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# Radiation-chemical Processes in Radioactive Compounds

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Publications on the effect of the natural radiation of radioactive inorganic salts on their radiation-chemical stability are analysed. The main rules governing radiation-chemical processes in radioactive salts are examined. The effects of recoil atoms produced in radioactive disintegration, chemical impurities, and the intrinsic charge on the mechanism of the radiolysis of radioactive compounds are discussed. A detailed account is given of the effect of variation in the intensity of self-irradiation on the yield of decomposition products from certain radioactive salts (sulphates of Group II metals). A list of 55 references is included.

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## I. INTRODUCTION

Within a few years of the discovery of radioactivity by Becquerel and the early papers of Mme Curie [1] radioactive isotopes were employed as indicators for the qualitative and quantitative determination of several elements, in studying the structure of chemical compounds, and also for observing the progress of processes involving substances containing a radioactive tracer. All such experiments were based on the assumption that the physicochemical properties of isotopes of the same element are identical, and that the effect of radiation from the radioactive isotope on the test materials could be neglected [2]. The first condition is satisfied if the difference in mass between the isotopes is relatively small: in practice it can be regarded as satisfied for elements of atomic number above ten [3]. The second condition by no means applies in all cases: very often radiation-chemical processes in the test systems have a significant influence on the physicochemical properties of radioactive compounds [4,5]. This applies especially to solid radioactive materials, in which disturbances due to the radiation may accumulate and remain for a long time.

With the development of atomic industry and the wider use of radioactive isotopes in science and various branches of the economy, it becomes increasingly necessary to study the properties of highly radioactive materials, which are subject to continuous self-irradiation. In atomic technology and in the preparation of labelled compounds, for example, materials must be handled whose specific radioactivity reaches several curies and tens of curies per gram. For practical purposes, therefore, it is extremely important to assess the effect of self-irradiation on various properties of highly radioactive materials, to determine their radiation stability.

Frequently these problems cannot be solved merely by investigating the effect of corresponding external irradiation on the systems. Even with bombarding particles of the same nature and energy there are definite differences between self-irradiation and external irradiation: (*a*) self-irradiation is continuous in time (as long as the radioactive isotope is present); (*b*) the dosage rate is usually low in self-irradiation; (*c*) the action of self-irradiation is usually uniform throughout a solid of any dimensions even with particles of low energy (provided, of course, that the radioactive isotope is uniformly distributed throughout the sample); (*d*) chemical impurities, which may be in various valency forms, are produced in the system by radioactive disintegration; and (*e*) recoil nuclei play a significant role in radioactive materials.

The above features of radioactive compounds demonstrate the need for a careful investigation of radiation-chemical processes occurring in radioactive salts. Unfortunately, not so many publications have yet appeared on this topic, and there have been no reviews of work that has been published. The present survey makes an attempt to fill this gap.

The chemistry of hot atoms (and also the self-radiolysis of organic compounds), which often exhibit problems similar to those of the radiation chemistry of solid radioactive compounds, will not be considered here. This field of research is of intrinsic value, and involves mainly the study of phenomena in neutron-irradiated materials, the measurement of the distribution of isotopes between individual chemical forms, and the separation of isotopes by means of the Szilard–Chalmers effect. Full information on these aspects can be found in several publications [3,6-9].

## II. PRIMARY RADIATION PROCESSES IN RADIOACTIVE MATERIALS

The nature and the accumulation of the primary radiolysis products of crystalline radioactive compounds has been studied most fully on the radioactive sulphates of barium, strontium, calcium, magnesium, and potassium [10-16]. Isolated experiments have also been made on several carbonates [17-21], cobalt formate [22], and other compounds.

Self-irradiation even by low-energy $\beta$-particles may lead to considerable radiation-chemical changes. In the $\beta$-disintegration of tritium ($\overline{E} \simeq 6$ keV), for example, the bonds in the chemical compound containing $^3H_1$ may be ruptured [23]. If conditions are produced in a radioactive material such that radiation disturbances are not annealed, defects may gradually accumulate to considerable concentrations [24,25]. Thus 5 min after the start of an experiment, Lambe detected by electron spin resonance the accumulation of paramagnetic centres in mixtures of tritium and krypton frozen at 4.2° and 77°K. [26,27]

The introduction of $\alpha$-emitters into crystals of complex salts produces more fundamental radiation-chemical changes than does the addition of $\beta$-radioactive isotopes.

Radiation disturbances (recorded by electron spin resonance) have been observed in $La_2Mg_3(NO_3)_{12}.24H_2O$ at room temperature immediately after the addition of americium-241 (3 mc $g^{-1}$).[28] Yet the $\beta$-radiation of promethium, present in this compound in similar amounts to americium ($\sim 3$ mc $g^{-1}$), has such a weak effect that an e.s.r. signal appeared only three weeks after preparation of the salt. The radiation defects observed in this salt were attributed to $NO_3$, $NO_2^-$, and $NO_3^{2-}$ radicals, which appear also after exposure of the salt to $\gamma$-quanta. Boyd and Ward showed[29] that the intensity of radiolysis of lithium bromate resulting from the fission of lithium-6 after capture of a neutron exceeds fivefold the intensity from the action of cobalt-60 $\gamma$-rays under similar conditions, the dose absorbed being $(1-40) \times 10^{22}$ eV $mole^{-1}$. The same products are formed in the two cases: i.e. the mechanism of radiolysis does not vary significantly with the method of irradiation. However, the experimental results are greatly affected by increase in the linear energy transfer on exposure to neutrons and subsequent fission of lithium-6. These processes are accompanied by a considerable rise in temperature in the tracks, which accelerates the radiation-thermal decomposition of lithium bromate.

