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Structural Disorder and Mechanochemical Reactions in Solids

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The present review is devoted to an analysis of the relationship between the changes in the structure and reactivity of solids, brought about by the development of a deformation. It has been shown that the principal regular features of mechanochemical transformations are determined by the extent of the structural disorder, the processes involved in its relaxation with the liberation of stored energy, and the mobility of the atoms. The part played by each of these factors has been examined for mechanically activated chemisorption, the ionisation of structural defects, the production of various non-equilibrium states on relaxation, the excitation of the mobility of the structure with the intensification of diffusion-controlled reactions, etc. The bibliography contains 87 references.

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I. INTRODUCTION

Deformation is the first response of a solid to the action of external mechanical forces. The external changes in the shape and dimensions of the solid reflect the changes in the order of the arrangement of the atoms, that is the structure of the substance with the development of the deformation. The nature of the internal changes depends on the type of solid and on the conditions of mechanical loading. They may be restricted to an increase or decrease in the interatomic distances, new defects (point, line, plane) may be produced, the type of crystal lattice may change, and in the limit the crystal may be transformed to an amorphous mass or, on the contrary, an amorphous substance may crystallise on deformation. Structural changes inevitably influence the structure-sensitive properties of a substance—its reactivity and transport phenomena (diffusion, thermal conductivity, electrical conductivity, etc.).

From the mechanochemical viewpoint, three aspects of these changes are important.

1. The structural disorder in the substance. The appearance of vacancies, interstitial atoms, and dislocations, which act as centres for the development of topochemical transformations, the production of broken bonds, which initiate various reactions, including chain processes, and the creation of chemically active freshly formed surfaces represent the most familiar examples illustrating the role of structural defects in the mechanical activation of solid reagents.

2. The second factor is structural relaxation, involving the most varied processes, which often have unexpected consequences. The wide variety of relaxation phenomena was revealed after the processes of deformation and breakdown in solids began to be studied by modern electrophysical and optical methods. The emission of fast electrons (with energy up to several keV, the Deryagin effect) and slow

electrons, mechanoluminescence, radiation in the radio and X-ray ranges, acoustic emission, the decomposition of a substance with the ejection of atoms and molecular fragments, and other phenomena have been discovered. It cannot yet be stated that all these phenomena are direct consequences of relaxation processes, but for each of them there exists at least one hypothesis relating the observed effect to the production, movement, and disappearance of structural defects. It should be noted that the energy liberated when defects disappear may reach several eV, that is it is quite sufficient for electronic excitation, ionisation, or bond rupture.

3. No less important is the third factor, which can be called the mobility or dynamics of the structure. In the development of a deformation, the new structure not only is formed, but also "lives". The internal stresses are weakened, and the forces of interatomic, intermolecular, or interionic interaction in the crystal are modified. Point defects are produced and displaced, dislocations multiply and move, grain boundaries are displaced, cracks appear and grow, etc. The mobility of the structure in the development of a deformation creates extremely favourable conditions for solid-phase chemical reactions.

Under real conditions, all three factors involved in the effect of deformation on the reactivity of a substance operate simultaneously. When the deformation of a substance and a chemical reaction are separated by an appreciable time interval, sufficient for the completion of relaxation processes, only the first factor—the existence of a changed structure in the substance—operates. The increase in reactivity due to stable changes in the structure of a substance is usually called mechanical activation.

There are also processes in which the principal rôle is played by the last factor, that is the mobility of the structure; these are associated with the intensification of chemical transformations in substances, where a reaction is possible, but the thermal motion, including translational diffusion, is completely "frozen", and the mobility of the particles, required for the reaction to take place, is brought about only by plastic deformation. The basic literature can be found in monographs, collected papers, and reviews.[1-20] The part played by structural disorder, its relaxation, and mobility in mechanochemistry is examined below for specific examples.

To compare the efficiencies of the action of the above factors, it is necessary to know the energy yield of the corresponding processes, since it is only in energy units that it is possible to compare the emission of electrons, the production of dislocations, luminescence, and chemical transformations. The measurement and calculation of these energy yields, which represent the quantitative basis of mechanochemistry, have not yet been sufficiently recognised; an exception is provided by ultrasonic chemistry.[21]

II. STRUCTURAL DISORDER

The treatment of various materials in mechanochemical reactors (apparatus for fine subdivision, the application of shock waves or pressure, shear combined with deformation, etc.) is accompanied by the production of structural disorder, which is preserved partly or completely for a fairly long time interval after the mechanical treatment has stopped. A clear and distinct indication of the extent of structural breakdown is provided by the change in the density of a substance after mechanical treatment. In quartz, the density decreases from 2.4 g cm^{-3} to 2.2 g cm^{-3},[13,22] corresponding to an increase in free volume by 8–9%. (For comparison it may be noted that the natural free volume of polymeric glasses is close to 2.5%.) These data reflect the state of quartz some time after mechanical treatment, when the structure has partly relaxed. During the development of the deformation, the extent of the decrease in the density of the substance is even greater, and the layer next to the surface is permeable to gases. The mechanically activated solubility of argon in quartz at 80 K and a pressure of 20 hPa is 10^{-2} mole kg^{-1}.[23] Similar effects are characteristic of metals, whose crystal lattices are much denser.[24]

In two-dimensional and one-dimensional systems such as highly anisotropic layer crystals and linear polymers, the degree of deformational disorder is even greater, and the state of limiting decrease in density may be frozen and preserved for study.[23,25] Since the excess free volume is so large that it is accessible to a gas, the extent of the disorder can be characterised by the sorptive capacity or the specific surface S, calculated using the BET equation from the isotherms for the reversible adsorption of argon or other gases at 80 K. The internal surface area generally corresponds to tens of hundreds of m^2 g^{-1}. In molybdenum disulphide (see Fig. 1*a*), thermal mobility of the atoms sufficient for healing appears at 150–200 K.

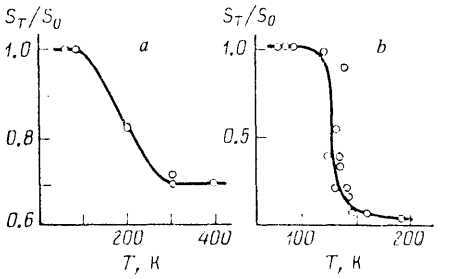


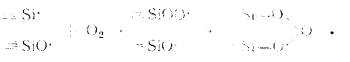
Figure 1. Thermal sintering of mechanically disordered powders of molybdenum disulphide (*a*) and polymethyl methacrylate (*b*);[23,25] S_0 and S_T are the specific surfaces at temperatures of 80 K and T.

The effect of structural disorder in polymers is even greater. For example, in polymethyl methacrylate after mechanical treatment at 80 K, the sorption of argon at a pressure of only 10 hPa is close to 10 mole kg^{-1}; the gas can be removed by evacuation, and adsorbed again. The internal surface area, calculated formally from the sorption isotherms, reaches 600–800 m^2 g^{-1}. The structure loosened to the maximum extent by deformation can be preserved for an unlimited time only at a temperature below 120 K (Fig. 1*b*). Above this temperature, spontaneous sintering begins, with a decrease in the internal surface area accessible to a gas by a factor of several hundred.[25] This extensive decrease in density is the clearest example of the effect of deformation on the structure of a solid.

The relationship between the changes in the structure and reactivity of a solid is important for mechanochemistry. Comparatively detailed information on the nature of mechanical defects, their concentration and reactivity, the direction of elementary reactions involving them, and the kinetic and thermochemical parameters has been obtained for the surface

of solids, where these defects are accessible to molecules from the gas phase. The friction and fracture surfaces of quartz,[15,26,27] silicon,[28] graphite,[29] and other crystals[30,32] have been studied.

