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The Effect of Ionising Radiation on Dissolution Processes

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The influence of various effects associated with the preliminary exposure to ionising radiation (γ-quanta, accelerated electrons, heavy particles) of a solid during its dissolution in aqueous media is analysed, particular attention being devoted to the relation between the rate of dissolution and the radiation-induced charge on irradiated and radioactive substances.
The mechanism of the intensification of the dissolution process when the entire solvent-solid system is irradiated is analysed in relation to the dissolution of uranium oxides in sulphate and carbonate solutions. Procedures involving the employment of ionising radiation for the regulation of the rate of dissolution of solids are considered.
The bibliography includes 105 references.

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I. INTRODUCTION

In many technological schemes dissolution is one of the principal operations which limits the economic parameters of the entire process. For this reason, the search for methods of improving the technology of the dissolution process is being prosecuted continuously. In this sense ionising radiation may be a very effective means of intensifying the dissolution of solids under certain conditions. However, despite the undoubted importance of the study of the influence of ionising radiation on the transfer of various substances to the liquid phase, until recently no systematic research in this field has been made.

The first report, by Simnad and Smoluchovski[1], concerning the considerable increase of the rate of dissolution of iron(III) oxide in hydrochloric acid after irradiation of the oxide with protons having an energy of 260 MeV was published in 1955. After this, the efforts of investigators were for a long time concentrated on the study of the radiation-stimulated corrosion and dissolution of various metals

and alloys, which was dictated, and is still dictated, by the requirements of "atomic technology".[2]

Various crystalline inorganic salts remain virtually uninvestigated. These include alkali metal halides and numerous oxyacid salts, many of which are widely used in the processing of nuclear materials[3]. The present review is in fact devoted to the dissolution of inorganic salt crystals which have been irradiated with γ-quanta, electrons, and heavy particles. Analogous examples involving metals and organic substances are quoted only as an illustration in the description of the main results[3]. One should note that no reviews have been published hitherto on the effect of ionising radiation on the kinetics of the dissolution of crystalline inorganic compounds. In the present survey an attempt is therefore made to discuss certain aspects of this complex phenomenon, to give a systematic account, to analyse critically the results obtained, and to outline the likely future use of ionising radiation for the regulation of dissolution processes.

The intrinsic mechanism of the dissolution of various simple and complex substances is not considered. It is assumed that the reader is familiar with this problem, which is dealt with in specialist publications[4-6].

II. THE INFLUENCE OF DISSOLUTION CONDITIONS ON THE EFFICIENCY OF THE ACTION OF IONISING RADIATION

The first report about the influence of γ- and X-radiation and of a stream of neutrons on the dissolution of ionic crystals was published as late as 1961.[7] The authors were able to show that the rate of dissolution of sodium chloride after irradiation is a structure-sensitive factor and depends on the nature and concentration of radiation-induced defects. Subsequently this type of research was extended to the accumulation of quantitative data concerning the influence of radiation on the dissolution of crystalline substances in water and aqueous solutions. It was found that the radiation effect depends to a large extent on the dissolution conditions.

Two regions in the dissolution process are usually distinguished: the diffusion region, regulated by processes involving the transport of material in the liquid phase, and the kinetic region, in which the rate of dissolution depends in many aspects on the properties of the solid[4,5]. It is known that, for the majority of ionic compounds, the stage involving the interaction of the solvent with the ions located on the surface of the solid takes place almost instantaneously and the rate of dissolution is determined by diffusion processes in solution. In this case the influence of radiation-induced defects may be obscured, since mass transfer in the liquid phase is the slowest stage in the dissolution process. However, for a whole series of compounds (with low and sparing solubilities) the transition of salt ions into the solution is fairly slow and the process as a whole depends on the rate of interaction of the solvent with the solid, i.e. on its nature and structure, and evidently on the presence of radiation-induced defects (if these exist).

The distinctive features of the heterogeneous dissolution process controlled by diffusion are as follows:

(1) dependence of the rate of the process on the rate and direction of motion of the solvent;

(2) dependence of the rate of dissolution on the diffusion coefficient and the viscosity of the liquid in the boundary layer at the surface of the solid in which the dissolved substances or reaction products accumulate;

(3) comparatively low temperature coefficients of the rate of dissolution.

Non-diffusional dissolution (kinetic region) has the following characteristic features:

(1) as a rule relatively low absolute dissolution rate constants (K_V);

(2) invariance of the dissolution rate constant K_V for different rates of stirring;

(3) rapid increase of the coefficients for the rate of dissolution v with temperature.

The above features permit the conclusion that in the kinetic region the transfer of the molecules (ions) of the solid to the liquid phase is determined by the chemical interaction of the compound undergoing dissolution with the solvent. Under these conditions, the dissolution rate constant is in fact a structure-sensitive quantity, whose value is determined by the properties of the solid, such as the type of bond between the crystal lattice elements, the number and nature of the defects, the lattice energy, the type of crystal structure, etc. Naturally dissolution under these conditions is of greatest interest for the study of the influence of radiation-reduced defects on the transfer of ions or molecules or solids to the liquid phase.

The initial postulate of the modern theory of dissolution is the recognition of the existence of a boundary layer of solution at the surface of the solid with composition different from that corresponding to the state of saturation. Accordingly, the equation for the rate of dissolution of the majority of compounds in water can be expressed as follows[4]:

$$dc/dt = \frac{\gamma D}{D + \delta\gamma} S (c_0 - c_t)^n , \qquad (1)$$

where D is the diffusion coefficient, γ the rate coefficient of the interfacial process, δ the effective thickness of the boundary layer, S the surface area of the compound undergoing distribution, n the order of the dissolution reaction, c_0 the solubility of the given compound, and c_t the concentration of the given compound in solution at time t. It is readily seen from Eqn. (1) that the dissolution rate constant corresponding to a constant volume of the liquid phase is defined by the expression

$$K_v = \frac{\gamma D}{D + \delta\gamma} . \qquad (2)$$

The order of the dissolution reaction in water is normally unity for the vast majority of compounds. Depending on the relation between the empirical coefficient γ and D/δ, a real dissolution process can have a diffusional or kinetic (interfacial) mechanism. In the latter case the entire process is determined by the kinetics (mechanism) of the interaction of the solvent with the surface of the solid. In conformity with these ideas, three main types of dissolution are possible:

(1) Purely diffusional: $\gamma \gg D/\delta$, i.e. $K_V \to D/\delta$ (diffusional region of the dissolution process);

(2) purely kinetic: $\gamma \ll D/\delta$, i.e. $K_V \to \gamma$ (kinetic region of the dissolution process);

(3) diffusion-kinetic region of the dissolution process, characterised by comparable rate coefficients for the interfacial and diffusion processes: $\gamma \simeq D/\delta$.

Usually the transition to the kinetic dissolution conditions is attained by increasing the rate of stirring of the liquid phase. The concentration difference between the surface layer and the bulk of the solution then becomes insignificant and diffusion processes may be neglected. One should also note that under industrial conditions it is more convenient to carry out the process in the kinetic region,

since the removal of the substance undergoing dissolution into the bulk of the solution as a result of the motion of the liquid is then faster than in the diffusional region.

In the study of dissolution processes, experimental problems are of primary importance. Particular attention must be devoted to the reproducibility of the hydrodynamic experimental conditions. Failure to meet this requirement leads to considerable discrepancies between the results even in a series of seemingly identical experiments. Virtually any defects in crystal structures influence the rate of transfer of the ions from the solid to the liquid phase under kinetic dissolution conditions, where the rate limiting stage is the interaction of the species of the solvent and the solid. For example, it has been shown[7] that, when NaCl crystals irradiated with X-rays are dissolved, the effect of radiation is not manifested in any way under diffusional conditions, being appreciable only under kinetic conditions. In experiments with irradiated crystals it is therefore necessary to make sure in the first place that the process proceeds via a diffusional mechanism.

In the study of the role of radiation-induced defects in the dissolution of salts experiments are usually performed with a limited amount of solvent, i.e. under conditions where Eqn. (1) is valid. The rate of dissolution, i.e. the variation of the quantity dc/dt with time, dose, intensity of irradiation, and other parameters is selected as the structure-sensitive characteristic. The majority of conclusions concerning the influence of irradiation on dissolution have been reached precisely by studying the dependence of v on the magnitude of the effects of radiation. However, the rate of dissolution is not a fully reliable criterion of the given process, because it depends [see Eqn. (1)] on the surface area of the crystals and very frequently also on their shape and the micro-relief of the crystal faces.

