. Japan, 71, 1345 (1968).
130. R. Schrader, Abhandl. Deutsch. Akad. Wissenschaften, Berlin, Kl. Chem. Geol., Biol., No. 5, 49 (1966).
131. R. Schrader, Silicat, Techn., 18, 8 (1967); 19, 6 (1968).
132. R. Scrhader and H. Rump, Ztschr. anorg. allgem. Chem., 350, 137 (1967).
133. R. Schrader, Ztschr. anorg. allgem. Chem., 343, 308 (1966).
134. R. Schrader, M. Arnold, and H. Rump, Ztschr. anorg. allgem. Chem., 350, 120 (1967).
135. R. Schrader, Ztschr. Phys. Chem., 227, 62 (1964).
136. R. Schrader, Silicat. Techn., 18, 8 (1967); 19, 6 (1968).
137. R. Schrader, Acta Chem. Acad. Scient. Tomus, 55, 39 (1968).
138. G. Naeser and W. Scholz, Kolloid Ztschr., 156, 1 (1958).
139. T. Shirasaki, M. Okada, and F. Sugamima, J. Chem. Soc. Japan, 72, 1198 (1969).
140. H. Takahashi, J. Chem. Soc. Japan, 32, 235 (1959); 32, 381 (1959).
141. J. Motooka, Hashizume, and M. Kobayashi, J. Chem. Soc. Japan, 71, 1412 (1965).
142. G. M. Gusev, in collected papers "Fiziko-Khimicheskie Izmereniya Mineralov v Protsesse Sverkhtonkogo Izmel'cheniya" (Collected Papers on Physicochemical Changes in Minerals During Superfine Size Reduction), Izd. Nauka, Novosibirsk, 1966.
143. A. T. Logvinenko and M. A. Savinkina, in Ref. 41.
144. V. A. Malinovskii, Tsvetnye Metally, 4, 38 (1933).
145. V. I. Molchanov, Dokl. Akad. Nauk SSSR, 182, 445 (1968).

Institute of Chemical Kinetics and Combustion,
Siberian Division,
Academy of Sciences of the USSR,
Novosibirsk