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Effect of Impurities on Radiation-chemical Processes in Crystals of Inorganic Salts

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Research results obtained on radiation-chemical processes in crystals of inorganic salts having composite anions (nitrates, sulphates, oxyhalides, etc.) containing various chemical impurities are analysed. The effect of water of crystallisation on the mechanism of the radiolysis and on the radiation-chemical resistance of inorganic compounds is examined. The role of heterophase additives (of a mixture of inorganic substances), the conditions of exposure, and the mechanism of transfer of energy in irradiated systems are discussed. The contributions of various factors (ionisation potentials of lattice ions, electron affinity of radiolysis products, lattice parameters, electrophysical properties of impurities, etc.) to the radiolysis of inorganic salts are estimated. Possible ways of controlling the radiation resistance of exposed materials are discussed.
The bibliography includes 121 references.

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I. INTRODUCTION

Research on the effect of ionising radiations on crystalline compounds has been especially widely developed during the past 15–20 years, largely because of the need to ascertain how corpuscular radiation and γ-rays affect the diverse structural materials employed in reactor engineering and also to establish the general features of radiation and radiation-chemical processes in various substances. Close attention has been paid in particular to the physical and chemical phenomena produced by ionising radiations in ionic compounds. This is associated e.g. with problems of trace techniques and the monitoring of radiations, study of the radiation stability of materials, and also attempts at a scientific approach to the change in properties of irradiated compounds. All these aspects require in some way a knowledge of the general mechanism (or mechanisms) of radiation-chemical processes in various classes of compounds.

Radiation and radiation-chemical processes have hitherto been most fully studied in crystals of alkali-metal halides, in nitrates, and in oxyhalides. Efforts have been directed mainly at identifying the products of radiolysis, studying the kinetics of their accumulation and annealing, establishing qualitative and quantitative relations between the yield of radiolysis products and the lattice energy,

linear energy transfer, pressure, and temperature, and recently at establishing the effect of various impurities on radiation-chemical processes. Impurities can sometimes have a decisive effect on the radiation-chemical resistance† of irradiated compounds, which can be utilised for controlling radiation-chemical processes in crystalline substances.

Although contributions increase annually, no systematic review and analysis has yet been made of the results scattered in many papers and journals, which may even in some degree hinder research in this field. The present Review attempts to fill the existing gap.

No claim is made to complete coverage of all the material. For example, the large section concerned with the radiation-thermal decomposition of solids is omitted, nor are many aspects of the action of radiation on alkali-metal halides considered. Attention is paid mainly to salts having composite anions. Deliberate restriction in the selection of material is due to the desire to adhere more closely to the essence of the question, without encumbering the paper with a mass of additional factual data. Nevertheless, references to the appropriate papers can always be found in the text.

II. GENERAL ASPECTS OF THE RADIOLYSIS OF INORGANIC SALTS

The experimental information that has accumulated on the radiolysis of salts of various acids shows that many features of radiation-chemical processes depend on the chemical composition of the test materials. Despite this, however, it is always possible to distinguish a large group (or groups) of typical primary and secondary reactions taking place whatever the compound irradiated. It is also noteworthy that the general processes do not exclude the presence of individual specific elementary reactions in the radiolysis of certain salts.

The primary processes of radiolysis comprise mainly the ionisation and excitation of anions A and cations C or the excitation of groups of ions according to fundamental schemes[1,2] of the type

$$h\nu \rightsquigarrow (K^{z_K}, A^{z_A}) \rightarrow (K^{z_K}, A^{z_A})^* \text{ or } (K^{z_K})^*, (A^{z_A})^* \quad (1)$$

$$h\nu \rightsquigarrow (K^{z_K}, A^{z_A}) \rightarrow K^{z_K-n}, A^{z_A-m}, (m+n)e^-, R_A^* , \quad (2)$$

where z is the ionic charge and R_A* are the excited radicals formed from the anions. Repeated ionisation is improbable, so that m and n are usually unity.

Because there are two main types of primary interaction of radiation with matter, the radiolysis of salts occurs in two ways—through secondary reactions of excited molecules and secondary interconversions of ionisation products—but it is often very difficult to determine the contributions of ionisation and excitation in the primary and subsequent stages of radiolysis. The reason is that present-day techniques (conductivity measurements, electron spin resonance) enable only ionised products to be reliably and fairly simply identified in a solid. The role of excited species in radiation-chemical processes must usually be assessed from indirect results. However, many analyses have recently been made of the formation of excited states and their role in various radiation processes.

† The radiation-chemical resistance of a salt is usually characterised by the extent of decomposition of the compound (Section II).

According to Lushchik, for example, a cascade of secondary electrons produces a series of electronic excitations of the ions of the main substance (of energy ~ 100 eV). These electronic states are unstable, and pass rapidly into stable electronic states of low energy—excitons and electron–hole pairs of energy ~ 10 eV—which determine the final radiation effects—luminescence, formation of colour centres, dislodged atoms, and subsequent radiation-chemical reactions—in ionic crystals[3,4]. Analogous phenomena can be observed as a result of the self-trapping of holes formed at low and even room temperature[5,6].

Elango et al.[7-10] showed in a series of experiments that colour centres are formed in alkali-metal halide crystals on exposure to light and soft X-rays. They consider that the main role is played by excitons, whose decay is able to initiate the formation of ionised species. In several papers the formation of excited species has been regarded as the primary stage of radiolysis[10-12].

Excited and superexcited electronic states evidently play an important part in radiation-chemical reactions[13,14]. However, analysis of numerous papers shows (without going into the mechanism of the primary act of absorption of the radiated energy and the intermediate stages of its transfer) that the conventional separation of all radiation-chemical reactions into two groups (reactions 1 and 2) is probably legitimate. It must be borne in mind that under certain conditions reaction (1) may precede the ionisation of cations and anions.