Even in the kinetic region, v depends strongly on the concentration of the substance undergoing dissolution in the liquid phase (apart from the dependence on S). Furthermore, in the initial stage of the process the rate of dissolution is frequently affected by different random factors, which are difficult to control. With increase of the concentration of the dissolved substance in the liquid phase, the accuracy of the determination of c_t diminishes. As a result of all these factors, the conclusions reached on the basis of the variation of v ultimately become to a large extent qualitative.

A more objective parameter, which characterises the dissolution of the solid, is evidently the dissolution rate constant, which is independent of the variation of the surface area of the crystals during dissolution†.

If it is desirable to obtain a more rigorous relation between the nature and concentration of the radiation-induced defects and the dissolution of the irradiated specimen uncomplicated by the influence of "structure-surface" factors, it is necessary to determine the values of K_V.[8]

It should be noted that, when v_{irr} and $v_{non\text{-}irr}$ are compared, a case may be encountered where the rates of dissolution of the same specimen differ in magnitude but change to the same extent under the influence of irradiation. Naturally the ratio $v_{irr}/v_{non\text{-}irr}$ will then differ from unity and on this basis it would seem possible to conclude that the point defects generated by irradiation affect the entire process[7,9,10]. However, under these conditions K_V does not change, since it is determined from the slope of the curves relating v/S_t to $c_0 - c_t$.

When $v_{irr}/v_{non\text{-}irr}$ changes, all the observed effects may be associated with the breakdown of the surface structure, a change in the surface area, micro-cracking or sintering, etc. If K_V is determined, all the surface effects are usually excluded and the relation between (the number of) radiation-induced point defects and the rate of dissolution of the irradiated crystal is revealed in a pure form, since the dissolution rate constant characterises the number of species of the solid abstracted under the influence of the solvent per unit surface and per unit time.

Furthermore, attention must also be drawn to the influence of the concentration of the dissolved salt in the liquid phase c_t, which affects dc/dt according to Eqn. (1).

The choice of the method and the conditions for the dissolution of the given compound after its irradiation are determined by the fact that point (and linear) defects generated by the radiation are manifested most effectively at low rates of dissolution[14-18]. This is because, for high rates of the given process, the entire surface of the solid in contact with the solvent is "operative" (the influence of the defects is blurred) and, for low values of v, the dissolution takes place at the weakest site—at the defects whose linkages with the crystal matrix are deformed[12-18].

If in the study of dissolution kinetics it is necessary to detect fine effects associated with structural changes in the crystal, one must carry out experiments with low rates of dissolution. For readily soluble salts, this can be achieved using virtually saturated initial solutions[11-13]. Under these conditions, dc/dt varies very strongly even when the crystal structure is altered only slightly. For sparingly soluble compounds, there is no such limitation on the concentration of the solvent.

For example, experiments have been carried out[11-13] with NaCl, KCl, KBr, LiF, and KI in almost saturated solutions, where dc/dt was low and the dissolution did not occur from all the surface points behaving as single "active centres", but only at sites where defects accumulated. Using this method, it was possible to detect many side effects in the dissolution of irradiated crystals.

III. DISSOLUTION OF COMPOUNDS IRRADIATED WITH HEAVY PARTICLES

All the known defects in crystal structures (point, linear, two-dimensional, or three-dimensional defects) may be formed as a result of the irradiation of solids by a particular type of ionising particle.

The displacement of atoms in the crystal lattices of solids is one of the main effects of bombardment by heavy particles (neutrons, protons)[19]. Naturally this is accompanied by ionisation and excitation processes with formation of various "electronic" defects with all subsequent transformations of the kind occurring on γ-irradiation.

The relation between electronic defects and their complexes and dissolution processes has been shown experimentally to be very complex and it is extremely difficult to predict beforehand the nature of their influence on the rate of dissolution. The role of the displacement of atoms, which facilitates the transfer of the ions of the solid to the liquid phase as a result of the weakening of the bond between the displaced atom and the crystal lattice, is clearer. One should also bear in mind that the influence of the same type of defects on the properties of solids of different kinds may differ sharply. The main effects in

† However, K_V may depend also on the surface relief. It is therefore more correct to compare the values of K_V for specimens with identical surface topographies.

metals are linked with the displaced atoms. On the other hand, for ionic crystals, electronic defects are of decisive importance.

The macrodefects in the structure of the surface of the irradiated crystals have a considerable influence on the dissolution, such defects including evaporation pits, growth projections, radiation-induced cracking, and partial fusion of rugosities, which is observed both on irradiation with electrons [20-23] and on bombardment with heavy particles [24-27]. One should note that irradiation does not always create an excess concentration of defects. It sometimes happens that, following radiation annealing, the crystal actually becomes more perfect owing to the decrease of the number of "biographical" defects [19]. Furthermore, the concentration and nature of radiation-induced defects arising on storage of irradiated crystals usually change gradually as they interact with one another. There is a simultaneous alteration also in the properties of the given specimen. Consequently, dissolution may in some cases be accelerated after a given specimen is acted upon by radiation, while in others the dissolution of the same specimen may be retarded. This has in fact been observed experimentally.

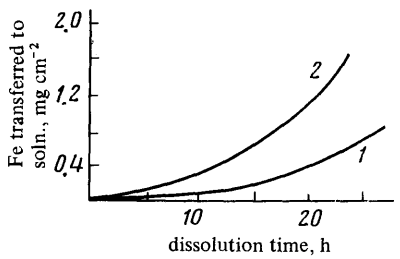


Figure 1. The rate of dissolution of Fe_2O_3 in 1 *N* HCl after irradiating the oxide with protons [1]: 1) non-irradiated specimen; 2) irradiated oxide; temperature 30° C.

Bombardment with neutrons or any accelerated heavy particles, which causes profound and persistent structural changes in the crystal lattice, has the greatest influence on the dissolution process. The first studies of radiation-kinetic effects on dissolution were instructive in this respect. Thus, Simnad and Smoluchovski [1] irradiated the oxide Fe_2O_3 with a stream of accelerated protons having an energy of 260 MeV, the density of the overall stream of protons reaching 10^{16} proton cm^{-2}. After irradiation, the oxide was dissolved in 1 *N* HCl solution and the liquid phase was analysed for iron by the periodic sampling method (Fig. 1). Fig. 1 shows that the irradiated oxide dissolves faster than the non-irradiated oxide. Such an increase in the rate of transfer of iron to the HCl solution can be explained by the appearance of a large number of bulk-phase defects (vacancies, displaced atoms, thermal peaks) as a result of the action of protons on the Fe_2O_3 crystal lattice. According to the authors [1], the characteristic change in the rate of dissolution as the latter proceeds is determined by two factors: the depletion of the surface in defects owing to their recombination, a greater ease of their diffusion in the surface region towards the interface (the loss of defects), and the gradual dissolution of the surface layer, which exposes the more damaged regions of Fe_2O_3. For this reason, an induction period is observed in the dissolution process.

The above publication was followed by a number of communications concerning the influence of irradiation with heavy particles on the rate of dissolution of purely ionic crystals in which not only the experimental results are described, but also an attempt is made to relate the observed effects to the formation of radiation-induced defects of a fully defined type.