Mechanically stimulated chemisorption on the surface of quartz has been described most systematically. The external manifestation of the phenomenon is that the initially inert surface of the solid, as a result of mechanical treatment, becomes chemically active in reactions with gases. Thus SiO_2, which is the highest oxide of silicon, does not react with oxygen under ordinary conditions; the product of the mechanochemical reaction is a previously unknown surface peroxide, assumed to have the structure $\equiv Si-O-O-O-Si\equiv$.[26] The formation of this peroxide can be represented as follows:



Oxygen is attached to the free radical $\equiv Si^{\bullet}$, produced at the point of mechanical rupture of the siloxane bond, after which the peroxide radical $\equiv SiOO^{\bullet}$ recombines with the $\equiv SiO^{\bullet}$ radical. The final result is that an oxygen molecule is "built into" the broken bond.

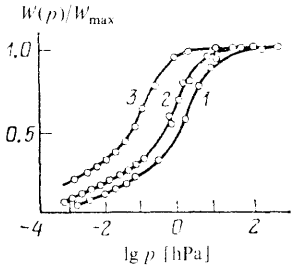


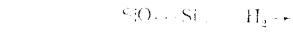
Figure 2. The mechanically activated chemisorption of hydrogen on the surface of quartz at different temperatures, K: *1*) 370; *2*) 300; *3*) 80.[26]

The regular features of mechanical chemisorption are illustrated by the graphs in Fig. 2. For a specific surface of quartz greater than 2–5 $m^2 g^{-1}$, the reaction is initiated by friction, that is by deformations in the layer next to the surface of the powder particles.[26] The graph giving the dependence of the reaction yield on the gas pressure $W(P)$ has a characteristic inflection.[33] At a high pressure, when the frequency of the collisions of the gas molecules with the surface is high, the reaction yield $W(P)$ has its highest value and is independent of pressure. Under these conditions, all the structural defects produced are involved in the reaction, and the consumption of the gas characterises the number of active centres formed by the friction of the particles of the powder against one another. The energy yield of the formation of the short-lived active centres is 10^{-1}–10^{-2} mole MJ^{-1}. At a low pressure, when the collisions of the molecules with the surface are infrequent, some of the short-lived centres are able to disappear before reacting with the gas, so that the yield of the reaction decreases.

In the absence of a gas, that is on mechanical treatment of the powder in a vacuum, up to 6×10^{16} m^{-2} free radicals $\equiv Si^{\bullet}$ and $\equiv SiO^{\bullet}$ are stabilised on the quartz surface.[15,34] The structure and chemical properties of the free radicals on a quartz surface have been studied in detail by EPR, chemisorption and thermal desorption, microcalorimetry, and luminescence. Detailed information on the reactivity of mechanical radicals, including a description of the stepwise mechanism, the kinetic law, the rate constants, and the heats of the reactions with CO, O_2, H_2, CO_2, and various organic molecules, have been published.[15]

The free radicals $\equiv Si^{\bullet}$ and $\equiv SiO^{\bullet}$ are not the only defects produced mechanically on the disordered surface of quartz. A smaller number of silicon atoms with two broken bonds, that is silylene centres =Si:, are stabilised.[15] It has been suggested that =C: atoms exist on the fracture surface of graphite,[29] =Ge: atoms on the surface of germanium oxide,[30] and Sn^{2+} ions on the surface of tin oxide.[16,31,32]

An important contribution to chemical activity is made by deformed bonds, which act as carriers of residual internal stresses. They were first detected in the elongation of polymers.[18] Deformed siloxane bonds are observed from the displacement of the stretching band in the infrared spectra.[35] The chemical properties of the deformed bonds on a quartz surface are similar to those of the radical pairs $\equiv Si...OSi\equiv$. Thus hydrogen reacts with them practically instantaneously at 80 K; the activation energy of the reaction



does not exceed 2–3 kcal $mole^{-1}$;[26] such a low activation energy is characteristic of free-radical, and not molecular reactions. The deformed bonds readily undergo not only hydrogenation but also hydrolysis[36,37] and carbonation. The energy of deformation is liberated in all these reactions.

To determine the surface concentration of deformed bonds, they are titrated with H_2 and CO_2. For the same exposure in the gas, the quantity of bonds reacting with CO_2 is several times greater than the quantity reacting with H_2; the difference is due to the non-uniformity of the distribution of the stresses in the bonds and the corresponding distribution with respect to reactivities. Judging from the consumption of hydrogen,[26] the concentration of deformed bonds on the surface of mechanically activated quartz at 80 K is approximately ten times the concentration of radicals, and reaches $(4–6) \times 10^{17}$ m^{-2}.

The curves in Figs. 3*a* and 3*b* illustrate the thermal stability of the active centres on the surfaces of quartz and magnesium oxide.[15,26,38] The concentration of radicals is independent of temperature; their stability is determined primarily by the purity of the reaction system; the more thoroughly traces of moisture are removed, the more stable the radicals. As expected, the concentration of deformed bonds, reflecting the magnitude of the residual stresses, decreases with increase in temperature.

Thus the nature of mechanical chemisorption on the surface of covalent crystals can be represented as follows. The friction and fracture of the particles of the substance leads to the production of disorder in the surface and to the deformation and rupture of chemical bonds. At room temperature, the deformed bonds undergo a spontaneous decrease in length, and some of the radicals disappear under the influence of friction; thus the complete utilisation of the work done in producing the disorder requires the creation of conditions in which the rate of the reaction of gases with the surface is greater than the rate of disappearance of the short-lived active centres.[39]

The disordered surface of magnesium oxide, which is a stable ionic crystal with melting point ~2900 K, has a high concentration of chemically active centres [up to 1×10^{14} cm^{-2} in the reaction with H_2, and $(3–5) \times 10^{14}$ cm^{-2} in the reaction with CO [38]]; the active centres are stable in a vacuum at

room temperature (see Fig. 3*b*). Hydrogen on this surface dissociates to give atoms with the formation of Mg–H and Mg–OH groups.

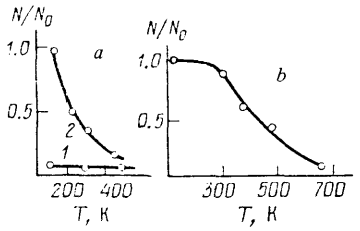


Figure 3. The thermal stability of the active centres on the surface of the oxides of silicon (*a*) (*1*—free radicals, *2*—deformed siloxane bonds) and of magnesium (*b*); N_0 and N_T are the initial and current concentrations of centres.[26,38]

For crystals made up of close-packed ions, the concepts of deformed and broken bonds become indefinite. Taking the extreme limiting case of a purely ionic structure (see Ref. 40, and also a criticism of this approach for alkaline earth metal oxides[41]), the high chemical activity of the disordered surface of MgO can be explained qualitatively as follows.[38] The MgO crystal consists of the chemically inert ions Mg^{2+} and O^{2-} with noble-gas electronic structures; these ions are energetically unfavourable in the free state. To obtain Mg^{2+} and O^{2-} ions in the gas phase from metallic magnesium and molecular oxygen, an energy of ~35 eV is required. When the small doubly-charged ions are close packed, however, there is a gain of electrostatic interaction energy, which more than compensates the loss. Thus the anions and cations are stable in the regular lattice, and the MgO crystal is inert and stable. After the mechanical production of disorder in the crystal, the packing of the ions becomes loose. The average number of neighbours of each ion becomes smaller, and the interatomic distances greater, compared with the regular lattice. Thus in the disordered regions there is a decrease in the strength of the electrostatic interaction responsible for the stability of the ions. Total loss of stability leads to the loss of an electron, that is to the conversion of the O^{2-} ion into the chemically active radical-ion O^-.