Certain workers usually distinguish two temperature regions when considering typical secondary reactions in the most thoroughly studied ionisation branch of radiolysis, in each of which a characteristic group of reactions takes place[1,14,15]. At low temperature (up to ~ 200°K) processes involving the recombination of radicals R with an electron are most often observed:

$$R + e \rightarrow (R^-)^* \rightarrow R^- + h\nu , \quad (3)$$

or

$$R + e \rightarrow (R^-)^* \rightarrow \text{product} . \quad (4)$$

In sulphates of alkali and alkaline-earth metals, for example, the reaction

$$SO_4^- + e \rightarrow (SO_4^{2-})^* \begin{cases} \nearrow SO_4^{2-} + h\nu \\ \searrow SO_3^- + O^-,\ (SO_3^- + O + e) \end{cases} \quad (5)$$

takes place[16], with formation of the initial sulphate ion and its radical dissociation products. At low temperatures dimerisation of the primary radicals

$$R + R \rightarrow R_2 \quad (6)$$

or

$$R_1 + R_2 \rightarrow R_2' \quad (7)$$

is also possible. The above reactions are typical of organic compounds and certain composite inorganic salts[17]:

$$ClO_3 + ClO_3 \rightarrow Cl_2O_6 . \quad (8)$$

In the region of ~ 200°K the most probable processes involve the decay of composite radicals into simple radicals and stable products:

$$R \rightarrow R_1, R_2, R_3 \ldots \text{(stable products)} . \quad (9)$$

For example[1,17]

$$ClO_3 + e \begin{cases} \nearrow ClO_2^- + {}^1/_2 O_2 \\ \searrow Cl^- + {}^3/_2 O_2 \end{cases} . \quad (10)$$

The above classification of primary reactions is, of course, extremely arbitrary, and individual deviations from the suggested scheme are possible in particular cases. Thus the dimerisation of radicals or processes resembling (8) are often observed at temperatures above 200°K.[1,15-19]

It is not only difficult but also dubious to introduce exact limits to these temperature regions without specifying the compounds. Even with a definite substance the temperature ranges within which particular radiation-chemical reactions occur may shift with the nature and the quantity of various impurities, the "biography" of the crystal, etc. It is therefore advisable to refine this concept (classification) in subsequent investigations.

Besides the above reactions there are still quite a large number of intermediate reactions of primary and secondary radicals, molecules, and fragments of composite anions or cations. Such processes fall into the main types[1]—(i) reactions between R and its breakdown products with the formation of composite radicals, e.g. $ClO-ClO_3^-$ and $N_2O_3^-$ in chlorates and nitrates respectively; (ii) interaction of thermalysed electrons with radicals and anions (processes 3–6); (iii) reactions of atomic oxygen with anions and radicals, e.g. the interaction of O and NO_2^- in the nitrates, and of ClO_3^- and O in chlorates and perchlorates; and (iv) reactions among excited molecules, ions (breakdown), and atoms with the formation of O_2 and O_3^- in oxy-salts, etc.

The formation of various products in irradiated salts may depend in larger or smaller degree on many factors. Substances that are less subject to the action of radiation possess several specific features responsible for their radiation.resistance[20]. *Radiation resistance* (or stability) is taken to be the ability of substances to withstand the action of radiation without change in their structure-sensitive properties, and could be measured by the stored energy[21-23]. This concept is close to the *radiation-chemical resistance*, which determines the extent of radiation chemical changes in an irradiated specimen, and is characterised by the yield G of the corresponding product (or decomposition of the whole compound).

The radiation-chemical yield of a particular product depends on a large number of properties of the solid, the radiation, and the conditions of irradiation. No unequivocal general quantitative relations have yet been established between G and the various parameters of the test systems. Only in isolated cases have the first steps in this direction been taken.

These two criteria, representing in different ways the interaction of radiation with a given compound, are almost identical. With alkali-metal halides, for example, a sharp distinction cannot be made between them, the differences being purely terminological. It is therefore more expedient (and even essentially more correct) to replace them by a concept such as *radiation resistance* defined by the totality of changes in the irradiated specimen due to the action of radiation. The *radiation yield* (G)—the quantity of various products (F-centres, localised holes, dislodged atoms, radicals, ions, new molecules, etc.) formed in the specimen by the absorption of 100 eV of radiant energy—must obviously be adopted as an [inverse] measure of radiation resistance. This preserves all the previously established relations for the variation in properties of exposed substances, determined by the stored energy or the radiation-chemical yield: it unites the purely "physical" and purely "chemical" approaches to the phenomenon.

The type of bond is usually very important. When various oxides are exposed in a reactor, for example, their radiation stability diminishes in the sequence

$$Al_2O_3 > BeO > ZrO_2 > SrO\ .$$

The covalent character of the bonds increases in a similar sequence[20]. Furthermore, radiation stability decreases from metallic to ionic, covalent, and molecular bonds[20,24]. These rules hold in series of compounds of the same type. However, the correlations are purely qualitative and extremely tentative.

The stability towards radiation usually increases with increase in the *lattice energy*[21-25], which is evidently one of the main characteristics determining the radiation resistance of solids. Thus the properties of ionic crystals of low lattice energy change considerably more strongly in the exposed zone than those of substances of high lattice energy. However, the resulting reversible radiation disturbances disappear far more slowly in compounds of the latter type[21,26].

The sensitivity of inorganic ionic compounds to radiation is largely dependent on the composition and on the nature of the bond. Thus in ionic crystals containing composite anions, in contrast to binary ionic salts such as alkali-metal halides, the bonds between elements in the lattice may be strong, with a small volume of free interstices‡, and hence little probability that atoms (ions) will be displaced from their normal positions. In many cases, therefore, a correlation is observed between the yields of radiolysis products from ionic salts and the free volume V_{fr} of the unit cell, defined as the difference between the volume of the cell and that of the ions occupying it[27-29]. The relation between radiolysis yields and free volume, noted by almost all authors, probably represents a cage effect. For a first-order or pseudounimolecular radiolytic process G and V_{fr} are related by the formula[29]

$$G = f[\exp(-k/V_{fr})]\ . \qquad (11)$$

The free volume—a phenomenological characteristic of the properties of crystals—is a parameter representing the cooperative character of the bonds in a solid that are responsible for solid-phase reactions. The disintegrating ion is usually more weakly bound in crystals with large free volumes (loose lattices): i.e. the probability of dissociation and of escape of radiolysis products from the cell is increased, while reverse processes of recombination diminish. Hence the initial yields of radiolysis products should increase, in series of compounds of the same type in which the cation or the anion is replaced (presumably also with bonds of the same character and the same lattice structure), as the free volume increases[27,28]. But macroscopic diffusion is also increased in loose crystals, which may tend to diminish the yields G.[30]

The nature of the cation has an appreciable effect on the yield G, which e.g. with nitrates increases in the sequence[28,30-33]

$$Li < Na < Rb < Cs < K$$

$$Cd,\ Ag < Pb < La < Ba\ .$$

In this case the properties of the cation must evidently also be taken into account, especially in series of salts having the same anion, besides the above role of the free volume.

‡ It makes sense to compare the volume of free interstices with the size of the lattice ions in series of salts of the same type.

Thus with silver and cadmium halides rise in the ionisation potential of the cation intensifies the irreversibility of radiolysis and increases the yield of decomposition products[34,35].