A study has been made [10] of the dissolution of alkali metal halide crystals (NaCl, KCl, KBr) in their aqueous solutions after irradiation of the specimens with neutrons. Neutrons from an Ra–Be source were used. The most interesting result is the dependence of the quantity $v_{irr}/v_{non\text{-}irr}$ not only on irradiation but also on the duration of storage of the specimens after bombardment with neutrons before the start of dissolution (Fig. 2). The authors [10] suggest that, during the storage of the irradiated crystals (at 20° C), processes involving the thermal annealing of defects take place, which decreases the rate of dissolution. Furthermore, there is a possibility of the formation of new types of defects owing to the interaction of the primary defects, which leads to the stabilisation of the NaCl structure and a decrease of $v_{irr}/v_{non\text{-}irr}$. Unfortunately, the authors [10] did not put forward any hypothesis concerning the relations between v and a definite type of radiation-induced defect, and the irradiation conditions do not allow an exact determination of the integral neutron flux; no account is taken of the influence of γ-quanta accompanying the bombardment with neutrons either. However, in the above study a negative effect of neutron bombardment on the rate of dissolution was established for the first time and it was stated that the nature of the defects may have a decisive influence on the rate of transfer of the species from the solid to the solution. Further studies on these lines showed that the sensitivity of the rate of dissolution to irradiation with neutrons depends to a large extent on the type of crystal face. Anisotropy of the effect of radiation is characteristic of virtually all alkali metal halides. For example, the (100) face is most sensitive in KCl and NaCl crystals, while dissolution of the (110) and (111) faces proceeds at the same rate both before and after irradiation with neutrons (integral flux of 1×10^8 cm^{-2}). [10] One cannot rule out the possibility that this is associated with differences in the packing density of ions on the crystal faces, which leads, according to Naumov and Savintsev [12], to the following experimental relations between v on the crystal faces and the relative unsaturation of the solutions σ [σ is expressed as a fraction or as a percentage and is equal to $(c_0 - c_t)/c_0$)]:

$$v_{(110)} = R_1\sigma^{1.18}, \quad (3)$$

$$v_{(100)} = R_2\sigma^{1.65}, \quad (4)$$

where R_1 and R_2 are constants.

Interesting results for the influence of bulk-phase defects on the rate of dissolution were obtained by the above workers [12]. A layer 50 μm thick ("etching" with water) was removed before dissolution from KCl, NaCl, KBr, and KI crystals irradiated with the neutrons from an Ra–Be source and also with protons (E_p = 4.5 MeV, the intensity of the proton beam was 6×10^{10} proton $cm^{-2}s^{-1}$), which made it possible to disregard the macrodefects on the faces caused by bombardment with heavy particles. This was followed by the dissolution of the crystals. Neutron

bombardment was accompanied by irradiation with γ-quanta having an energy of approximately 2 MeV, the crystals being exposed to a dose of 1.8×10^4 r. The energies of the protons and the neutrons were approximately the same and amounted to about 4 MeV. Experiments showed that, for large doses of heavy particles, the rate of dissolution, particularly under the conditions of low unsaturations, increases appreciably. The ratio $v_{irr}/v_{non\text{-}irr}$ decreases with increasing dilution of the solution (with increase of σ) and the influence of irradiation with heavy particles gradually becomes inappreciable. Irradiation with protons leads to a very marked increase in the rate of dissolution throughout the structure-sensitive region even for doses of the order of 10^{14} proton cm^{-2}.

Crystals such as those of LiF, the rate of dissolution of which is low, dissolve in pure distilled water ($\sigma \simeq \infty$) much more rapidly than the non-irradiated crystals, and a small change in the experimental temperature does not affect the nature of this relation. However, no hypothesis has been made concerning the relation between the change in v_{irr} and the type of radiation-induced defects [12].

The increase in the rate of dissolution as a function of defects such as displaced atoms, dislocations, thermal peaks (wedges), etc. is more definite. For example, the density of dislocations in neutron-irradiated KCl crystals has been determined by an etching method [28] and it was found that immediately after irradiation the density of dislocations increases by a factor of 2.5 (to 7×10^5 cm^{-2}). Next, the number of dislocations decreases smoothly during storage at room temperature in accordance with the curve equivalent to the variation of $v_{irr}/v_{non\text{-}irr}$ for the same crystals (Fig. 2).

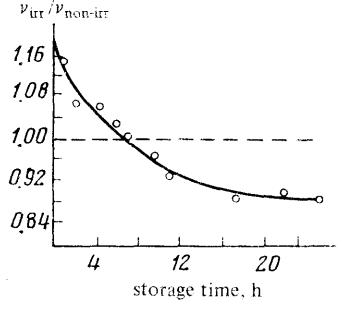


Figure 2. Dependence of the ratio of the rates of dissolution of irradiated and non-irradiated NaCl crystals on the duration of storage of the specimen at room temperature [10]. Solvent—25.85% solution of NaCl in water; integral neutron flux ~ 10^{11}–10^{12} neutron cm^{-2}.

An increase of v_{irr} with increase of the integral flux of heavy particles was observed in all the systems investigated, and for equal fluxes the effect was greater for heavier particles. However, these conclusions are to a large extent qualitative, since neutron bombardment was always accompanied by intense γ-radiation, the influence of which was disregarded. Furthermore, even for equal integral fluxes and neutron and proton energies, the densities of the defects generated by these two types of radiation were different. Unfortunately, the concentration of even the total number of defects was not estimated. If this had been done, it would have been possible to compare the effects of neutrons and protons.

Naumov and coworkers [10–12] showed clearly for alkali metal halides that, under identical conditions, the greatest increase in the rate of dissolution is observed for crystals with the highest crystal lattice energy. This very important experimental fact can be used for the qualitative estimation of the influence of radiation on the dissolution process.

An increase in the rate of dissolution has been observed for the oxides Al_2O_3 and NiO and formica [29] irradiated with accelerated krypton ions. The energy of the ions varied within a wide range (5–100 keV) and the integral fluxes were 5×10^{12} and 5×10^{13} cm^{-2}. The solvents were 3% HF for mica, NaOH solution for Al_2O_3, and concentrated HNO_3 for nickel oxide. The observed effect was attributed wholly to surface macrodefects on the irradiated specimens. This explanation appears to be quite likely, because krypton ions were absorbed by a thin layer of the test specimens, which made the surface amorphous, facilitating dissolution [29].

Table 1. Variation of the surface areas of solids as a result of exposure to neutrons and γ-quanta [30].

Substance	Type of radiation	Dose of No. of particles	Change in specific surface, % (the minus sign indicates a decrease and a plus sign indicates an increase)
TiO_2	γ	$1 \cdot 10^{22}$ eV g^{-1}	−15
C	neutrons	$7 \cdot 10^{19}$ neutron g^{-1}	0
α-Al_2O_3	neutrons	$2 \cdot 10^{18}$ »	0
γ-Al_2O_3	neutrons	$2 \cdot 10^{18}$ »	0
MgO	neutrons	$1 \cdot 10^{19}$ »	−25
SiO_2 (xerogel)	neutrons	$7 \cdot 10^{18}$ »	−3.3
SiO_2 (aerosil)	neutrons	$1 \cdot 10^{20}$ »	−69
BeO	neutrons	$4 \cdot 10^{18}$ »	+300
α-Al_2O_3	neutrons	$4 \cdot 10^{19}$ »	+300

It is not always possible to attribute the radiation-induced changes in the rate of dissolution solely to the effect of radiation on the structure and the surface area. For example, a study has been made [30] of the dissolution of oxides irradiated in a nuclear reactor in various media (H_2SO_4, HCl, NaOH). Measurements were made of the surface areas of the irradiated systems (Table 1) and it was found that, as a result of atomic displacements, thermal peaks, and sintering, the surface changes appreciably after irradiating the test specimens in the atomic reactor. Apart from all other factors, this process depends on the properties of the specimen: porosity, moisture content, degree of dispersion, and even the type of radiation-chemical reactions in the specimen. As a rule, the surface area decreased under the influence of irradiation with heavy particles. However, in these experiments [30] it was impossible to establish a clear relation between the changes in the rate of dissolution and the surface area.

Nevertheless in individual instances the role of the radiation-induced changes in the surface is shown quite clearly. Thus a study of the rate of transfer of uranium to the liquid phase when U_3O_8 irradiated with neutrons interacts with 0.1 N H_2SO_4 solution showed that the decisive

factor in this process is the damage of the surface structure of the oxide[31], which causes complete surface amorphisation for integral fluxes in excess of 10^{17} neutron cm^{-3}.[32] Under these conditions, the rate of dissolution of the oxide increases. Fig. 3 shows that, for the doses investigated, there is an increase in the rate of transfer of uranium to the solution. There is a distinct difference in the behaviour of the irradiated and non-irradiated U_3O_8. One should note that the radiation-chemical decomposition of U_3O_8 under the influence of neutrons was scarcely observed, so that the solubility of this oxide in H_2SO_4 remained constant. This led to a gradual mutual approach of the dissolution curves for the irradiated and non-irradiated specimens, as the saturated solution was formed and the damaged surface layers dissolved. The time required for the equalisation of concentrations was approximately 10 days.