The stability of ions can be characterised by the energy required to transfer an electron from the anion to the cation:

$$Mg^{2+}O^{2-} \longrightarrow Mg^{+}O^{-} .$$

In a regular crystal, this energy, which is equal to the width of the band gap, is close to 8 eV. On a surface disordered by friction, the energy of electronic excitation should be smaller. In principle, it can be estimated from the position of the long-wave edge of the absorption band in the spectrum of the surface.

Fig. 4 gives the diffuse reflectance spectrum for a disordered MgO surface (curve *1*). The edge of the band corresponds to an energy of ~4–5 eV, compared with 8 eV for the regular crystal.[38] A similar effect was recently detected in other disordered oxides.[32] The displacement of the boundary of the absorption band by 3–4 eV can be regarded as a measure of the energy of disorder of the surface. After the chemisorption of hydrogen, as a result of which the most active parts of the surface are "worked out", the boundary of the spectrum is displaced to the left by ~1 eV (curve *2* in Fig. 4).

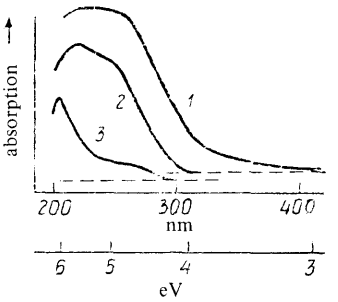


Figure 4. Diffuse reflectance spectra of magnesium oxide powders: *1*) after mechanical treatment; *2*) after reaction with hydrogen; *3*) after heating in a vacuum.[38]

The initial energy yield of the mechanically stimulated chemisorption of hydrogen for MgO is greater than that for quartz, and is equal to ~0.2 mole MJ^{-1}.[38] The excess energy of the disordered surface, calculated from the displacement of the long-wave boundary of the spectrum (by 3–4 eV) and the concentration of active centres (~5 × 10^{18} m^{-2}), is on the average 2–3 J m^{-2} or 100 kJ $mole^{-1}$ for all the ions of the surface.[38]

For the chemical behaviour of a substance, it is important that the mechanical work is used up in increasing the strength of the electron-donor properties of the anions. In the approximation being considered, the energy of chemical reactions on the disordered surface of an ionic crystal is explained by the following thermochemical cycle:

$$\begin{array}{l} Mg^{2+}O^{2-} \longrightarrow Mg^{+}O^{-} \\ O^{-} + XY \longrightarrow OX^{-} + Y \\ Mg^{+} + Y \longrightarrow Mg^{+}Y \\ \hline Mg^{2+}O^{2-} + XY \longrightarrow YMg^{+}OX^{-} \end{array}$$

where XY is a chemisorbed molecule, for example H_2, H_2O, etc. When the energy required for electron transfer (first stage) is lowered to the value of the thermal effect of the two subsequent exothermal chemical reactions, the overall reaction becomes energetically favourable.

Thus whereas in photochemistry the transfer of an electron takes place as a result of the absorption of a quantum of light, and the lifetime of the active excited state $\{Mg^{+}O^{-}\}$ is short, in mechanochemistry the ionisation is facilitated by the production of structural disorder, and the active state is metastable at room temperature.

In magnesium oxide (see Fig. 5), the ionisation energy is lowered to 4 eV. In crystals with a narrower band gap (GeO_2, SnO_2 [32]), the absorption spectrum of the surface states after the production of disorder extends to the long-wave boundary of the visible range; in this case the first stage of the thermochemical cycle examined above takes place spontaneously. Similar processes are possible in organic compounds. Calculations[42] have shown that a local increase in the C–C bond in polyethylene should be

accompanied by a decrease in the ionisation potential to half its value; the transfer of an electron from the deformed bond into a structural trap then becomes possible.[43]

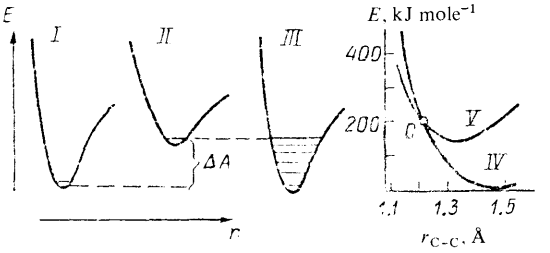


Figure 5. The relaxation of elastically deformed bonds (for explanation see text).

These examples are given here to emphasise that in the band gap of deformed ionic and covalent crystals, donor and acceptor electron levels localised on structural defects are created. These levels may be ionised thermally, and may capture biographic electrons or holes, that is electrons or holes previously existing in the crystal, including those from impurity atoms with variable valence.

The existence of easily ionisable defects is confirmed by their partial ionisation during the mechanical treatment of solids, and also by the anomalously high radiation yield for the formation of paramagnetic centres under the influence of ionising radiation on mechanically disordered crystals.[20,44] Thus after mechanical treatment and irradiation with a dose of less than 1 Mrad, 10^{17} g^{-1} F-centres are produced in radiation-stable magnesium oxide.[44] Their concentration does not increase with increase in the dose, since the vacancies are created during mechanical treatment, and irradiation leads only to their occupation by electrons.

The production of structural disorder in inorganic salts containing complex polyatomic anions should apparently increase their tendency to decompose. In fact, complex anions such as N_3^-, $C_2O_4^{2-}$, NO_3^-, etc., after the loss of an electron, are converted into a singly-charged form or a neutral species; this state is generally unstable, and the loss of the electron initiates the subsequent breakdown of the anion into individual fragments. The probability of breakdown is naturally much greater on the surface or close to defects, where there are no geometric restrictions on the formation of products.

Thus the increase in the donor properties of anions in the production of disorder must be regarded as one of the most important factors in the processes involved in the mechanical decomposition of inorganic compounds. This approach to the nature of the decomposition is confirmed by the influence of metal oxides on the extent of the mechanical degradation of nitrates.[45] This work was begun about 20 years ago, but was subsequently neglected.

III. STRUCTURAL RELAXATION

The chemical and physical effects accompanying the restoration of a mechanically disordered structure are extremely varied, and this variety is the most interesting feature of the processes involved in the deformation and breakdown of solids. The variety is due to the partial ionisation of structural defects and the existence in the deformed solid of both neutral and electrically charged centres. It is usual[2-5] to divide conditionally the entire range of phenomena into mechanochemical and mechano-emission phenomena, the former being produced by the relaxation of neutral disordered parts of the structure with the liberation of elastic energy, and the latter involving the recombination of charges and the decay of electric fields. There is obviously no distinct boundary between these overlapping groups of phenomena.

1. Excited States

In the restoration of a mechanically disordered structure, vibrational and electronic excited states are produced.[46,47] Vibrational excitation is possible as a result of the transformation of elastic energy into vibrational energy on free contraction of a previously elongated chemical bond.[46] This process is explained by Fig. 5, where *I* is the potential curve for the interaction of the atoms, *II* is the same for the elastically deformed bond, and ΔA is the work of deformation. The change *II* → *III* illustrates the relaxation of an elongated bond under conditions when no work is done against external forces. When the deformational energy liberated on bond relaxation is comparable with even half of the bond strength, the level of vibrational excitation will correspond to an effective temperature of tens of thousands of degrees. The excited bond can either undergo thermalisation (Joule heat) or take part in a chemical reaction.