The effect of the free volume is usually decisive where the variation of ionisation potential in a series of salts of the same type is small. In salts with like anions and the same or almost the same free volumes the radiation resistance is higher in the compound whose cation has the lower ionisation potential. This is probably due to the polarising effect of the cation on the anion. Such interaction was reflected in the empirical dependence of the efficiency of decomposition of salts of the same type on the ratio of the ionisation potentials of the cations[1,36]:

$$G = G_A E_A + G_c E_c \frac{I_{M_1^+}}{I_{M_2^+}} , \qquad (12)$$

where G_A and G_C are the efficiencies of decomposition of the salts calculated per 100 eV of energy absorbed solely by anions and by cations respectively, E_A and E_C their ionicities, and the I the ionisation potentials. This formula describes well the radiolysis of several halogenates at not very high temperatures (Fig. 1).

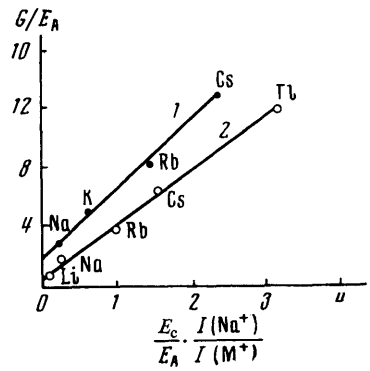


Figure 1. Dependence of radiolysis of salts on ionicity of anion and cation allowing for ionisation potential of cation[1]: 1) chlorates; 2) bromates.

Where ionisation processes predominate in the formation of the primary products, increase in their *electron affinity* involves a decrease in the radiolytic decomposition of the salts. This rule is illustrated by the selenates, sulphates, and carbonates of alkaline-earth metals (barium, calcium). In these compounds the primary products of radiolysis are the radical-ions SO_4^-, SeO_4^-, and CO_3^-, whose relative electron affinities are approximately 1 : 1.3 : 2§. The total yield of paramagnetic species from the salts follows the same sequence.

Where the formation of the primary radiolysis products involves rupture of bonds in the anion, the subsequent radiation processes depend on the electron affinity of these products. Alkali-metal nitrates, chlorates, bromates, and iodates can be included in this group of salts (with a readily broken bond in the anion). In this case increase in the electron affinity of the primary products is accompanied by an increase in the overall efficiency of decomposition of the salt. Thus because ClO_2 in chlorates possesses a greater electron affinity than does NO_2 in nitrates, the reaction

$$ClO_2 + e^- \rightarrow (ClO_2^-)^* \rightarrow ClO^- + O \qquad (13)$$

goes more strongly than does

$$NO_2 + e^- \rightarrow (NO_2^-)^* \rightarrow NO^- + O . \qquad (14)$$

Therefore the total yield of radiolysis products should be higher (under the same conditions) e.g. in potassium chlorate than in potassium nitrate, as is observed experimentally. The electron affinity of ClO_2 actually governs reaction (13) to some extent. However, the final yield of radiolysis products from reaction (14) largely depends on competition between deactivation of the excited state and dissociation of $(NO_2^-)^*$ into NO^- and O. Salts of this type conform to the relation

$$A_1/A_2 = K \frac{G_1(O_2)}{G_2(O_2)} , \qquad (15)$$

where A_1 and A_2 are the electron affinities of the primary products of radiolysis in the salts, and K is a constant representing all the factors other than electron affinity that influence the radiolysis (type of cation, free volume of lattice, energy of bond, etc.). In the above salts, for example, $A_{NO_2} = 1.62$ and $A_{ClO_2} = 3.43$, while $G(O_2)_{KClO_3} = 2.0$ and $G(O_2)_{KNO_3} = 0.8$.[31] Formula (15) is probably general in character, and can be used for the approximate comparison of radiation resistance in series of analogous salts of the second group.

The above examples show that radiation-chemical processes in salts, and hence the yield of individual products, depend on many factors governing the individual and collective interactions in the undisturbed and irradiated crystal lattice.

The linear energy transfer and the dosage rate are also very important in radiolysis[37-45]. Several investigations have recently been made on these aspects, including experiments on the exposure of various salts to heavy accelerated particles. For example, the bombardment of nitrates with protons changes substantially the rate of formation of nitrite, the initial yields of which are 0.50, 0.92, 1.65, and 2.00 for sodium, rubidium, caesium, and potassium nitrates respectively[38-41]. The γ-irradiation of these salts results in lower initial yields—approximately 0.3, 0.6, and the range 1.0–1.2 for the potassium and caesium salts[27,31].

Exposure of compressed pellets of sodium nitrate to protons produces a maximum yield of nitrite if the specimens are at +180°C.[40,42] At the same time a monotonic decrease in $G(NO_2^-)$ from 1.6 to 0.6 is observed with increase in the linear energy transfer from 2 to 6 eV $Å^{-1}$. At lower temperatures the yield of nitrite first increases and then falls with increase in the linear energy transfer (Fig. 2). These effects are well explained by the enhanced probability of reverse processes with large linear energy transfers (too high density of primary defects in the track), which ultimately lowers $G(NO_2^-)$. It is assumed further that local heating in the track tends to accelerate the radiation-chemical processes. Two regions of radiolysis are therefore distinguished: in the low-temperature range (the track is at a higher temperature than the matrix) local heating in the tracks is of decisive importance; in the high-temperature region the

§ The electron affinities were taken for the species in the gas phase (from standard tables).

yield of radiolysis products is affected mainly by processes of recombination in regions having a high content of primary products (the yield $G(NO_2^-)$ decreases).

It has been concluded[43] from a study of the radiolysis of alkali-metal azides, perchlorates, and nitrates by cobalt-60 γ-quanta and by protons that the variation in yield of products cannot be explained by thermal effects in the track even with large linear energy transfers. It was also shown that the bombardment of azides, nitrates, and especially perchlorates by protons diminishes the dependence of the yield on the free volume of the unit cell.

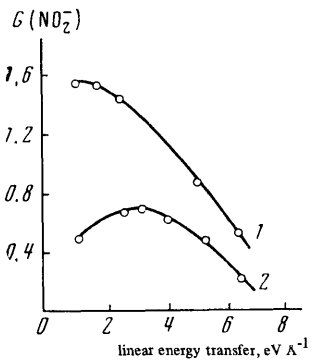


Figure 2. Variation in yield of nitrite in proton-irradiated compressed sodium nitrate pellets for radiolysis at: 1) 180°C; 2) 25°C[40].

Several investigators prefer to explain the variation of yield with linear energy transfer solely by thermal effects in the tracks[37,38]. It was also suggested that charges may be displaced in the region of the tracks, with intensified dissociation of lattice ions[39].

The effects of dosage rate on radiation-chemical processes in various salts involve problems closely similar to the influence of linear energy transfer on yield, but have not yet been studied in adequate depth. Most of the relevant publications reveal no variation in yield at different dosage rates[39,44-50]. For example, variation in the rate of electron irradiation from 10^{17} to 10^{20} eV g^{-1} s^{-1} produces hardly any change in $G(NO_2^-)$ in potassium, sodium, caesium, and lead nitrates[48], a conclusion supported by other work[46,47] for a wider range of dosage rates (10^{15}–10^{20} eV g^{-1} s^{-1}) and other forms of radiation. Similar conclusions can be reached also for chlorates and bromates[49,50].