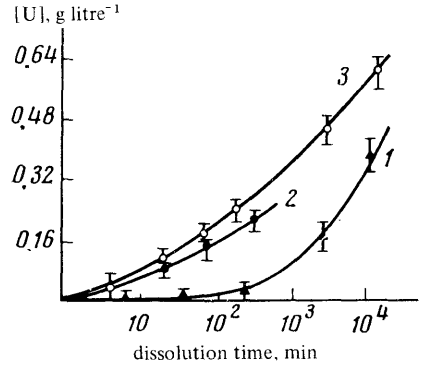


Figure 3. Kinetics of the transfer of uranium to the solution from neutron-irradiated U_3O_8: 1) non-irradiated U_3O_8; integral neutron flux (neutron cm^{-2}): 2) 1.2×10^{16}; 3) 1.2×10^{17}; temperature $30 \pm 1°C$.[31]

Table 2. The rate constants for the dissolution in water of various strontium sulphate specimens[33].

Specimen	$K_v = 10^7$ $cm^{-2}\,s^{-1}$
Non-irradiated	6.0
Irradiated with γ-quanta, dose 10^{20} eV g^{-1}	4.6
Irradiated by reactor radiation, 1×10^{18} neutron cm^{-2}	7.1
Radioactive crystals (50 mc of ^{35}S per gram of salt)	2.1

All the above examples involving crystalline compounds irradiated with neutrons are to some extent indefinite, since the contribution of the γ-quanta accompanying the neutron bombardment from any source was completely ignored in these experiments. In this respect the data of Gromov and Bespalova[33] throw some light on the problem, because they determined for the same object ($SrSO_4$ crystals) the influence of the mixed neutron and γ-radiation of the reactor, the separate effect of the γ-quanta from a cobalt source, and pure β-radiation (radioactive crystals) (Table 2). It was found that γ- and β-radiations retard the dissolution of strontium sulphate in water, while bombardment with neutrons accelerates it. Bearing in mind that neutrons and γ-quanta are active simultaneously in an atomic reactor, the acceleration of the dissolution process owing to the neutron flux alone is in fact much greater. One cannot rule out the possibility that neutrons, which cause very appreciable structural damage in the crystals, always promote dissolution. However, their influence may be masked and even completely suppressed by effects associated with the γ-radiation and the decrease of the surface area (see Jech and Kelly[29]), which was disregarded in the majority of investigations.

Summarising the discussion of the available experimental data, one may conclude that defects of the type of displaced atoms, dislocations, displacement zones, and interstitial atoms, which are very effectively generated on bombardment of the crystals with heavy particles, as a rule promote a more vigorous dissolution of the compounds.

IV. RELATION BETWEEN THE RADIATION-INDUCED DEFECTS AND THE DISSOLUTION OF COMPOUNDS IRRADIATED WITH γ-QUANTA AND ELECTRONS

In the first studies of the influence of X- and γ-rays and accelerated electrons on the kinetics of the dissolution of ionic crystals the extremely complex dependence of the rate of dissolution on the absorbed dose, on the degree of saturation of the liquid phase by the dissolved salt, and on the duration of storage of the irradiated compounds was already noted[7,9-12,28]. For example, it was found that a change in the concentration of the dissolved salt, even within narrow limits, has a significant influence on the ratio $v_{irr}/v_{non\text{-}irr}$ (Fig. 4). The data illustrated in Fig. 4 refer to the dissolution of NaCl crystals after exposure to X-rays[6]. According to the experimental conditions, the process occurred in the kinetic region of the dissolution reaction (Reynolds number $Re = 4000$). It is of interest to note that the ratio $v_{irr}/v_{non\text{-}irr}$ increases with increase of the NaCl concentration in solution, while the absolute difference between these rates diminishes, approaching zero as saturation is reached. The latter finding shows that the solubility of the irradiated crystals is equal to that of the non-irradiated crystals, i.e. radiation affects only the kinetic characteristics of the interphase interaction between the solid and the solvent.

In order to detect the change in solubility (c_0), which is a thermodynamic parameter, it is necessary to carry out experiments under adiabatic conditions; the energy evolved on dissolution (stored in the crystal during irradiation) then increases the temperature in the system, which affects c_0. Another procedure is evidently possible. The effect of radiation should then be strong enough to cause qualitative changes in the solid phase (the generation of chemical impurities, "fragments" of compounds, etc.), which might affect both the composition of the solution and c_0.

Berzina et al.[10] reached this conclusion in a study of the variation of the rate of dissolution of NaCl, KCl, and KBr crystals in aqueous solutions after irradiation on X-ray apparatus. In addition, they compared the changes in $v_{irr}/v_{non\text{-}irr}$ for the same specimens but different exposure doses (Fig. 5). Fig. 5 shows that, with increase of the radiation dose, the ratio of the linear rates of dissolution increases smoothly, other conditions being equal. Comparison of the data obtained for different salts also

made it possible to establish the following empirical rule: if irradiation with X-rays leads to an increase of the rate of dissolution, the observed effect is greater the higher the energy of the crystal lattice of the given substance [10]. This rule holds in practice for a series of similar compounds (Table 3).

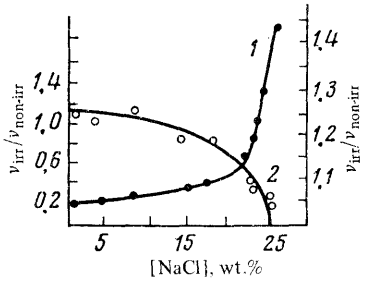


Figure 4. Dependence of the ratio (curve *1*) and the difference (curve *2*) of the linear rates of dissolution of irradiated and non-irradiated NaCl crystals on the salt concentration in solution; temperature 21°C; irradiation with X-rays [7].

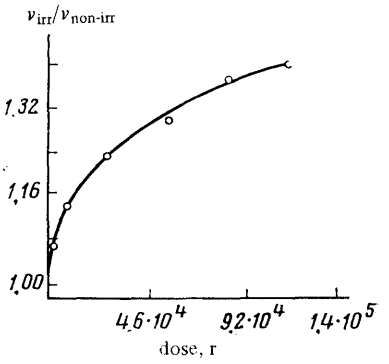


Figure 5. Dependence of the ratio of the rates of dissolution of X-irradiated and non-irradiated NaCl crystals on the dose [10]. NaCl concentration in solution used for the dissolution reaction 26 wt.%; temperature 21°C.

More detailed studies of the influence of X-rays (energy 8 keV) on the transfer of the ions of NaCl, KCl, etc., to the solution as a function of the degree of unsaturation σ have been made [11,12]. Anisotropy in the effect of radiation on different crystal faces was observed and it was established that irradiation not only accelerates, but also retards dissolution in certain ranges of σ. Thus, for a relative unsaturation of the solution less than 0.007, irradiation of an NaCl crystal leads to an increase in the rate of dissolution of the "100" face. When $\sigma > 0.007$, the rate of dissolution of this face is found to decrease, the maximum decrease corresponding to a dose close to 1×10^5 rad. With increase of the dose above 1.6×10^5 rad, the (100) face of the irradiated NaCl crystals then begins to dissolve once more at a higher rate than the non-irradiated face. For irradiated KCl crystals, the corresponding critical relative unsaturation resulting in a change in the sign of the effect of radiation on dissolution is $\sigma = 0.005$.

Table 3. Variation of the relative rates of dissolution on the (100) face of various X-irradiated alkali metal halide crystals (dose 1.2×10^5 rad). [12]

Crystal lattice energy, kcal mole^{-1}	Compound	Relative unsaturation σ					
		0.003	0.006	0.009	0.012	0.015	0.018
180	NaCl	1.65	1.10	0.90	0.90	0.90	0.93
164	KCl	1.15	0.97	0.83	0.78	0.76	0.82
158	KBr	1.06	0.99	1.00	1.00	1.00	1.00
149	KI	0.94	1.00	1.00	1.00	1.00	1.00

This complex relation between the rate of dissolution of the crystal face, the relative unsaturation of the solution, and the irradiation dose can be explained, according to the authors [11,12], by the fact that different structural defects in the crystal lattice affect the rate of dissolution of the irradiated compound to different extents (and sometimes in the opposite way). The above features are characteristic of the dissolution of the (100) face only, while along the other directions, (110) and (111), NaCl, KCl, and other alkali metal halide crystals are insensitive to the action of radiation [13].