The simplest example of the almost free contraction of bonds is provided by the relaxation of an elongated chain of atoms after its rupture. The model of a contracting chain has recently been the subject of computer experiments. The chain consisted of 20–100 spheres with the mass and dimensions of carbon atoms,[48] and the potential of the interaction between them was given by a Morse function. The preliminary deformation reached 0.5–1.5 Å per bond. After elongation, one end of the chain was "released" and the coordinates of all the atoms were followed. At a definite level of the excess energy, the contraction was accompanied by bond rupture. The calculated mass spectra of the fragments (for preliminary elongation of all the bonds of the chain by 1 Å) are given in Table 1.

Since the lifetime is short, the participation of vibrationally excited states in bimolecular reactions with species of the surrounding medium is less probable than monomolecular transformations such as, for example, decomposition of the substance. Decomposition is studied (see Fig. 6) by deforming or rupturing the specimens before their introduction into the mass spectrometer or chromatograph, which records the ejection of atoms of molecular fragments. The elongation and rupture of polymers gives a whole series of low-molecular compounds,[18,49,50] from hydrogen atoms to compounds containing 2–6 carbon atoms. The fracture of alkali metal halide crystals is accompanied by the ejection of neutral metal and halogen atoms,[51,52] whereas the carbonates under the same conditions decompose with the liberation of carbon dioxide,[14] the nitrates with the liberation of oxygen and oxides of nitrogen,[53] etc.[55] Not all of these effects can be fully explained by the decay of vibrationally excited states.[54]

In early studies,[51] most attention was directed to proving the existence of mechanical decomposition of the substance, and the quantity of fragments formed was not always measured. In polymers, the yield of low-molecular compounds is much lower than the number of ruptures of the

macromolecules. In the fracture of different crystals, the yield of fragments (calculated for 1 m^2 of surface formed) apparently varies from 10^{15}–10^{17} molecule m^{-2} in alkali metal halide crystals[51,52] to 10^{18}–10^{19} molecule m^{-2} in alkaline earth metal carbonates.[14] In a number of cases, the yield is possibly too high, because not all authors have taken account of the intensive sputtering of the substance in the initial period of growth of the crack; the part played by this phenomenon has been analysed.[52]

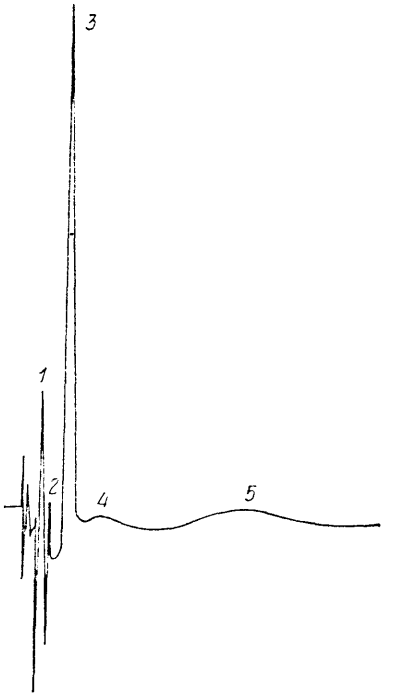
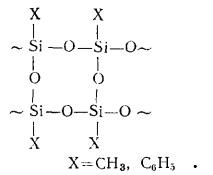


Figure 6. Chromatogram of the low-molecular products of the mechanical degradation of polypropylene: *1*) methane, *2*) ethane, *3*) propane, *4*) propylene, *5*) butane fraction.[49]

Table 1. The calculated number of fragments[48] in the free contraction of a chain of carbon atoms.

Number of C atoms in the chain	Number of C atoms in the fragment						
	1	2	3	4	5	6	7
30	4	5	1	—	1	—	1
50	6	12	1	4	—	—	—
100	14	13	7	6	4	—	1

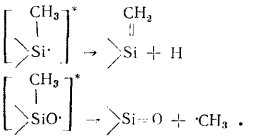
A quantitative study of low-temperature (80 K) mechanical decomposition has been carried out for polysiloxanes with a ladder structure, namely polymethyl- and polyphenylsilasesquioxanes:[50]



X = CH_3, C_6H_5 .

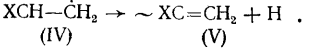
Contrary to widespread opinion, the rupture of the siloxane bonds takes place by a free-radical mechanism.[56] At 80 K, the degradation is accompanied by the ejection of hydrogen atoms and methyl radicals (for X = C_6H_5, benzene is ejected) with a probability of ~0.8, calculated for each bond rupture. As a result of secondary reactions, the H atoms and $CH_3^{\cdot}$ radicals are converted into H_2, CH_4, and C_2H_6.[50]

The primary radicals formed at the moment of rupture of the elongated polymer chain are apparently excited, and have an excess of vibrational energy; thus in spite of extensive cooling, they decompose at the β-bond with a probability close to unity:



This decomposition route is facilitated by the fact that the expenditure of energy in the rupture of the C–H and Si–C bonds is partly compensated by the gain on the formation of unsaturated groups.

The excitation of vibrations with a high amplitude changes the nature of the interaction between the atoms at the points of maximum separation from and closest approach to one another. The removal of atoms may be completed by bond rupture, and when there is appreciable approach of the carbon atoms at the end of a ruptured polymer chain, when the distance decreases to the value characteristic of a double bond, rearrangement of the atoms may take place. This situation was first analysed for the removal of a hydrogen atom from a vibrationally excited terminal radical of the type ~$CHX-\dot{C}H_2$:[57]



(IV) (V)

The potential curves (see Fig. 5) corresponding to the initial (IV) and final (V) states intersect at the point *C*. For reaction to take place, that is the transformation (IV) → (V), it is necessary that the level of excitation reach the crossing point of the potential curves.

A characteristic feature of ionic compounds is that the mechanical rupture of the bonds is preceded by the transfer of an electron from the anion to the cation.[7] This characteristic feature of ionic compounds has been used to explain the emission of neutral atoms during the fracture of alkali metal halide crystals;[58] it was assumed that in the mouth of the growing crack there is excitation of the vibrations of ions, whose amplitude is such that electron transfer from a halide ion to a metal ion takes place at the point of maximum separation from one another. Neutral atoms, which are not held by forces of electrostatic interaction, leave the surface. The results of calculations[58] showing that the emission of the atoms amounts to 10^{19} m^{-2} are too high, since for this yield, the energy used up in the sputtering of the substance is greater than the energy of breakdown; this mechanism may however make a contribution to the overall yield of the emission of atoms (see Ref. 54 for other mechanisms).

The range of mechanochemical relaxation phenomena is not restricted to the vibrational excitation of bonds. When various structural defects disappear, energy is liberated in

quantities of up to several eV, which is sufficient for electronic excitation. Under favourable conditions, the production of electronically excited states can be detected from the characteristic luminescence of the specimen. Comparatively bright mechanoluminescence (or triboluminescence) is characteristic of materials whose structures contain luminescent centres, that is luminophores. Substances in which luminescent defects are formed as a result of mechanical treatment are more interesting; examples of solids of this kind are provided by quartz[59] and copper.[60] In quartz, the luminescent structural defects are atoms with one or two broken bonds, the free radicals $\equiv SiO^{\bullet}$, and the silylene centres =Si:. The excited electronic state of the $\equiv SiO^{\bullet}$ radicals corresponds to an energy of 1.91 eV, and these radicals show luminescence in the red range of the spectrum. The silylene centres correspond to a blue luminescent band with a maximum at 2.65 eV.[59]

When fine quartz powders are subjected to mechanical treatment, the structural defects, including luminescent defects, are localised chiefly on the surface of the particles. Under these conditions, luminescence is observed when the surface is excited by ultraviolet light or friction, or by the heat of chemical reactions with gases.[59] The relaxation of residual stresses is also accompanied by luminescence. In the first studies, the excitation of triboluminescence in quartz was related to the processes involved in the disappearance of short-lived active states, for example the recombination of neighbouring radicals and the relaxation of extensively deformed siloxane bonds. The subsequent determination of the details of the electronic excitation routes encountered considerable difficulties. It was found that the contribution of processes involving the transfer of energy to the luminescence centres is small,[59] and it appears that during friction or on the relaxation of stresses, at least some of the $\equiv SiO^{\bullet}$ and =Si: centres are produced even in the electronically excited state.