The above examples still do not give complete clarification of this field. Thus there are indications that yields of primary radicals vary with different intensities of self-irradiation in radioactive alkaline-earth metal sulphates[51-53]. Experiments with strontium sulphate crystals exposed to cobalt-60 γ-quanta have also shown that at room temperature the radical concentration ratio $C_{SO_4^-}/C_{SO_3^-}$ decreases from 2.9 to 2.1 with increase in the dosage rate from 6.2×10^{13} to 6.2×10^{16} eV g^{-1} s^{-1} (in both cases the absorbed dose was $\sim 10^{20}$ eV g^{-1}). At low dosage rates the total concentration of paramagnetic centres increases at the same time by almost 30%. The observed effects are probably caused by accelerated recombination of radicals in "hot zones" (or points), whose concentration is higher at high dosage rates[54].

The nature of the cation can exert a great influence on primary radiation-chemical processes (in series of salts of the same type, e.g. alkali-metal nitrates). Several workers consider that the yield of radiolytic decomposition products from the anion depends not only on its ionicity but also on interaction of the cation with the radiation[30,31,33,55]. Ionisation of the cation and the transfer of excitation energy (charge) from cation to anion play an important part here[1,33,56].

In concluding this Section we note that such factors as degree of dispersion, pressure, and temperature also affect the occurrence of radiation-chemical processes in crystals of inorganic salts. Increase in the dispersity of crystalline nitrates is accompanied by increase in $G(NO_2^-)$, an effect attributed to oxygen trapped in the crystal surface[55], which usually promotes the reverse reactions. Furthermore, gaseous products may migrate to the surface of fine particles, where they may react chemically among themselves and with the surrounding medium, as has been observed in the radiolysis of powdered succinic acid[57].

The effect of temperature is largely dependent on the mechanism of radiolysis and the reverse reactions, which are accelerated by heating. In sodium, potassium, and rubidium nitrates, for example, the yield of NO_2^- increases with rise in temperature above $\sim$ 130°C[41,57-61]. With sodium nitrate this is attributed[59,60] to an increased probability that excited $*NO_3^-$ ions will break down into NO_2^- and O. In the case of rubidium[41] and potassium[59] nitrates the observed increase in $G(NO_2^-)$ is ascribed to polymorphic transitions in crystals. The irradiation of potassium[16], barium, calcium, and strontium sulphates at high temperatures stimulates the breakdown of excited sulphate ions resulting from the recombination of primary SO_4^- radical-ions with electrons:

$$SO_4^- + e \rightarrow \overset{*}{SO_4^{2-}} \rightarrow SO_3^- + O^-(O + e)\,. \qquad (16)$$

A reaction of type (4) without destruction of $*SO_4^{2-}$ occurs between −196° and −50°C. There are examples in which temperature has hardly any effect on radiolysis. Thus the yields of Cl, ClO^-, Cl_2^-, O_2^-, and ClO_2 in potassium chlorate remain almost unchanged between 77° and 300°K[58].

Changes in the crystal lattice caused by pressure have an appreciable influence on the yields of radiolysis products, owing to the slowing down or acceleration of radiation-chemical reactions. Increase in pressure (preliminary compression) usually lowers $G(NO_2^-)$ in nitrates[41]. Analogous effects occur if the irradiated crystals and the surrounding medium (air, an inert gas) are under pressure[61]. The dependence of the yield of radiolysis products on pressure and temperature (both these parameters usually vary in experiments) is quite complex, and largely determined by the mechanism of primary and secondary reactions[61].

All the above features of the radiolysis of inorganic compounds depend in considerable measure on the presence of impurities, which are directly or indirectly involved in radiation-chemical processes.

III. EFFECT OF WATER OF CRYSTALLISATION ON RADIATION-CHEMICAL PROCESSES IN CRYSTALS

The effect of water of crystallisation (which can also be regarded as an impurity in the matrix of the main material) on radiolysis was first noted in 1952 during an

investigation of the photochemical decomposition of lanthanum nitrate[62]: the crystal hydrate was found to decompose more rapidly than the anhydrous salt. Somewhat later a similar effect was observed in the same salt on exposure to γ-quanta[46]. Baberkin and Proskurin then undertook a detailed study of the radiolysis of a series of hydrated nitrates of bivalent cations[63,64]. On exposure to cobalt-60 γ-rays at room temperature the tetrahydrate of calcium nitrate decomposed several times more rapidly than the anhydrous salt (Table 1).

Table 1. Effect of water of crystallisation on the radiolysis of calcium nitrate[63].

Compound	$G(NO_2^-)_{part}$	$G(O_2)_{part}$*
Cryst. $Ca(NO_3)_2$	0.25	—
Cryst. $Ca(NO_3)_2.4H_2O$	1.50	0.37±0.02
Molten $Ca(NO_3)_2.4H_2O$	0.13	0.02±0.01

* G_{part} represents the yield of radiolysis products taking into account the ionicity and the weight of the component of the hydrate from which they have been formed.

The yield of nitrite in aqueous calcium, cadmium, zinc, and magnesium nitrates varies with the dosage rate of γ-rays[64], passing through a minimum at 0.8×10^{16} eV g^{-1} s^{-1} (dose 7×10^{19} eV g^{-1}) in the case of the calcium and cadmium salts. The other two nitrates show a similar variation in $G(NO_2^-)$, but at an exposed dosage rate of 1.2×10^{16} eV g^{-1} s^{-1}. This is evidently connected with a change in the rate of certain radiation-chemical processes depending on the density of ionisation of the crystals with increase in the linear energy transfer. Furthermore, the increased yield of nitrite was attributed to reactions such as

$$H_2O + e^- \rightarrow H_2O^- \rightarrow H + OH^- \text{ aq.} \quad (17)$$

$$2H + NO_3^- \rightarrow NO_2^- + H_2O. \quad (18)$$

On present-day views it is legitimate to introduce these reactions, since the nitrate ion is considerably more efficient than water in capturing electrons.

Study of the radiolysis of sodium nitrate containing various quantities of adsorbed water (this salt is hygroscopic) shows[65] that the yield of the nitrite ion increases smoothly with increase in the content of water molecules in the crystal lattice of the nitrate (Fig. 3). A possible explanation of this increase in yield was the involvement of H and OH radicals of water in the decomposition of the nitrate ion, e.g.

$$NO_3^- + H^\cdot \rightarrow NO_2^\cdot + OH^-. \quad (19)$$

More probably increase in the water content of sodium nitrate is accompanied by a diminution of the cage effect, and the reverse reactions involving recombination of NO_2 are inhibited. It must be noted that the investigation was in effect made on the heterogeneous system $NaNO_3$–H_2O; nevertheless the yield of NO_2^- was determined by the energy absorbed not by the salt but by the whole "mixture". When the ionicity of the components is taken into account, therefore, the dependence of $G(NO_2^-)$ on the water content of sodium nitrate may be different.