The retardation of the transfer to the liquid phase of the ions of different substances irradiated with electrons, observed by many workers, is probably a fairly general phenomenon, which is frequently encountered. The same effect was noted for the dissolution of γ-irradiated uranium oxides U_3O_8 and UO_3 in sulphuric acid [31,34]. One cannot rule out the possibility that this type of action of γ-quanta can be accounted for by the radiation annealing of biographical defects owing to their recombination with the radiation-induced defects of opposite sign (for example, a vacancy and an atom in the interstices) generated under these conditions. The crystal then, as it were, becomes more perfect [35].

The first attempt to establish a relation between the change in the rate of dissolution of irradiated crystals and the concentration of defects of a particular type was apparently undertaken by Gromov and Bespalova [33], who investigated the influence of γ-quanta on the dissolution of strontium sulphate crystals in water. It was found that, with increase of the absorbed dose (regardless of the dose rate), the dissolution rate constant decreased smoothly to a constant value. For example, K_V for the non-irradiated salt was 6×10^{-7} cm^{-2} s^{-1}, while its minimum value (obtained for a dose of approximately 10^8 rad) was 3×10^{-7} cm^{-2} s^{-1}. Special experiments showed that electronic defects, i.e. holes and electrons localised at biographical defects, consisting mainly of the radical-ions SO_4^- and SO_3^- as well as e_{st}^- (the amount of SO_4^- exceeded that of SO_3^- almost by a factor of 10), are mainly formed in $SrSO_4$ under the influence of cobalt-60 γ-quanta [36-39]. The displacement of atoms and even more so of dislocations does not occur under these conditions. This facilitates the

determination of the relation between the concentrations of definite radiation-induced defects and the rate of dissolution.

It was found that K_V decreases with increase in the concentration of SO_4^-, SO_3^-, and e_{st}^- (Fig. 6), i.e. there is a definite correlation between K_V and the number of electronic defects R. Without analysing the mechanism of the influence of the above defects on the transfer of Sr^{2+} and SO_4^{2-} ions to the liquid phase and solely on the basis of experimental data, the authors[33] represented the dissolution rate constant in the following form:

$$K_v = K_0 + K_{irr}, \quad (5)$$

where $K_{irr} = f(R)$, while K_0 is a constant. Bearing in mind that K_{irr} decreases exponentially with increase of the amount of R (Fig. 6), it is easy to obtain the final formula in the following form:

$$K_v = K_0 + K_1 \cdot \exp(-\alpha [R]), \quad (6)$$

where K_1 is a constant and α an empirical parameter with the dimensions particle^{-1}. When $[R] = 0$ (no irradiation), we have $K_V = K_0 + K_1$; when $[R] = [R]_\infty$ (maximum concentration of defects), we have $K_V \simeq K_0$. The values of K_1 and K_0 are determined from experimental data. The parameter α is found graphically from the slopes of the corresponding curves. Calculations have shown that the proposed formula describes satisfactorily the variation of K_V with the concentration of the radiation-induced defects of the electronic type.

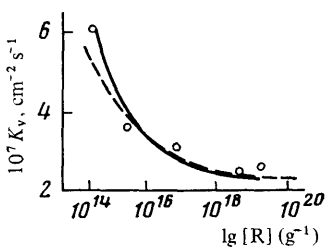


Figure 6. Dependence of the rate constant for the dissolution of $SrSO_4$ crystals on the concentration of defects (R) of the type SO_4^-, SO_3^-, and e_{st}^- in the crystal[33]. The dashed curve represents calculations by Eqn. (6).

Experiments with annealed $SrSO_4$ crystals provided satisfactory evidence for the relation between the decrease of K_V and the increase of the number of electronic defects. It was found that heat treatment at 400° C for 2 h restored the properties of the γ-irradiated specimens and that K_V for such specimens approached the value for the non-irradiated specimens[33]. In the course of this type of annealing, the SO_4^- and SO_3^- radical ions as well as e_{st}^- disappeared from the crystals, as shown by ESR.

The next step in refining the role of structural defects arising on irradiation was taken by Parkhaeva et al.[40] Crystals of natural (celestite) and synthetic strontium sulphate were subjected to the action of a stream of electrons with an energy of 3.5 MeV; the difference between these specimens was determined by impurities (thus the celestite contained approximately 1% of calcium, barium, magnesium, and potassium ions). Furthermore, the natural celestite crystals contained even before irradiation a fairly large number of SO_4^-, SO_3^-, and SO_2^- radical-ions, formed as a result of the β-decay of ^{87}Rb and the permanent level of background radiation. Thus the natural strontium sulphate had a fairly large number of biographical defects (an excess of dislocations cannot be ruled out either), which could serve as sites for the trapping of holes or electrons as well as sinks for the newly formed radiation-induced defects. As a result of irradiation with electrons having such large energies, displaced atoms should be formed in the $SrSO_4$ crystals in addition to the electronic defects and should be capable of stimulating the dissolution process. Indeed it was shown by ESR that in this instance the SO_3^-, SO_2^-, and SO_2^+ radical-ions as well as oxygen in the interstices are formed almost exclusively in the first stages of irradiation (up to 10^5 rad). SO_4^- radical-ions then gradually accumulate as well. Accordingly, the dissolution rate constant initially increases to a maximum and then gradually falls (Fig. 7).

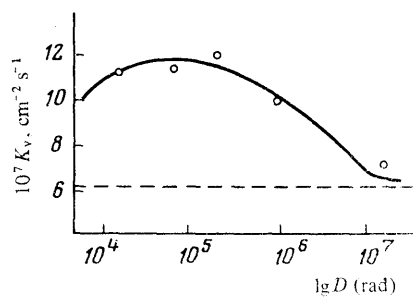


Figure 7. Variation of the rate constant for the dissolution of strontium sulphate as a function of the absorbed dose D after irradiation with fast electrons having an energy of 3.5 MeV. K_V for the non-irradiated crystals is represented by a dashed line[40].

Here there is competition between two types of defects—those which accelerate and those which retard dissolution. The gradual decrease of K_V is probably associated with the accumulation of point defects of the electronic type, in the present instance of SO_4^- and e_{st}^-, while the appearance of displaced atoms promotes dissolution. We may note that with increase of electron energy to 5 MeV (the number of displaced atoms naturally increases under these conditions) the dissolution rate constant for a dose of $\sim 10^5$ rad increases approximately by a factor of 1.5 compared with K_V for specimens irradiated with electrons having energies of 3.5 MeV (also for a dose of 10^5 rad).

Extremely interesting results were obtained in a study[41] of the dissolution of γ-irradiated LiF crystals in distilled water containing iron ions. The authors showed that γ-radiation promotes the formation of two-dimensional defects in LiF crystals, which accelerated dissolution of the given salt on the (100) face. This was demonstrated by the appearance of double helices on the face undergoing dissolution, which did not occur in the absence of the radiation. The dissolution figures vanished almost completely and v correspondingly decreased after the annealing of the crystals in the course of 4 h at 550° C.

Summarising the data concerning the influence of γ-radiation and accelerated electrons on the dissolution of ionic crystals, certain conclusions may be drawn. Simple radiation-induced defects created by γ-quanta or accelerated electrons retard dissolution on irradiation under "milder" conditions (primary electronic or hole defects, for example, radical-ions, trapped electrons, etc.). The formation of displaced atoms, vacancies, and linear defects, which weaken the bonds in the crystal lattice and increase its free energy, promote the transfer of ions or molecules of the solid to the liquid phase. The formation of various associations of vacancies and displaced atoms as a result of postradiative processes can also retard dissolution. The sign of the effect of radiation on dissolution rate is therefore frequently reversed during the storage of such crystals.

V. THE INFLUENCE OF THE RADIATION-INDUCED CHARGING OF SOLIDS ON THE RATE OF THEIR DISSOLUTION

One cause of the retardation of the dissolution of irradiated crystals containing simple defects of the electronic type may be the radiation-induced charging of the dielectric crystals[40,42-47]. The appearance of an excess electric charge in irradiated solids was encountered for the first time after the discovery of radioactive elements and their accompanying radiations. Thus in 1900 Pierre and Marie Curie published the results of their experiments on the measurements of the charge of radium-containing barium salts[48]. This in fact has been used widely in the preparation of radioactive current sources (atomic batteries)[49-52].