Thus one of the elementary acts in the relaxation of stresses may be the reaction of a $\equiv SiO^{\bullet}$ radical with an adjacent highly deformed $\equiv Si...O...Si\equiv$ bond:

$$\equiv SiO^{\bullet} + \equiv Si..O...Si\equiv \rightarrow \equiv Si-O-Si\equiv + [\equiv SiO^{\bullet}]^{*} \ . \quad (1)$$

The reaction gives the electronically excited radical $[\equiv SiO^{\bullet}]^{*}$ and a non-deformed siloxane bond. Reaction (1) describes not only the production of electronically excited states but also the migration of defects with scattering of the energy, that is the development of plastic deformation.

The mechanoluminescence of copper has been observed[60] during strong impact on the end face of a metal bar; the luminescence was produced on its opposite side. Several years after the detection of the luminescence of metals, a theory was proposed, relating this phenomenon to the annihilation of edge dislocations in the volume or on the surface of the metal.[61] The energy required for the excitation of the luminescence (2.15, 1.25, and 0.85 eV) is liberated in the recombination of electrons with holes localised on the copper atoms at the centre of the edge dislocation; at these atoms there are broken bonds similar to those of free radicals at the centres of the dislocations in covalent semiconductors. The characteristic luminescence times correspond to the times taken for the dislocations to reach the surface after impact.

Thus the pictures of the build-up and quenching of the mechanoluminescence in quartz, copper, and other substances reflect the processes involved in the production, migration, and disappearance of structural defects.

2. Mechano-emission Phenomena

The emission of fast and slow electrons, including exo-emission, electrical conductivity pulses, X-rays, static electricity, gaseous discharge, and various forms of luminescence, that is a complete range of electrophysical phenomena accompanying deformation and cohesion and adhesion breakdown, are usually distinguished in the group of mechano-emission effects. Mechano-emission phenomena have been examined in comparative detail in a number of reviews, collected papers, and monographs.[1-5,9,54,55]

As noted above, the factors responsible for mechano-emission phenomena are to be found in the production, interaction, and scattering of electric charges, and one of the principal directions of research in this field still involves the interpretation of the mechanisms of the ionisation of a substance and the creation of electric fields. Several mechanisms have been discussed. The thermo- or auto-ionisation mechanism was examined above; it involves the capture of electrons (or holes) on the local levels of structural defects.

The dislocation mechanism involves charge transfer by mobile dislocations. The dislocations in crystals are electrically charged;[62,63] their charge is compensated by a cloud of charges of opposite sign, localised on point defects. During deformation and breakdown, the dislocations carry their charge on to the surface. When fracture is unsymmetrical, different parts of the crystal are deformed in different ways, and in the mouth of the growing crack there is a component of the movement of the dislocations directed towards the thicker part of the crystal; the excess charge is carried with the dislocations. In alkali metal halide crystals, the excess charge reaches $10^{5}-10^{7}$ CGSE unit m^{-2} or $10^{14}-10^{16}$ centre m^{-2}. In this case the results of calculations[64] agree with the results of measurements of the magnitude of the charge.[65]

The polarisation mechanism is the simplest to explain. The electric fields are produced in this case as a result of the orientation of the polar molecules during the development of the deformation; a similar effect is observed when there is a relative displacement of ions of opposite charge. Thus for identical orientation of all the side groups of polymethyl methacrylate, the charge density would be 9×10^{7} CGSE unit m^{-2}; the experimental value is approximately 10 times smaller, 6×10^{6} CGSE unit m^{-2}. The polarisation mechanism plays the principal role in the production of electrets in polymers;[66] an appreciable polarisation EMF is produced when shock waves pass through a substance.[67]

The mechanism of the separation of the electrical double layer is characteristic of the breakdown of adhesion contact. An electrical double layer is always produced at the boundary of contact between two surfaces of different kinds, and from this viewpoint the breakdown of adhesion contact is identical to the separation of the plates of a capacitor.[9] The charges produced when a polymer film is torn from a support, or when plates of mica are split, represent the most familiar examples of the consequences of electrification by this mechanism.

The production of electric fields during the deformation or breakdown of solids is usually accompanied by scattering of the excess charge. The charged centres preserved after mechanical treatment are responsible for post-effects—a decrease in electrical conductivity, the emission of electrons or ions, and luminescence excited by the recombination of charges.[68] These processes are completed with increase in temperature (exo-emission, thermoluminescence) and by the adsorption of gases and vapours on the surface.[69]

In the deformation and breakdown of solids in air or in another gas atmosphere, the principal route for the scattering of the charges is by electrical breakdown, that is gaseous discharge accompanied by characteristic luminescence, acoustic effects, etc. In a vacuum, the charges may be scattered in several ways. When the electron is firmly bound to a centre, for example to a structural defect, the decisive factor in the scattering of charges is the stability or mobility of the defects themselves. Thus in polymers, electrons may be stabilised in so-called structural traps or vacancies. On deformation or with increase in temperature, the structural traps are destroyed, with the liberation of electrons and the excitation of emission, conductivity, or recombination luminescence.[43] Processes of this type include the capture of *F*-centres by moving dislocations with subsequent recombination of charges. In the other limiting case, when the concentration of charges is high, and the electrons are not so firmly bound to the traps, the principal role in the relaxation of charges is played by the emission of electrons, brought about by their repulsion from one another. The intensity of the emission of electrons in a vacuum is determined by the fluctuations in the surface charge density; for a local charge density of 10^8 CGSE unit m^{-2}, the energy of the emitting electrons may reach 10^1–10^2 keV.[54,68]

A radiation mechanism of charge scattering has been proposed to explain the mechano-emission effects accompanying the splitting of alkali metal halide crystals.[54] The electrically charged walls of the growing crack represent a rapidly separating capacitor, in the field of which the velocity of the electrons and ions leaving the surface is increased. The accelerated particles bombard the opposite wall of the crack, producing excitons; some of the excitons decay with the ejection of a free cation. The cation is accelerated by the field of the capacitor, bombards the opposite wall of the crack, etc. The consequences of the individual stages, that is the emission of accelerated electrons (Deryagin effect), exciton luminescence, the emission of excited cations, and the appearance of radiation defects on the walls of the crack, have been detected by various methods.[51,52,70,71]

IV. DEFORMATIONAL MOBILITY AND THE KINETICS OF DIFFUSION-CONTROLLED REACTIONS

During the deformation of solids, different forms of mobility are excited. These include both the usual forms of thermal motion, but mechanically activated, and also purely mechanical deformational mobility. In the first case, the mobility is clearly activational in character, and the movement of particles requires that an energy barrier be overcome. In the second case, the motion is practically athermal, and the contribution of thermal fluctuations to the mobility is negligible compared with the role of internal stresses. The movement of dislocations and grain boundaries can be classified as deformational mobility.

Familiar examples of the mechanical activation of thermal motion include ascending diffusion, diffusion creep, diffusion along dislocations, etc. The role of super-equilibrium defects in activated diffusion has been less extensively studied. For the vacancy mechanism, the diffusion coefficient is directly proportional to the concentration of vacancies. For many materials at room temperature this is negligible, but it may be increased sharply by mechanical treatment, reaching 10^{16}–10^{17} g^{-1}.[20,44] The diffusion coefficient is also increased by many powers of ten. This effect is apparently important for the mechanical activation of sintering processes.