Formation of H·, OH·, $HO_2^\cdot$, and O_2^-—radicals whose concentration increases with increase in the number of molecules of water of crystallisation—is usually observed in irradiated crystalline hydrates of various salts[66–75].

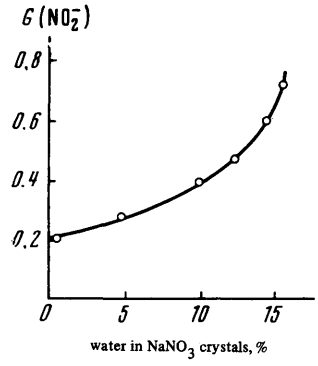


Figure 3. Variation of yield of nitrite in γ-irradiated sodium nitrate with water content of crystals[65].

Furthermore, electron spin resonance has revealed in certain salts (e.g. $BeSO_4.4H_2O$, $BeSO_4.2H_2O$, $CaSO_4.2H_2O$, $ZnSO_4.6H_2O$, $ZnSO_4.H_2O$) a paramagnetic centre (g = 2.000 ± 0.001, H = 4 ± 1 oersteds), probably due to a stabilised electron[69]. Water of crystallisation impedes[68,75] the radiation decomposition of certain salts. Thus Table 2 shows that the total yield diminishes by a factor of ten on passing from the anhydrous salt to the tetrahydrate.

Table 2. Yields of radiolysis products from beryllium sulphate and its crystalline hydrates*[69].

Compound	Temperature	G_{total}	$G_{part}(SO_3^-)$	$G_{part}(H, OH, HO_2)$
$BeSO_4$	room	0.12	0.12	—
	−196°	0.43	—	—
$BeSO_4 \cdot 2H_2O$	room	0.02	0.045	—
	−196°	0.22	—	3.3
$BeSO_4 \cdot 4H_2O$	room	0.005	0.016	—
	−196°	0.13	—	0.8

* Irradiation with γ-quanta (^{60}Co); dosage rate 1000 r s^{-1}.

However, radiolysis products accumulate in the same way in beryllium sulphate and in its hydrates: the concentration of paramagnetic centres increases initially, and then decreases slightly from absorbed doses of ~ 3×10^{20} eV g^{-1} (Fig. 4). Similar relations are obtained even at low temperatures, and also if the distribution of absorbed energy in the crystal according to the ionicities of the main substance and of water is taken into account[68,69].

The above results suggest that water of crystallisation exerts some "protective" action on the crystalline matrix. In the radiolysis of sulphates the water molecules may donate electrons to the primary SO_4^- radicals formed on exposure, tending to transform them to the initial state SO_4^{2-}. It is also possible that the water of crystallisation

"takes to itself" part of the radiant energy and disseminates it through the lattice, which ultimately leads to heating of the whole specimen. The hypothesis that products of the radiolysis of water take part in radiation-chemical processes with radicals of the main substance is not considered [68,69], since the yield of radiolysis products in specimens having a high content of water of crystallisation remains depressed as the temperature of the experiments is lowered to −196°C (Table 2), when reactions between radicals can be neglected.

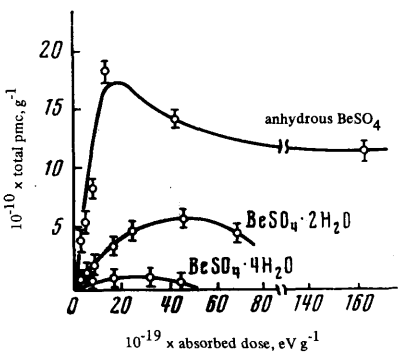


Figure 4. Accumulation of sum of paramagnetic centres (pmc) in γ-irradiated beryllium sulphate and its hydrates at room temperature [69].

Interaction between products of the radiolysis of water molecules probably occurs in the crystalline hydrates of transition metals ($MnSO_4.H_2O$, $NiSO_4.6H_2O$, $CoSO_4.7H_2O$). [73] Thus the suggested mechanism of the radiolysis of manganese sulphate hydrate by γ-irradiation may involve a reaction such as

$$MnO(SO_4) + H_2 \rightarrow MnO_2 + 2H^+ + SO_3^{2-} . \qquad (20)$$

The hydrogen and the intermediate compound of quadrivalent manganese are formed by radiolysis of the initial compound. The crystalline hexahydrate of ammonium iron(II) sulphate undergoes extensive decomposition after treatment with hard X-rays, to give products such as Fe^{3+}, SO_3^{2-}, and H_2 in maximum yields of 1.8, 0.43, and 0.35 respectively [74]. Chemical interaction between products of the radiolysis of water and the main compound is assumed also here.

Aqueous sulphates of copper, magnesium, zinc, and chromium remain almost undecomposed by cobalt-60 γ-rays. The radiant energy is mainly adsorbed by the water of crystallisation, which decomposes into oxygen and hydrogen. In $Li_2SO_4.H_2O$ exposed at the temperature of liquid nitrogen to accelerated electrons (1 MeV), for example, appreciable decomposition of the sulphate ion could not be detected even by such a sensitive method as electron spin resonance [72,75,76].

Although the effect of water of crystallisation on the radiolysis of salts has not yet been finally settled, existing experimental results indicate that the water is able to protect the matrix of the main substance from destruction when the radiolysis products do not undergo chemical reactions with ions or radicals of the compound [68,69]. If, however, water or its radiolysis products are involved in radiation-chemical processes, decomposition of the salts is promoted.

Further investigations on these lines will help to provide a deeper understanding of radiation-chemical processes in crystalline hydrates.

IV. RADIATION-CHEMICAL PROCESSES IN CRYSTALS OF INORGANIC SALTS CONTAINING IMPURITIES

Experimental workers encountered the effect of impurities on the radiolysis of solid compounds literally in the first investigations of radiation-chemical processes in inorganic compounds. However, systematic research on this aspect has been undertaken only recently.