In atomic batteries the source of radiation is usually surrounded by a weakly conducting medium—vacuum or a solid dielectric. In the latter case a space charge is gradually formed in the layer of the dielectric. The charging of dielectric materials is also observed, when they are irradiated with a stream of accelerated electrons and γ-quanta[51,53-65]. The concept of the charging of the bulk and surface of radioactive preparations has been used quite successfully recently to account for the characteristics of certain physicochemical processes involving the participation of radioactive solids[42,47,66-69].

The conditions for the formation of electric charges in irradiated materials have been fairly thoroughly investigated as a function of their dielectric properties[54,56,70-73]. A general theory of this phenomenon has been devised[51,52,59,61,73,74] and both empirical and theoretical formulae have been proposed, which make it possible to estimate both the magnitude of the radiation-stimulated charge[61,62] and the degree of polarisation of various specimens charged on irradiation[65,72]. A theory has been developed and measurements have been made of the accumulation of electric charges in radioactive crystals of inorganic salts[42,75-77].

Experiments have shown that, regardless of the mechanism of the formation of the radiation-induced charge and its distribution in the bulk of the solid, electric breakdown is observed under certain conditions, which is sometimes accompanied by the appearance of Lichtenberg figures[71,78-80]. This means that an electric field gradient, exceeding the breakdown potential, i.e. $E > 10^4$–10^6 V cm^{-1}, arises within the irradiated specimen. For example, when LiF crystals are irradiated with electrons having an energy of 1–2 MeV, tree-like channels—the tracks of electrical breakdown both during and after irradiation—develop within the crystal (for exposure doses of 1×10^{15}–1×10^{17} electron cm^{-2}). At the same time a large number of edge dislocations and particles of colloidal lithium appear along the channels and in the bulk of the crystal. All these features are superimposed on the radiation-induced defects[81]. The absence of electrical breakdown does not imply the absence of an excess of radiation-induced charge in dielectrics which have been irradiated with a stream of ionising particles; charging naturally leads to the appearance of bulk-phase polarisation, which persists for a long time after irradiation ceases.

Despite the fact that the charging of solids and the formation of a radiation-induced charge have been fairly thoroughly investigated, there has been virtually no systematic research concerning the influence of the electric field on the properties of solid specimens, the radiation-induced and radiation-chemical reactions in the latter, and also various heterogeneous processes. However, interesting information about the relation between the charge and properties of solids may be found in individual communications.

The formation of a radiation-induced charge has a marked influence on the kinetics of the formation and distribution of the radiation-induced defects in crystals[21,82], on the electron work function, and on the catalytic properties of solid oxide catalysts[66-68,83]. The influence of the electric field on the chemical and radiation-chemical processes in gases and liquids has been studied in detail (see Tal'roze's review[84]).

There are experimental data (admittedly only qualitative) concerning the appreciable influence of an external electric field and the charging of the solid phase on sorption phenomena in both liquid[47,85,86] and gaseous[68,69,87,88] phases. For example, anions[86] and negatively charged colloidal particles[85] are sorbed more effectively from solutions on positively charged crystals. Consequently the presence of an external electric field in a heterogeneous system, such as a solid–solvent system, or the appearance of excess charge at the interface on irradiation or polarisation alter appreciably the rates of processes involved in dissolution (sorption, crystallisation, orientation or disorientation of molecules at the interface, the rate of their migration in solution, etc.). All these factors make it possible to assume that the dissolution proper should also depend to a definite extent on the electric field in the system. The first experiments carried out on these lines confirmed the above hypothesis[45,46].

The theory of the dissolution of charged crystalline substances (dielectrics) has been most thoroughly developed at the present time. A possible relation between the charging of the crystals and the rate of their dissolution was postulated for the first time by Gromov and Bespalova[89] in a study of the dissolution of radioactive strontium sulphate crystals in water. Direct experiments then showed that NaCl, $SrSO_4$, etc. crystals, polarised by a permanent external electric field, dissolve more slowly than non-polarised compounds[45,90]. The polarisation of the solvent also has a definite influence; for this reason, the change in K_V depends in many respects on the ratio of the dielectric constants of the solid and liquid phases[90]. The intrinsic solubility of compounds is also very important (Fig. 8). Indeed, according to Fig. 8, with increase of the strength E of the field in which the crystals were polarised, K_V for celestite (the solubility of which is lowest among the substances investigated) decreases to the

greatest extent. The relative decrease of K_V in series of salts of the same type (NaCl, LiF, NaF) is greater for lithium fluoride—a compound which is less soluble than NaF and which has a higher dielectric constant.

The observed changes in the rate of dissolution can be explained in terms of the general ideas of the dissolution theory and the hypothesis that K_V can be represented in the form of two multipliers, one of which does and one of which does not depend on the polarisation of the crystal[45]. Theoretical analysis of the influence of the charging of the crystals on the kinetics of their dissolution showed that the dissolution rate constant depends in a fairly complex manner on the dielectric properties of the crystal, the surrounding medium, the structure of the double layer at the crystal–solution interface, and the electric field strength within the crystal[45,91]. It has been established[45] that, with increase of the electric field strength in the crystal and for not unduly low bulk-phase concentrations in the liquid phase, K_V diminishes regardless of the sign of the charge localised in the crystal. The essential feature of this influence is that the polarised molecule (dipole) must perform additional work to overcome the electrostatic interaction forces on transfer from the charged specimen to the liquid phase.

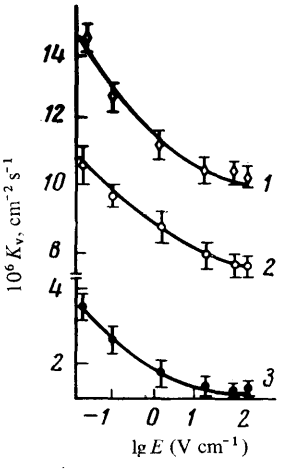


Figure 8. Variation of the rate constant for dissolution in water corresponding to different electric field strengths E (and hence different polarisations of the crystal)[90,91]: 1) NaF; 2) LiF; 3) $SrSO_4$.

Experiment showed that, in the dissolution of irradiated salts whose charge (and polarisation) is due to a non-uniform distribution in the bulk of the crystal of the carriers generated on irradiation, it is usually extremely difficult to isolate the influence of any one factor: charge, radiation-induced electronic defects, displaced atoms, or structural changes in the surface. This is because all the above consequences of the irradiation of the crystal are closely interrelated. However, we shall attempt to analyse the change in K_V for irradiated crystals which may be attributed to radiation-induced charging.

It has been established[36,38,39] that defects such as SO_4^-, SO_3^-, and e_{st}^- arise in $SrSO_4$ crystals irradiated with a stream of γ-quanta or accelerated electrons. At temperatures below −100° C for γ-irradiation or at room temperature for irradiation with electrons having an energy of approximately 1 MeV, only the SO_4^- radical-ions and thermalised electrons captured by traps are formed. Defects of the type of displaced atoms are not produced. Experiments with $SrSO_4$ crystals of this particular type were carried out by Parkhaeva et al.[40] The variation of the rate of dissolution of natural celestite ($SrSO_4$) irradiated with accelerated electrons having an energy of approximately 1 MeV is illustrated in Fig. 9.

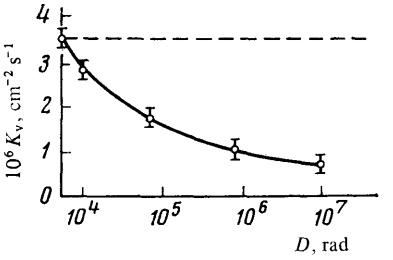


Figure 9. Dissolution of celestite single crystals in distilled water at 25° C after irradiation of the crystals with a stream of electrons having an energy of 3.5 MeV. The dashed line corresponds to non-irradiated crystals[40].