At a concentration of vacancies of $\sim 10^{17}$ g^{-1}, a solid is saturated by defects to almost the same extent as on fusion, when there is one vacant site for every 10^3–10^4 atoms in lattice sites. This state differs from fusion in that it is produced at a comparatively low temperature, when jump-over by the atoms is difficult. As the deformation develops, however, this restriction is removed, since the internal stresses lower the barrier to jump-over. Thus the state of a substance at the moment of intensive deformation can be represented as "cold fusion". This terminology is already encountered in the literature.[72]

The mechanical mobility of a structure should also be revealed in the kinetics of chemical reactions. The relationship between reaction rate and molecular mobility is one of the basic characteristic features of chemical reactions in solids. The mobility produced by internal stresses is no exception to this rule.

A convenient system for the study of the mobility of a structure subjected to different mechanical treatments may be provided by diffusion-controlled completely frozen reactions between particles which are distributed in a solid matrix and which do not react with one another only because of the absence of mobility. These processes include so-called static reactions between adjacent particles, for example between radicals in pairs or between a radical and a neighbouring molecule of the matrix, and also reactions between particles situated at an appreciable distance from one another, for example the recombination of radicals or charged centres. It has been established experimentally that reactions of both types are much more intensive in a deformed material.[72–76]

To determine how the rate of a chemical reaction is related to the development of deformation, and to estimate the work done in bringing about a reaction, quasi-monomolecular statistical reactions and bimolecular diffusion-controlled reactions in systems with frozen translational mobility are examined separately below.

1. Statistical Pseudo-monomolecular Reactions

The mechanical intensification of reactions between adjacent particles has been observed in dilute frozen solutions of polymers at 80 K.[73] Mechanical treatment was accompanied by degradation of the macromolecules P with the formation of radicals $R^{\bullet}$ and their secondary reactions with molecules of the matrix: hydrogen atom donors HX or the monomer M:

$$P \rightarrow R^{\bullet} \qquad (2)$$

$$R^{\bullet} + HX \rightarrow RH + X^{\bullet} \qquad (3a)$$

$$R^{\bullet} + M \rightarrow RM^{\bullet} \ . \qquad (3b)$$

The extent of the transformation in replacement (3a) or addition (3b) reactions was followed by EPR. Fig. 7*a* shows the changes in the concentration of the radicals $R^{\bullet}$ (curve *1*) and $RM^{\bullet}$ (curve *2*) and the total concentration $R^{\bullet} + RM^{\bullet}$ (curve *3*). On prolonged mechanical treatment of the specimens, reactions (3a) and (3b) were accompanied by the disappearance of the radicals, and when this process stopped, the reactions stopped. The curves giving the change in the concentrations of the radicals $R^{\bullet}$, $RX^{\bullet}$, or $RM^{\bullet}$ during the mechanical treatment of the powders were used to calculate the rates of the free-radical replacement and addition reactions at 80 K. The rates of most of the addition reactions studied corresponded, to within a factor of 10–100, to the value extrapolated to 80 K using the Arrhenius equation with the parameters k_0 and E characteristic of the liquid phase. The method involving the

mechanical treatment of frozen solutions has been used to compare the reactivities of various radicals and molecules at low temperatures.[73]

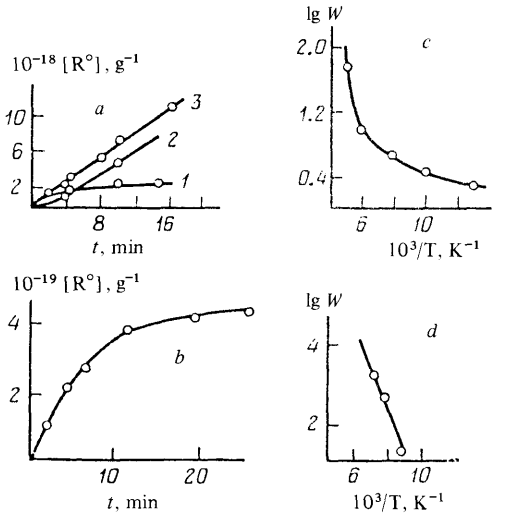


Figure 7. Free-radical reactions during the mechanical treatment of polymers (*b*) and their solid solutions (*a*, *c*, *d*);[73,77,81] rate of supply of mechanical energy in the range 1–10 W g^{-1}; *a*) addition of $\sim CH_2\dot{C}(CH_3)COOCH_3$ radicals to tetrachlorobenzoquinone at 80 K; *b*) formation and disappearance of free radicals in polystyrene at 80 K; *c*) replacement $R^{\bullet} + CH_2(COOH)_2 \rightarrow RH + \dot{C}H(COOH)_2$; *d*) addition $R^{\bullet} + CH_2{=}CH(C_6H_5) \rightarrow R{-}CH_2\dot{C}H(C_6H_5)$.

As an illustration, Fig. 7 compares the results of measurements of the rates (w) of mechanically intensified reactions involving the transfer of a hydrogen atom and addition (Fig. 7*d*) over a wide temperature range.[59] The temperature coefficient of the addition reaction in the frozen solutions is close to the activation energy of this reaction in the liquid phase (Fig. 7*d*). For the replacement reaction (Fig. 7*c*), the Arrhenius law is not observed, since at a low temperature, the transfer of a hydrogen atom takes place by a tunnelling mechanism.

A rigorous description of the kinetics of mechanically intensified random reactions was recently carried out[78] using the concept of the mechanical movement of kinetically non-uniform systems in which there is a wide distribution of reaction centres with respect to reaction rate constants. In solids at a low temperature, when the mobility is frozen, the non-uniformity is due to differences in the nature of the immediate environment of the particles.[79]

Under ordinary conditions, the relative arrangement of the particles remains unchanged during the reaction, and the function $n(k)$ characterising the distribution of the particles with respect to the rate constants remains constant; the reaction leads to gradual "burn-out" of the fractions of the distribution with rate constants close to the maximum value k_{max}. Deformation influences the structure of the immediate environment of the particles and displaces the reaction system, restoring the burnt-out "rapid" fractions. As a result, a varying distribution of the particles with respect to rate constants $n(k, t)$ is established, depending on the frequency of the mechanical displacement ν and the time t.

The number of particles in an arbitrarily selected fraction of the current distribution with respect to rate constants $n(k, t)$ is determined by the ratio of the rates of three processes:[78]

$$\frac{d}{dt}\{n(k, t)\} = -kn(k, t)\,dk - \nu n(k, t)\,dk + \nu N(t)\,\frac{n(k, 0)\,dk}{N(t)} .$$

The first two terms characterise respectively the loss of particles from the fraction as a result of the reaction with rate constant k and mechanical displacement with frequency ν. The third term describes the replenishment of the fraction k as a result of a redistribution of the particles from other fractions on mechanical displacement: of the total flux $\nu N(t)$, where $N(t)$ is the current concentration of particles, only the fraction $n(k)dk/N(t)$ corresponding to the contribution of this fraction to the current concentration $N(t)$ enters the fraction k.

Under conditions of intensive displacement, the current distribution function $n(k, t)$ does not differ greatly from the original function $n(k)$, since for $\nu \ll k_{max}$ the loss of the rapidly burnt-out fractions is immediately made good by replacement; the rate of the process is therefore described by the equation for a first-order reaction

$$-\frac{dN(t)}{dt} \approx k_{max}\frac{N(t)}{\ln(k_{max}/k_{min})}$$

but the effective concentration is lower than the total concentration by a factor of $[\ln(k_{max}/k_{min})]^{-1}$. The factor $[\ln(k_{max}/k_{min})]^{-1}$, determined by the width of the hyperbolic distribution of the particles with respect to rate constants,[80] takes account of the fact that the reaction develops only as a result of the particles in that part of the distribution adjoining k_{max}. In other words, in spite of strong displacement, the reaction rate remains slower than the maximum possible.