In 1958 Cunningham and Heal expressed the view that impurities and lattice defects have no significant influence on the radiolysis of potassium nitrate [47]. This largely unfounded statement was very soon refuted. For example, not only the yield of nitrite but also the kinetics of the accumulation (annealing) of the radiolysis products are changed in potassium nitrate contaminated with strontium, lead, thallium, and sulphate ions [77]. The strongest effect is exerted by strontium and lead(II) ions, which produce cationic vacancies in potassium nitrate (the impurities were introduced into the crystals by fusing the nitrates and potassium sulphate with potassium nitrate at 340°C). It was also noted that thallium(I) ions, which are electron donors, increase the yield of nitrite, whereas strontium and lead(II) ions lower the yield. This is due to competition between impurities and radiolysis products for the electrons involved in the radiation-chemical processes. It is significant also that sulphate ions, which give anionic vacancies, hardly affect the rate of annealing of defects, whereas lead and strontium impurity ions accelerate the annealing.

Tervalent rare-earth metal ions inhibit the radiolysis of crystalline nitrates; those which are able to pass into the quadrivalent state (primarily Ce^{3+} and Pr^{3+}) are less effective [78]. Donor–acceptor interaction between impurity and radiolysis products probably occurs here also. The authors assume, as in their early papers [77,79], that the inhibition of radiolysis by impurity rare-earth metal ions is due to the resulting cationic vacancies, which facilitate recombination processes in the irradiated system.

A similar view was developed [80] in an investigation of the radiolysis of sodium nitrate contaminated with calcium ions replacing sodium isomorphously in the crystal lattice. However, decomposition of the nitrate is intensified in this case, although the proportions of the radiolysis products remain unchanged.

Impurities in potassium nitrate crystals which should produce neither cationic nor anionic vacancies (potassium hydroxide was introduced by fusion) nevertheless do affect radiolysis [81,82]. The yield of nitrite in potassium nitrate contaminated with the hydroxide is higher than in pure specimens. Furthermore, the yield at a dosage of $\sim 2.5 \times 10^{18}$ eV g^{-1} first increases with the alkali concentration, and then decreases, approaching the value of $G(NO_2^-)$ for the pure salt. These results are explained by the effect of hydroxide ions on the localisation and the decay of excited states of nitrate ions. It is also possible that hydroxide ions may take part in radiation-chemical reactions with radiolysis products of potassium nitrate.

The radiolysis of potassium nitrate is inhibited by contamination with nitrite and perchlorate ions [83]. The yield of nitrite in the impure crystals is 1.15, which compares

with the 1.7 obtained[81] for the pure crystals. A mechanism of acceptor–donor interaction[71-80] probably operates here.

According to the views developed earlier, univalent anionic impurities, included isomorphously in the lattice of potassium nitrate, compete with radiolysis products in reactions involving electrons, which may either accelerate or retard (depending on the mechanism of radiolysis) breakdown of the crystalline matrix.

It has also been shown[83] that the yields of radiolysis products from potassium nitrate (NO_2^- and O_2) increase sharply at temperatures above 128°C, when potassium nitrate undergoes a transition from a rhombic to a trigonal structure.

Lykhin and Boldyrev made a detailed investigation of the radiolysis of sodium nitrate contaminated with silver, thallium(I), strontium, and lead(II) ions, introduced into the crystals by fusing the nitrates with sodium nitrate[84]. The products were exposed to X-rays in air. The experiments support the main concept of the authors that bivalent ions facilitate breakdown of an excited nitrate ion by generating cationic vacancies in the potassium nitrate lattice. This occurs because the cage effect diminishes in the vicinity of a cationic vacancy. Therefore the yield of the nitrite ion is increased in sodium nitrate contaminated with bivalent cations. On the other hand, vacancies promote annealing reactions (the yield falls), which occur at an appreciable rate at high temperatures. As a result of competition between these processes the yield of nitrite becomes even smaller in the impurity crystals, relative to that in the pure crystals, as the temperature of irradiation is raised (Fig. 5).

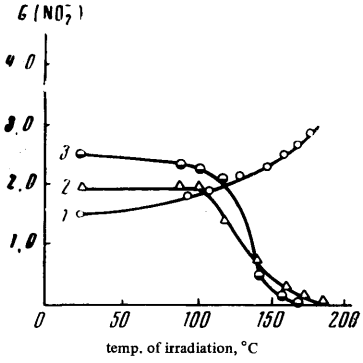


Figure 5. Dependence of yield of nitrite on temperature of irradiation[84] for: 1) pure KNO_3; 2) KNO_3 + 2.5 mole % Sr^{2+}; 3) KNO_3 + 2.5 mole % Pb^{2+}.

Several workers have observed that annealing processes are accelerated in crystals in which impurities have created cationic vacancies (and thereby facilitated the movement of products of radiolysis)[15,59,77,85-87]. Thus Mohanty has demonstrated that aluminium ions present in lead nitrate increase appreciably the rate and the degree of annealing of radiation disturbances in exposed crystals[87]. Contamination with bivalent cations (strontium, lead) accelerates considerably annealing processes in potassium nitrate[59,77]. The effect of impurities is especially noticeable during the initial periods of annealing (Fig. 6). It is significant that the sulphate ion, which should form anionic vacancies, has no effect on annealing (curves *1* and *2*).

An investigation of annealing in proton-irradiated crystals of sodium, potassium, and rubidium nitrates (contaminated with calcium, cadmium, and strontium) has led to the conclusion[15] that annealing is decisively affected by impurities producing cationic vacancies, on which intermediate products of radiolysis may even "accumulate". The donor–acceptor properties of the impurities are regarded as of no significance. This view cannot be fully accepted, since the acceleration of annealing observed in crystals of alkali-metal nitrates is not entirely unambiguous.

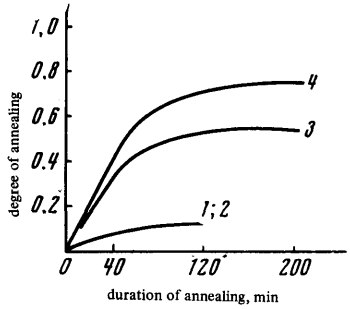


Figure 6. Effect of impurities on the post-radiation (absorbed dose 20.8 Mrad) annealing of potassium nitrate crystals at 130°C[85]: 1) pure specimen; 2) KNO_3 + 1.5 mole % K_2SO_4; 3) KNO_3 + 2.5 mole % $Sr(NO_3)_2$; 4) KNO_3 + 2.5 mole % $Pb(NO_3)_2$.

The slowing down of annealing processes in rubidium and caesium nitrates contaminated with carbonate ions (0.6–3 mole %) is attributed to an increase in the yield of nitrite when the crystals are irradiated with protons[88]. The carbonate ions are assumed to be balanced in the nitrate lattice by an increase in the number of interstitial ions and a decrease in the number of cationic vacancies. The increased yield is therefore due to a slowing down of radiation annealing on cationic vacancies. In addition to this mechanism, colour centres formed on anionic vacancies (some result from the incorporation of carbonate ions) may prevent the recombination of electrons with radicals by promoting the breakdown of radical products to nitrite.