The experiments were performed as follows. The crystals were irradiated at 20–30° C (experiment showed that this entails the generation of the radiation-induced charge, SO_4^- radical-ions, and e_{st}^-) and were dissolved in distilled water at 25° C immediately after irradiation. Before dissolution, the outer layer of the crystal damaged by irradiation was removed by partial dissolution. Under these conditions, the changes in K_V could be attributed only to radiation-induced charging and the formation of electronic defects. Fig. 9 shows that celestite crystals freshly irradiated by electrons dissolve more slowly than the non-irradiated specimens. Evidently radiation-induced charging, the influence of which swamps that of radiation-induced effects, is of decisive importance in this instance. During the storage of crystals (for several months), the charge generated by irradiation partially leaked away (more precisely, the part of the charge not associated with the radiation-induced defects formed, whose concentration did not change during this period) and K_V increased somewhat, approaching the rate constant for the non-irradiated specimen. After thermal annealing, when all the defects disappeared, the properties of the irradiated and non-irradiated crystals were identical.

The results obtained for crystals of irradiated celestite can be explained satisfactorily by experiments with polarised specimens of the same mineral (Fig. 8, curve 3)[90]: K_V decreases smoothly with increase of the strength of the electric field causing the polarisation of the crystal (cf. Figs. 8 and 9).

In another series of experiments, LiF crystals were irradiated with fast electrons[91]. The thickness of the LiF plates was chosen so that virtually all the electrons

were absorbed in the specimen. In conformity with the theory of the radiation-induced charging and experimental determinations, the average excess space charge was negative. One of the irradiated crystals was placed in an electric field, the direction of which enhanced the radiation-induced polarisation. Others were placed in the field in such a way that its action promoted the depolarisation (the discharge) of the irradiated lithium fluoride. The results of these experiments are presented in Table 4, which shows that the smallest value of K_V is that of crystals in which the radiation-induced polarisation, caused by the non-uniformity of the distribution (and excess) of the charges, has been enhanced by the electric field. The decrease of polarisation as a result of the induced discharge of the irradiated LiF increases the rate of dissolution.

Table 4. Variation of the dissolution rate constant for electron-irradiated lithium fluoride crystals subjected to subsequent polarisation in an external 1500 V cm^{-1} electric field[91]*.

Experimental conditions	$10^6 K_V$, $cm^{-2} s^{-1}$
No field, crystal not irradiated	12.4
Field not applied to irradiated crystal	11.2
Electric field promotes discharge of irradiated crystal (depolarisation)	11.4
Electric field enhances polarisation of irradiated crystal	9.4

*The dose absorbed on irradiation amounted to 5×10^6 rad. Polarisation (depolarisation) time 48 h.

The experiments showed that on irradiation the influence of the radiation-induced charging can be observed in a pure form in certain cases. It is usually masked and partly swamped by the effect of radiation-induced defects. Evidently at least two opposed factors are manifested simultaneously in the irradiated compounds: the retardation of dissolution owing to the radiation-induced polarisation and the acceleration of the transfer of ions to the solution as a result of the formation of radiation-induced defects.

VI. RADIATION-CHEMICAL PROCESSES IN THE LIQUID PHASE AND DISSOLUTION

When the energy of ionising radiation is used to regulate dissolution processes, one can not only irradiate crystals before their interaction with the solvent, but an attempt can be made to act on the entire solvent–dissolved substance system. In this case the energy of the radiation is absorbed mainly by the liquid phase, because its amount is as a rule many times greater than that of the compound being dissolved. Furthermore, dissolution is usually rapid, and the radiation doses absorbed by the solid are much smaller than those which alter the rate of dissolution on preliminary irradiation of the crystals. Consequently the main radiation-induced processes occur in the liquid phase and the effect of radiation on dissolution is indirect—it is due to the interaction of the products of the radiolysis of the solvent with the solid phase.

Somewhat different conditions are possible in the dissolution of radioactive salts (the special case of dissolution directly during irradiation). It can be readily understood that here all the phenomena accompanying the dissolution of irradiated solids take place: radiation-induced charging, the accumulation of radiation-induced defects, breakdown of the structure of the surface, and radiolysis of the liquid phase. Bearing in mind that such salts are used in "atomic technology", the study of dissolution directly under irradiation is clearly of special interest.

The dissolution process has been studied directly in the field of γ-radiation, using the dissolution of the uranium oxides UO_2 and U_3O_8 in acid or alkaline media[92–94]; the rate of this process depends on the heterogeneous oxidation of uranium(IV) to uranium(VI)[95]. In the hydrometallurgical processing of uranium ores various oxidants (H_2O_2, O_2, MnO_2, etc.) are usually added to the liquid phase, which promotes the conversion of uranium(IV) into uranium(VI) and, in view of the higher rate of dissolution of uranium(VI) oxides compared with uranium(IV) oxides, this results in a more effective extraction of uranium from ores[96,97].

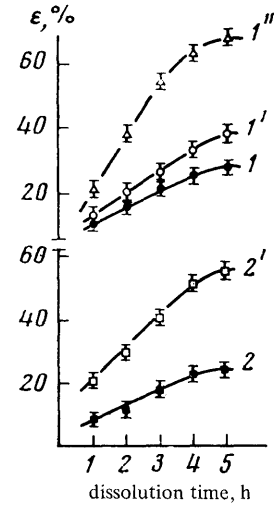


Figure 10. Variation of the degree of transfer of uranium ϵ to the liquid phase on dissolution of UO_2 and U_3O_8 in 0.1 N H_2SO_4: 1) U_3O_8, system not irradiated; 1′) and 2″) U_3O_8, system irradiated during dissolution using dose rates of 20 and 1.2×10^3 rad s^{-1} respectively; 2) UO_2, system not irradiated; 2′) UO_2, system γ-irradiated during dissolution using a dose rate of 1.2×10^3 rad s^{-1}.[92]

Experiments designed to investigate the dissolution process in the field of γ-radiation were performed with finely dispersed UO_2 and U_3O_8 powders, which were prepared by the usual methods[95]. Irradiation with ^{60}Co γ-rays was performed in air in open thermostatted vessels, with free access of air (aerated solutions). The dose rates used in the experiments were varied from 20 to 10^3

rad s^{-1}. The solvents consisted of 0.1 N H_2SO_4 and a carbonate solution (40 g $litre^{-1}$ of Na_2CO_3 and 30 g $litre^{-1}$ of $NaHCO_3$, pH ~ 10), which are used most frequently in the technology of the processing of uranium ores[96-98].

Fig. 10 presents the results of the determination of the degree of transfer of uranium (ϵ) to the solution for different dose rates. ϵ was determined from the expression

$$\varepsilon = ([U]_{soln.}/[U]_{solid}) \cdot 100, \quad (7)$$

where $[U]_{soln}$ is the amount of uranium in the liquid phase at time t and $[U]_{solid}$ is the initial amount of uranium in the solid phase. Fig. 10 shows that, under the influence of γ-radiation, the degree of transfer of uranium to the liquid phase increases. At a dose rate of 1.2×10^3 rad s^{-1} ϵ increases approximately by a factor of 2.5 for U_3O_8 and 2.1 for UO_2. For higher radiation intensities, during prolonged dissolution (lasting more than 2 h), when the liquid phase was saturated with uranium and the consumption of H_2SO_4 began to have an effect, the increase in the rate of dissolution diminished. A similar relation between ϵ and the dose rate is characteristic of the dissolution of uranium oxides in the carbonate solution[93]. The influence of γ-radiation on the transfer of uranium to the solution was estimated in the above studies by comparing the rates of dissolution referred to unit surface area of the oxides.

The experiments showed that v is independent of the integral dose at least during the first hour, since the rate of dissolution of UO_2 remains constant in the course of γ-irradiation at a fixed dose rate. With increase of the dose rate, v steadily increases. The time interval corresponding to a constant value of v diminishes with increase of the dose rate, mainly owing to the gradual saturation of the liquid phase with uranium. The above features of the variation of v are characteristic of the dissolution of uranium oxides both in 0.1 N sulphuric acid and in the carbonate solution.

According to Gromov and coworkers[92,94], this shows that the decisive factor accelerating the transfer of uranium to the liquid phase (at least in the first stages of the dissolution process) is the interaction of the oxide undergoing dissolution with the radical products of the radiolysis of water, the concentration of which depends on the intensity of the radiation. This conclusion is confirmed also by experiments with radical acceptors, the addition of which to the solution sharply reduces the efficiency of γ-radiation. Thus the addition to the sulphuric acid solution of 1×10^{-4} M CH_3OH, which is an acceptor of OH radicals, decreased ϵ by a factor of 1.3 for a dose rate of approximately 400 rad s^{-1}.[94] Naturally, one cannot fully rule out the influence of the molecular products of the radiolysis of water, for example H_2O_2, etc., but their effect may be manifested only in later stages of the dissolution process when they have accumulated in sufficient amounts. At least during the first two hours, their influence may be disregarded.