Thus intensive mechanical displacement moves a slow reaction, retarded because of the absence of mobility, into conditions close to kinetic. On less intense mechanical treatment, or in a reaction system with high values of k_{max}, when $k_{max} > \nu > k_{min}$, the observed rate constants are determined by the frequency of the displacement:[78]

$$-\frac{dN(t)}{dt} = \nu\frac{\ln(k_{max}/\nu)}{\ln(\nu/k_{min})}N(t) .$$

2. Bimolecular Reactions

The displacements of structural elements, associated with the development of a deformation, through distances which are large compared with the lattice parameters can readily be detected from the intensification of reactions involving the recombination of radicals (by EPR) or charged centres (from the luminescence). Bimolecular reactions of this type have been observed during the mechanical treatment of polymer powders in mills,[73,74,81,82] during the plastic deformation of substances on Bridgman anvils,[6,11,12] during the monoaxial elongation of polymer films,[75,76] in the shear deformation of alkali metal halide crystals,[83] and in other systems.

The limit of the accumulation of active centres during the mechanical treatment of solids is related to deformational recombination. This phenomenon has been detected during the subdivision of polymer and quartz powders, and its essential feature is that the number of free radicals at first increases according to a linear law, but after some time their

accumulation stops, in spite of the fact that the mechanical degradation continues at a constant rate[74] (see Fig. 7*b*). During fine subdivision, work is done chiefly to deform the shape of the particles of the powder and in friction. For polymers, for which the yield stress is low ($\sim 10^7$ N m^{-2}), even under comparatively mild dispersal conditions, for an energy intensity of 0.1–1.0 J g^{-1} s^{-1}, bulk deformation conditions are produced, that is the mechanochemical transformations are due chiefly to plastic deformation of the particles, and not to their splitting or to friction against one another.

For solid quartz powders under the same conditions, friction takes place.[26] The deformation is localised in a thin layer of the particles next to the surface, and all the active centres are concentrated on the surface and accessible to molecules from the gas phase. For solid materials, the change from surface deformation (friction) conditions to bulk deformation conditions is possible when there is a decrease in the particle size[46] or a sharp increase in the energy intensity.[84]

Bulk and surface deformations lead to the rupture of chemical bonds and the migration of radicals, and hence to their encounter and disappearance. Migration may be due either to the direct displacement of the structural elements with localised active centres or to the breakdown of macroradicals with the subsequent diffusion of low-molecular fragments, or to various relay mechanisms, such as the gliding of dislocations or the displacement of free-radical states to the quartz surface according to scheme (1).

Thus the current concentration of defects such as radicals or other active centres during mechanical treatment is determined by the competition between the processes of their formation and disappearance.

The formation of defects is characterised by the magnitude of the energy yield $G_M(R^\bullet)$, which is determined from the slope of the initial section of the accumulation curve (see Fig. 7*b*). On the stationary section, where the concentration of defects is equal to the limiting concentration $[R^\bullet]_\infty$, the energy yields for their formation $G_M(R^\bullet)$ and disappearance $G_M(-R^\bullet)$ are equal to one another.

Table 2. The energy yield and the limiting concentrations of free radicals during the mechanical treatment of powdered polyethylene and quartz (calculated from published data[15,74,81]).

Substance	Degradation conditions	G_M, mole MJ^{-1}	$[R^\bullet]_\infty$	σ, N m^{-2}
Polyethylene	volume deformation	$\sim 10^{-3}$	~ 10 mole m^{-3}	$\sim 10^7$
Quartz	friction	$\sim 10^{-3}$	$\sim 10^{-7}$ mole m^{-3}	10^9–10^{10}

The values of the parameters $G_M(R^\bullet)$ (to within an order of magnitude) and $[R^\bullet]_\infty$, characterising the processes involved in the formation and disappearance of radicals during the mechanical treatment of polyethylene and quartz in a vibration mill (intensity ~1 W g^{-1}), are given in Table 2. Unfortunately, these parameters cannot be estimated for other materials, since the appropriate papers do not give the expenditure of mechanical energy.

Plastic deformation may be homogeneous and cover the entire volume of the substance. The softer the material and the greater the load, apparently, the closer the dynamics of mechanochemical transformations are to this homogeneous model. Much more frequently, however, plastic deformations develop in local zones: in the glide planes of dislocations, in the layers between crystallites, in shear bands, etc. The micro-heterogeneity of the development of deformation is clearly revealed in the processes involved in the disappearance of radiation defects as a result of deformation. Thus when there is appreciable shear deformation of γ-irradiated alkali metal halide crystals, only 5–10% of the defects, situated in the glide planes of the dislocations, disappear.[83] During the monoaxial elongation of polymer films, ~50% of the radiation-induced radicals disappear.[75] In the binary systems hydrocarbon–halogen, etc., γ-irradiated at a low temperature, slight initial deformation initiates a chain reaction covering ~1/4 of the volume of the substance;[85,86] the chain process apparently develops according to the following scheme: deformation–reaction with a change in volume–shrinkage deformation–reaction etc.

Displacement within the entire volume of a substance at the molecular level has been observed during the mechanical treatment of powders in mills, where the particles are subjected to repeated impact. Under these conditions, practically all the radicals produced by γ-irradiation in polymers disappear,[78] but the mechanochemical reaction of metals with halogens, sulphur, selenium, or tellurium takes place explosively.[87]

The nature of the relationship between deformation and the yield of a bimolecular reaction depends on the mechanisms of the development of the deformation and the migration of the reaction centres. The dynamics of the development of a reaction in the glide plane of dislocations can be considered first: a geometric model of the process is shown in Fig. 8*a*. Moving from left to right, the dislocation covers all the reaction centres in the glide plane, and they react with one another in a narrow zone close to its centre.

The change in the concentration of reaction centres on the dislocation line (n_L, m^{-1}) as it moves in the direction x is given by the relationship

$$\frac{dn_L}{dx} = (1 - r_0 n_L) n_s - r_0 n_L n_s$$

where r_0 is the capture cross-section radius, and n_S the concentration of centres in the glide plane of the dislocation, m^{-2}. In all cases, $n_L = bn_S$ and $n_S = bn$, where b is the lattice parameter, and n the volume concentration of reaction centres, m^{-3}. For $L = 1$, the product $r_0 n_L$ characterises the degree of filling of the dislocation line by reaction centres, the first term corresponds to the fraction of centres captured on the free sections of the dislocation line, and the second term corresponds to the number of collisions leading to reaction and the liberation of centres from the dislocation line. The expression for the current concentration of centres on the moving dislocation line has the form:

$$n_L(x) = \frac{1}{2r_0}\{1 - \exp(-2r_0 n_s x)\} + n_0 \exp(-2r_0 n_s x) .$$

The number of centres disappearing on collision with a dislocation is given by

$$-dn_L = 2r_0 n_L(x) n_s dx .$$

Substituting the function $n_L(x)$ and integrating gives

$$\Delta n = n_s x - \frac{1}{2} n_\infty \{1 - \exp(-2r_0 n_s x)\} .$$

This equation describes the development of the bimolecular reaction in the glide plane of a dislocation. Initially, in the acceleration section, the reaction centres accumulate on the

dislocation line; after the limiting concentration of centres $n_{\infty,L}$ (equal to half the number of positions on the dislocation line) has been reached, stationary reaction conditions are established, when all the centres appearing react immediately. The distance x_{cr} at which the change in conditions takes place is $x_{cr} \cong n_{\infty,L}/n_s$. When the critical mean free path is greater than the average distance between dislocations, the most favourable conditions for the reaction, for which $\Delta n \cong n_s x$, cannot be established, since the dislocations will arrive too early at an area free from reaction centres.