The decrease in rate of radiolysis of sodium nitrate containing isomorphous silver nitrate as impurity is explained by Cunningham solely by the acceptor properties of silver ions[89,90].

Similar conclusions have been reached for the radiolysis (by X-rays) of lead azide containing a homophase impurity (silver or copper ions)[91,92]. The radiation decomposition of the azide is accelerated quite considerably by silver ions, the effect tending to saturation at an impurity content of ~ 10 mole %. The introduction of copper ions into the azide produces a sharp decrease in rate of radiolysis proportional to their content. Experiment shows that radiolysis is accelerated by impurities that increase the concentration of electrons in the material,

and slowed down by impurities that diminish the number of free electrons. This rule holds, of course, only if electrons are involved in reactions tending to increase the yield of radiolysis products[29,79,93].

We cannot in general confine our attention to the donor–acceptor action of impurities when considering the effect of foreign ions on radiolysis. Indeed, change in the nature and concentration of various defects in the preparation of crystalline compounds may affect also the fate of excited states. This indicates the complicated and multistage character of the influence of homophase additives on the radiolysis of solid compounds. When the impurity enters the lattice isomorphously, replacing ions of the main substance at lattice points and producing no vacancies, the impurity may act mainly by taking part in radiation-chemical reactions. For example, the increase in the yield of radicals observed in experiments with irradiated crystals of potassium perchlorate is due to the diminished probability of the recombination of electrons with radicals caused by the impurity silver ions, which act as acceptor centres for electrons[94]. But the effect of impurity copper ions in accepting electrons is probably balanced by a diminished concentration of anionic vacancies, and the copper ions act only as centres of recombination:

$$ClO_4^- + Cu^{2+} + e \rightarrow ClO_4 + Cu \rightarrow ClO_4^- + Cu^+ . \qquad (21)$$

As a consequence of these reactions the degree of decomposition of potassium perchlorate decreases[94].

The results of experiments with impure crystals can sometimes be explained by redistribution of the radiant energy and the localisation of electrons (holes) in specimens with defects. Thus powdered crystalline barium sulphate contaminated with nitrite and nitrate ions exhibited inhibited radiolysis of the main substance with intense decomposition of the impurity. This is explained by a hole–exciton mechanism of transfer to the impurities of the energy absorbed by the whole crystal lattice. Defects such as vacancies formed in the vicinity of an impurity may serve as sites for the localisation of holes and the destruction of excitons, which will lead to decomposition of the impurity[95–98].

Preferential radiolysis of impurities has been observed in crystals of sodium sulphate, lithium sulphate monohydrate[99], and strontium phosphate[100]. Various impurities of both donor and acceptor types—nitrite, sulphite, nitrate, and formate ions, hydrogen peroxide, methanol, benzene—were studied in the latter work. In all cases the impurity ions underwent considerable radiolysis. Their effect on the course of radiolysis of the carrier material largely depended on their donor–acceptor properties and on the transfer to the impurities of the energy absorbed by the crystal.

One consequence of the work on the radiolysis of contaminated barium sulphate is to establish that energy absorbed in an irradiated crystal can be transmitted to considerable distances[97]. Such a process is evidently quite possible, since energy transfer has already been observed between spatially separated rare-earth metal ions in crystals of the chlorides and bromides of various elements[101,102].

A purely electron–hole mechanism of the effect of impurities on the concentration of radiation defects has been postulated[103]. The number of localised holes in γ-irradiated α-alumina at 77°K increases proportionally to the content of the impurity ion Ti^{4+}. The latter, being located at an Al^{3+} lattice point, captures an electron, thus presenting its recombination with a hole.

There are indications that radicals formed from impurities may interact chemically. In fused potassium chloride crystals containing hydroxide and cyanide or nitrite impurity ions, for example, photolysis was followed by formation of a radical type of impurity HNO_2^-. Such reactions as

$$\rightsquigarrow HO^- \rightarrow H^\cdot + O^-$$

and

$$H^\cdot + NO_2^- \rightarrow HNO_2^- \qquad (22)$$

probably occur in this system[104].

At the conclusion of this Section it must be noted that the concept of the donor–acceptor effect of impurities on radiolysis, the vacancy mechanism, the transfer of the radiated energy from the matrix to impurity ions, and the mutual stabilisation of defects have long been successfully used in investigating the radiolysis (or coloration) of alkali-metal halide crystals. The literature on this problem is vast, so that it is sufficient to give merely a few examples. Thus transition-metal impurities (nickel, copper) in sodium chloride accelerate the decay of F-centres[105]. Traces (0.01 wt.%) of chromium, manganese, iron, cobalt, and nickel are electron traps and sources of vacancies (potassium chloride and bromide crystals)[106]. Contamination with sulphate, nitrate, and hydroxide ions diminishes the probability of the formation of F-centres, since radiolysis products of the impurities (O_2^-, O, etc.), being centres for the capture of electrons, compete with anionic vacancies for electrons[107]. A detailed analysis has been made[108,109] of the effect of bivalent cations (Pb^{2+}, Sr^{2+}, Ca^{2+}) and anions (S^{2-}) on the kinetics of accumulation and the stability of colour centres in potassium chloride and other alkali-metal halide crystals. Fairly complete reviews of the effect of impurities on the accumulation of various colour centres in alkali-metal halide crystals can be found[20–24,110–112].

In all cases the results have been explained (independently of the test material) in terms of the effect of vacancies created in the crystal lattice by the introduction of impurities. The donor–acceptor properties of impurities and ions of the main substance have also frequently been considered. Mechanisms involving the transfer of excitation energy from the lattice to impurities have been far more rarely analysed, although the role of such processes in a solid is quite large[3–9,20,113].

Little study has been made of the participation of impurities in intermediate reactions with radicals produced by irradiation of the crystalline matrix, the effect of the mode of inclusion of the impurity in the lattice (isomorphous or non-isomorphous), and other questions.

V. RADIOLYSIS OF MIXTURES OF INORGANIC SUBSTANCES

Although the effect of foreign impurities on radiation-chemical processes has now been studied fairly thoroughly, little work has yet been done on the radiolysis of salts with heterophase additions[90,114–118]. The first paper on the effect of impurities forming an independent phase on the radiolysis of inorganic compounds appeared only in 1967[114]. This showed that powdered thorium dioxide and nickel and zinc monoxides (particle size 90–140 μm) added in amounts of 1.5–7 mole % accelerate the radiolysis of ammonium nitrate by X-rays (the degree of radiolysis was assessed

from the total gas evolution). The efficiency of catalysis by the additives varied in the sequence

$$ThO_2 > ZnO > NiO > \text{pure } NH_4NO_3 .$$

The electronic work function φ in these oxides increases from nickel to thorium. Impurities of low work function were regarded as donors of electrons in the irradiated system. Therefore the above additives, by raising the concentration of electrons, accelerate the intermediate stages of radiolysis, which leads to the more intense gas evolution observed experimentally.