Experiment showed that the increase of v with increasing dose rate (I) is not associated with the effect of radiation in the solid phase, since preliminary γ-irradiation of U_3O_8 or UO_2 *in vacuo* actually retards dissolution somewhat[31,34]. Consequently the acceleration of dissolution is caused by the oxidation of uranium(IV) to uranium(VI) by the products of the radiolysis of the liquid phase on the surface of the dissolving oxide. On this basis, the authors relate the rate of dissolution of uranium oxides to the intensity of γ-radiation. It was shown that, in the initial stages of the dissolution in both acid and carbonate media, the following relation holds[92]:

$$\lg v_I = \text{const} + {}^1/_2 \lg I, \quad (8)$$

where v_I is the contribution to the overall rate of dissolution determined by the action of radiation. The main assumption in the derivation of the above formula is that the radical products of the radiolysis of water[99,100] namely OH and HO_2 in the sulphuric acid solution and O_2^- and CO_3^- in the carbonate solution, which are strong oxidants[101,102], play the main role in the dissolution process. These radical products oxidise uranium on the surfaces of the dissolving oxides to the hexavalent state, which accelerates the dissolution processes as a whole. In conformity with the adopted radiolysis mechanism, the steady-state concentration of the radical products of the liquid phase proved to be proportional to $I^{1/2}$, which in fact determines the final form of Eqn. (8).

The dependence of $\lg v_I$ on $\lg I$ in the dissolution of uranium oxides in sulphuric acid is illustrated in Fig. 11, which shows that the slope of the straight lines is 0.5 within the limits of experimental error, for both UO_2 and U_3O_8, in agreement with Eqn. (8). Deviations from the linear relation are observed for a dose rate of 1.2×10^3 rad s^{-1}, when the accumulated hydrogen peroxide (a molecular radiolysis product) probably accelerates the dissolution of the oxides. It was also noted that, after 2–3 h of dissolution, the experimental results ceased to agree with Eqn. (8). According to the authors[92] this is caused by the consumption of H_2SO_4 and the change in the surface area of dissolving oxides [in the derivation of Eqn. (8) the above parameters were assumed to be constant], which cannot be taken into account with adequate accuracy by the available methods. Eqn. (8) also holds fairly accurately in experiments involving the dissolution of UO_2 and U_3O_8 in the sodium carbonate solution[93,94]. The slope of the $\lg v_I - \lg I$ straight lines for the carbonate medium is likewise 0.5, indicating the validity of the main assumptions made in the derivation of Eqn. (8).

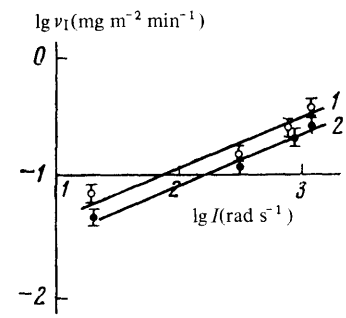


Figure 11. Dependence of $\lg v_I$ on the logarithm of the γ-radiation dose rate for UO_2 (line *1*) and U_3O_8 (line *2*) in the dissolution of the oxides in 0.1 N H_2SO_4. The values of v_I were calculated by Eqn. (8) for the range of dissolution times 0–60 min.[92,94]

Additional intensification of the dissolution of uranium dioxide can also be achieved as a result of the preliminary radiation-chemical solid-phase oxidation of uranium(IV)

when the dry oxide is γ-irradiated in the presence of air. Thus X-ray diffraction showed that UO_2 acted upon by γ-quanta in air, for absorbed doses of approximately 10^8 rad, is converted into U_3O_8 to the extent of 20%. The radiation-induced oxidation of UO_2 in air probably proceeds via the following mechanism

$$UO_2 \xrightarrow{\gamma} (UO_2)^* + O_{2(air)} \text{ and } UO_2 \cdot mU_3O_8 \text{ or}$$
$$UO_2 + O_3 \xrightarrow{\gamma} n\,UO_2 \cdot m\,U_3O_8 \quad . \qquad (9)$$

The oxygen involved in the oxidation of UO_2 may be present in the dioxide itself (within pores and cracks) or can come from the surrounding medium.

The formation of uranium(VI) in uranium dioxide subjected to preliminary γ-irradiation affects also the rate of dissolution of UO_2, since the U(IV) $\rightarrow$ U(VI), transition limiting the rate of dissolution, takes place partly even in the solid phase under the influence of γ-irradiation [103-105].

Unfortunately the study of dissolution processes directly in the field of ionising radiation, which appears to be promising from the practical point of view, has so far been limited to the above system comprising uranium oxides and a sulphuric acid or carbonate solution [92-94, 103-105].

Further studies on these lines will evidently yield much new and interesting practical and theoretical information.

VII. CONCLUSION

It follows from the data discussed that the rate of dissolution of irradiated solids is affected by many factors, which frequently act in opposition. Depending on the dissolution conditions, defects of only one type can be of decisive importance, while others play a passive role, although their concentration is in fact high.

The main effects of the radiation-kinetic phenomena in the dissolution process are associated with the formation of radiation-induced defects, a change in the structure of the surface, and the charging of the irradiated solid. However, their contribution is in many respects determined by the nature of the specific substance. For example, in the case of metals there is no point in taking into account the radiation-induced charging, since charges rapidly leak away and recombine with carriers of the opposite sign. This also applies to any non-metallic specimens whose intrinsic conductivity is more than 10^{-5} Ω^{-1} cm^{-1}.

The wide variety of the effects of radiation and their influence on the rate of dissolution creates certain difficulties in the study of the given phenomenon [43]. However, there are ways of reducing the influence of a particular change in structure on the dissolution process (Table 5). Table 5 shows that, in principle, it is possible to select conditions such that, after appropriate treatment of the irradiated compound, the effect of radiation on the dissolution process becomes insignificant.

A promising field for the utilisation of radiant energy in order to stimulate heterophase reactions (including dissolution reactions) involves the irradiation of the entire solid–solvent system. A necessary condition in this instance is the oxidation (or reduction) at the interface of the compound undergoing dissolution. If it limits the rate of dissolution, then ionising radiation may constitute an effective means of influencing the process as a whole.

Further development of studies on the practical utilisation of radiation-induced dissolution of solids depends on the solution of many theoretical and experimental problems.

Table 5. The influence of radiation-induced defects on the kinetics of the dissolution of solids [43].

Effect of radiation	Change in rate of dissolution	Method of reducing the influence of given effect
Displaced atoms and linear defects	acceleration	annealing
Trapped electrons or holes, radicals (electronic defects)	acceleration or retardation	annealing
Loosening of surface	acceleration	annealing, recrystallisation, dissolution of surface layers
Radiation-induced polishing of surface	retardation	annealing, prolonged storage of crystals before dissolution
Radiation-induced charging	retardation	
Dissolution of radiolysis products of solid	acceleration or retardation	annealing, change in liquid phase
Radiolysis products of liquid phase	acceleration (provided that dissolution process is accompanied by heterogeneous oxidation or reduction)	introduction of radical acceptors into liquid phase, experiments with non-oxidisable salts
	have no influence on dissolution in the absence of oxidation (reduction) of solid phase	

1. The development of a theory of the influence of point defects of various types (primarily electronic) on the rate of dissolution.
2. The study of the effect of various impurities in the crystal lattice on the subsequent dissolution of the irradiated substances.
3. The study of the influence of a single definite type of defect on the values of K_V for various systems; the development of methods for suppressing (or forming) radiation-induced defects which are undesirable in the given specific instance. Evidently the use of the effect of light on the given system is extremely promising in this connection.
4. A wider employment of the effects of the irradiation of solid and liquid phases simultaneously; the selection of optimum conditions for the selective acceleration of the dissolution of complex systems under irradiation.

The development of these fields will not only extend and deepen our knowledge of the mechanisms of the dissolution of solids, but will undoubtedly make it possible to develop new practical methods for regulating heterophase processes.

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