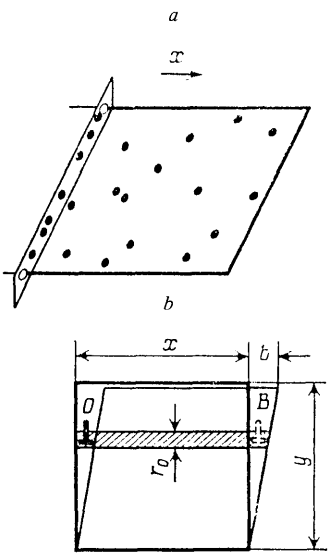


Figure 8. Diagrams explaining the development of a bimolecular reaction in the glide plane of a dislocation (for explanation see text).

To estimate the energy yield of a bimolecular reaction stimulated by the movement of dislocations, Fig. 8*b* can be considered. The volume V corresponding on the average to one dislocation and equal to $V = xy : 1$, is outlined by the continuous line in Fig. 8*b*. Under the influence of the shear stress σ, the dislocation is displaced from the position O to the position B, at the boundary of the volume V, which is equivalent to a displacement of all the substance above the glide plane by an amount equal to the lattice parameter b. The relative deformation ε is then given by $\varepsilon = b/y$. The work A done by the shear force in the path b is equal to $A = \sigma bx.1$, and the number of particles Δn reacting in the path x in the glide plane of the dislocation is equal to $\Delta n = nr_0 x.1$. Since the path x is the average distance between the dislocations in the glide plane, paths whose length is greater than x will be "superfluous". Under the most favourable conditions, the energy yield of the reaction G_M is given by the expression:

$$G_M = \frac{\Delta n}{A} = \frac{r_0 n}{b\sigma} \quad \text{or} \quad G_M \simeq \frac{n}{\sigma_y} \ .$$

In the last relationship it is assumed that $r_0 \cong b$, and that the stress σ is close to the yield stress σ_y.

For $\sigma_y \cong 10^7$ N m^{-2} and $n = 10^2$–10^3 mole m^{-3} (which corresponds to a number of centres ~10^{20} cm^{-3}), the energy yield may reach 10–100 mole MJ^{-1}, that is in the example being considered, the work done in carrying out the reaction should be comparable with the heat required to fuse the reaction system.

The energy yield of the reaction when the deformation develops by a slip mechanism can be estimated similarly. When the atom planes slip relative to one another, the particles of one plane encounter particles situated in the other. To a first approximation it can be assumed that for a relative displacement of the planes through a distance Δl, the number of reacting particles in unit area is given by:

$$\Delta n_s = r_0 \Delta l n_s^2 \quad \text{or} \quad \Delta n = r_0 b \Delta l n^2 \ .$$

The work A done in the displacement of the planes relative to one another is equal to $A = \sigma\Delta/b$, and the energy yield of the reaction $GM(-R^{\bullet})$ is given by

$$G_M(-R^{\bullet}) = \frac{\Delta n}{A} = \frac{V_0}{\sigma} n^2 \ .$$

Here, the product $r_0 b^2$ is taken as equal to the reaction volume V_0. In contrast to the dislocation mechanism, in the case of the slip mechanism the energy yield is directly proportional to the square of the concentration of centres. A similar relationship will be observed when there is external friction:

$$G_{fr}(-R^{\bullet}) = \frac{r_0}{\sigma_{fr}} n_s^2 \ .$$

Here, the tangential stress σ_{fr} is equal to $\sigma_{fr} = \mu p$, where μ is the coefficient of friction, and p the normal pressure.

In internal and external friction, the free radicals are formed at the point of rupture of the bonds and disappear. Under stationary conditions, the yields of the formation $G_M(R^{\bullet})$ and disappearance $G_M(-R^{\bullet})$ of radicals are equal to one another, and the concentration is equal to the limiting value $[R^{\bullet}]_{\infty}$. Since for polyethylene and quartz, $G_M(R^{\bullet})$ and $[R^{\bullet}]_{\infty}$ are known (see Table 2), it is possible to estimate the magnitude of the tangential stresses under the conditions of the mechanical treatment of the powders. The results of the estimates are given in the last column of Table 2. In the calculations it was assumed that $r_0 \cong 3 \times 10^{14}$ m mole^{-1}, and $V_0 \cong 1 \times 10^4$ m^3 mole^{-1}. In polyethylene, the stresses are of the same order of magnitude as the yield stress (10^7 N m^{-2}), whereas in quartz they are 10^2–10^3 times greater.

Under real conditions, the energy yield may be influenced by several factors. In the first place, the probability of the reaction when the particles meet may be less than unity. Next, to complete the reaction it is necessary to have plastic deformation of the entire volume of the crystal, and not merely the regions adjoining the glide planes, so that the stresses should be much greater than the yield stress. Finally, under real conditions it is difficult to avoid superfluous displacement of the dislocations, and superfluous deformation. Nevertheless, deformation recombination provides a convenient and informative method for studying the processes involved in the development of deformation; the first studies in this direction have already been carried out.[83]

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Mechanical stresses, like ionising radiation and other physical methods of acting on a substance, initiate and accelerate chemical reactions. In photochemistry and in radiation chemistry, the energy quanta interacting with a

substance are comparable to or greater than the strength of the chemical bonds, so that the chemical action of the radiation is natural. In mechanochemistry, on the other hand, the average level of the elastic potential is usually very low, and the possibility of the production of chemical effects is not always obvious; it is therefore necessary to assume that mechanisms for concentrating the energy exist. One of the principal ways in which the elastic energy can be concentrated is by the formation of structural defects.

The production of vacancies and interstitial atoms, dislocations, and internal and external surfaces of separation by various treatments reflect a general tendency shown by crystals to transform energy supplied from outside into the energy of crystal lattice defects. On thermal treatment, Frenkel defects are stabilised in crystals; the energy used in their formation is compensated by the increase in the configurational entropy of the crystal when vacancies and (or) interstitial atoms are produced in its volume.

In exactly the same way, in the elastic deformation of a crystal, the state of the crystal in which the dislocations or other defects at which the excess energy is concentrated are distributed in the volume is theremodynamically more favourable than the state in which there is a uniform distribution of the elastic stresses throughout all the interatomic bonds. The stabilising factor in this case also is the contribution of the configurational entropy S_c to the free energy of the crystal. Since $S_c = k \ln W_D$ (where W_D is the thermodynamic probability of the crystal with defects, equal to the number of ways in which these defects can be arranged in the lattice sites), the increase in free energy on production of the defects is given by:

$$\Delta F = F_D - F_0 = -kT \ln W_D .$$

Here, F_0 is the free energy of the elastically deformed crystal, and F_D the same for a crystal in which all the energy of deformation is concentrated in structural defects.

Thus the tendency for the excess energy to be concentrated in structural defects is a characteristic feature of the crystalline state of a substance. The nature of mechanochemical transformations is to a considerable extent related to this characteristic feature of solids.

It follows from the experience gained in mechanochemistry, and partly reflected in the present review, that the production of defects and the subsequent production of structural disorder are unavoidably accompanied by a perturbation of the electronic sub-system of a substance, ionisation, various relaxation processes, and excitation of the mobility of the structure; this provides the means by which mechanical stresses have an effective action on the reactivity of solids.

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