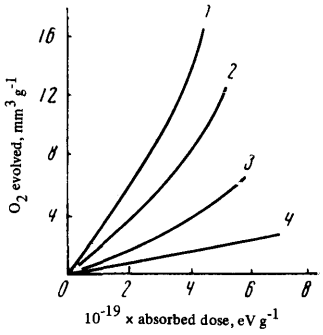


Figure 7. Radiolysis of sodium nitrate by X-rays at room temperature: 1) $NaNO_3$ (+3.5 mole % ZnO); 2) $NaNO_3$ (+3.5 mole % ThO_2); 3) pure $NaNO_3$; 4) $NaNO_3$ (+3.5 mole % CoO).[115]

This conclusion was confirmed by these workers on several new systems[92,115]. Thus Fig. 7 illustrates the radiation-chemical decomposition of potassium and sodium nitrates containing mechanically admixed powdered oxides of thorium, nickel, cobalt, and zinc. In these experiments, too, impurities of low work function accelerated radiolysis, and those with high values of φ slowed it down. By analogy with homophase additives, the impurities probably affected reactions such as[115]

$$\rightsquigarrow NO_3^- \rightarrow NO_3 + e , \quad (23)$$

$$NO_3 + e \rightarrow NO_2^- + O , \quad (24)$$

$$NO_3^- + e \rightarrow \overset{*}{N}O_3^{2-} \rightarrow NO_2^- + O^- . \quad (25)$$

A comprehensive investigation has been made of the effect of heterophase additions on the radiation-chemical stability of lead azide[116,117]. The additives used were the oxides of zinc, cadmium, cobalt, and nickel. The first two accelerate considerably the evolution of nitrogen from the azide when the mixtures are exposed to X-rays. Nickel and cobalt oxides retard the radiolysis of the azide under the same conditions. It was also found that these additives have no effect on the activation energy of radiolysis. From the results of numerous experiments the fully justified suggestion was made[116] that donor–acceptor interactions between the compounds in the mixture undergoing irradiation were of decisive importance. Introduction of a heterophase impurity of donor type increases the steady-state concentration of electrons in the irradiated system, whereas acceptor impurities have the opposite effect. As a result, radiation-chemical reactions involving electrons in silver azide are either slowed down or accelerated, e.g.

$$\rightsquigarrow N_3^- \rightarrow N_3^0 + e , \quad (26)$$

$$N_3^0 + e \rightarrow N_3^- . \quad (27)$$

Analogous effects have been observed in perchlorates[117]. It should also be noted that the donor or acceptor character of impurities is greatly dependent on the type of systems in contact during exposure, and may not coincide with assessments based on the measured work functions of the pure oxides in the absence of irradiation.

Processes entailing the redistribution (and primary distribution) of energy in heterogeneous systems under irradiation (transfer of charges, migration of excitons) should also be very important in these cases. These phenomena accompanying radiolysis can be represented by the proposed[117] empirical relation

$$v_d/v_0 = 1 + f\left(\alpha \frac{I_d}{I_0} - 1\right), \quad (28)$$

where v_0 and v_d are the rates of radiolysis of the pure salt and of the salt with the additive, I_0 and I_d are the corresponding absorbed dosage rates, α is a constant defining the transfer (redistribution) of energy between the components, and f is the fraction by weight of the heterophase additive. Experiments show that the radiant energy may actually undergo redistribution even when particles of the mixtures are in poor contact. The mechanism of such transfer is not yet clear. However, there is direct evidence that radiant energy absorbed in crystalline mixtures is able to migrate at least to distances up to 60 Å.[118]

Heterophase impurities would probably have a weaker effect than similar homophase impurities on the radiolysis of the main substance. For example, the yield of NO_2^- radicals falls with increasing contamination of barium sulphate with the nitrate ion, to reach a minimum when the latter forms a separate phase[97,98]. Hence transfer of the radiant energy, absorbed in the matrix of the main substance, to the heterophase nitrate impurity is difficult. Although heterophase additives are less effective, study of the effect of foreign mechanical inclusions on the radiolysis of various salts is a promising line of research on the radiation chemistry and the physics of solids. Heterophase additives are very easy to "introduce", a factor which may be decisive in work with impurities, limiting the experimental possibilities. Investigations in this field will probably enable new methods to be developed for systematically varying the radiation resistance of various compounds.

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Experiment shows that external actions on a crystal, varying the mobility and the steady-state concentrations of charged species and excited states, change the rate of radiation-chemical processes. The direction of these changes can be predetermined and even controlled if the mechanism of radiolysis is known. The introduction of impurities into a crystal may be an effective method for monitoring and controlling processes of radiolysis.

Analysis of the experimental results shows that several mechanisms have been suggested for the effect of impurities on radiolysis, corresponding to the actual processes occurring in the crystal lattice.

1. Donor–acceptor interaction of impurity and products of radiolysis. The specific effect of an impurity is

largely dependent in this case on radiation-chemical processes in the exposed crystals. For example, stages of radiolysis having a radical mechanism or involving excited states will be relatively insensitive to donor or acceptor impurities.

2. Generation of vacancies by impurity ions. Vacancies may provide a site for the localisation of electrons or holes capable of increasing the mobility of the products of radiolysis, which will accelerate recombination processes. The same defects can often have opposite effects on the rate of radiolysis. For example, the addition of cadmium ions, which create cationic vacancies in the lattice of silver salts, enhances the radiation resistance of silver oxalate[119] but promotes decomposition of silver carbonate[119-121]. In this case the mechanism of the radiolysis of the specific compound is also decisive.

3. Transfer of the energy of the radiation absorbed by the lattice to the impurity, as occurs in organic systems[113]. The impurity itself decomposes, protecting, as it were, the main compound.

4. Acceleration and extension of the radiolytic decomposition of salts by interaction of radiolysis products of "impurity" molecules and matrix components. This mechanism is typical of crystalline hydrates or compounds with considerable inclusions of water molecules.

Research workers have so far paid less attention to the role of impurities in the intermediate stages of radiation-chemical reactions. The mechanism of the introduction of foreign atoms into the lattice, and hence the specific mode of participation of the impurity in radiation and radiation-chemical processes, have not always been studied in detail.

The preparation of specimens—quenching, thermal and radiation conditioning—is very important in radiation-chemical investigations. Due attention will probably also be paid to this factor in future work.

In conclusion it must be noted that the action of an impurity is usually a complicated multistage process: only in very rare cases is its role determined by a single one of the above mechanisms. And the first advances in this direction support the hope that reliable methods (and a theoretical basis) will be developed for controlling the radiolysis of inorganic compounds.

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