Careful investigations on radioactive (sulphur-35) sulphates of barium, calcium, strontium[10-12], magnesium, and potassium[14-16,31,32] show that radiation defects of the same nature arise in radioactive and in inactive salts. In this respect the actions of external irradiation and of self-irradiation are equivalent. The radical-ions $SO_4^-$ and $SO_3^-$ are the chief primary products ("defects") in the above salts. Prolonged storage of the radioactive materials involves gradual formation of the ions $SO_3^{2-}$ and $SO_2^-$ and probably of $SO_2$.[16,32] At low temperatures an appreciable quantity of other, less stable radiation defects, whose nature has not been established, is also formed. The main features of the mechanism of radiolysis which applies to non-radioactive sulphates are preserved:

$$c \rightsquigarrow SO_4^{2-} \rightarrow SO_4^- + 2e\,(SO_3^-,\ O^-,\ e) \quad (1)$$

$$SO_4^- + e \rightarrow \overset{\bullet}{SO}{}_4^{2-} \begin{cases} \nearrow SO_4^{2-} + h\nu \\ \searrow SO_3^- + O^-\,(O + e) \end{cases} \quad (2)$$

$$SO_3^- + e \rightarrow \overset{\bullet}{SO}{}_3^{2-} \begin{cases} \nearrow SO_3^{2-} + h\nu \\ \searrow SO_2^- + O^-\,(O + e) \end{cases} \quad (3)$$

$$SO_3^- + SO_3^- \rightarrow SO_3^{2-} + SO_2 \quad (4)$$

The main difference between externally irradiated and radioactive salts lies in the variation in the concentration ratio of paramagnetic centres. Thus $SrSO_4^*$ of initial specific radioactivity $\sim 100$ mc $g^{-1}$ gave the ratio $[SO_4^-]/[SO_3^-] = 16.5$ after 4 years (absorbed dose $2 \times 10^{22}$ eV $g^{-1}$). In externally irradiated strontium sulphate (dose $5 \times 10^{22}$ eV $g^{-1}$) this ratio is 0.5. Hence the main product in radioactive materials is the radical-ion $SO_4^-$, with very little formation of $SO_3^-$ radicals. Yet the concentration of the latter radicals is increased appreciably by irradiation with fast electrons and $\gamma$-rays (comparable temperature conditions and doses). The probable explanation is that the mean energy of sulphur-35 $\beta$-particles ($\sim 55$ keV) is approximately one-tenth of that of the Compton electrons from cobalt-60 $\gamma$-radiation (410 keV) and far smaller than the energy of the fast electrons. In the former case (or with an external source of low emitted energy), therefore, ionisation effects predominate with the formation of $SO_4^-$ radical-ions in the crystals of the radioactive sulphates, but the probability of cleaving sulphur–oxygen bonds to form $SO_3^-$ radical-ions increases, on $\gamma$-irradiation (cobalt-60) and exposure to fast electrons. This interpretation of the results requires further experimental verification.

The temperature of irradiation also affects the relative proportions of $SO_4^-$ and $SO_3^-$ radical-ions: in the main the former predominate at low temperatures, and the latter at room temperature. Hence rise in temperature accelerates the dissociation of excited sulphate ions by reactions (2).[31,32] This is consistent also with experimental results on the thermal stability of radical-ions in sulphates[31-33]: the most stable is $SO_3^-$, which, for example, is annealed in strontium sulphate only at $\sim 500^\circ$C; the radical-ion $SO_4^-$ begins to disappear even at room temperature. Probably the interconversion and recombination of paramagnetic centres during the prolonged storage of radioactive salts even at room temperature also determine in considerable measure differences in the proportions of the radicals compared with externally irradiated specimens.

Variation in the ratio of primary and secondary products of radiolysis may depend not only on the duration of self-irradiation but also on the appearance of impurities and the influence of ionisation processes accompanying radioactive disintegration on the course of subsequent radiation-chemical changes. Thus in the $\beta$-disintegration of radioactive lanthanum-143 some 60% of the cerium atoms formed are in the quadrivalent state, and the remainder in the tervalent[34]. External irradiation by accelerated electrons does not produce such effects.

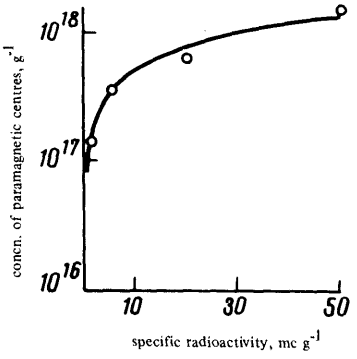



**Figure 1.** Dependence of concentration of paramagnetic particles on specific radioactivity of $SrS^*O_4$ at room temperature on keeping for 55 days.[11]

The radicals formed on exposure gradually accumulate to reach a limiting concentration[35-37]. This is a consequence either of kinetic effects directly in the irradiated zone or of afterprocesses in the thermodynamically non-equilibrium system. If the radicals are stable at room temperature (i.e. if they disappear slowly after exposure has ceased), it is easy to obtain curves representing the accumulation of paramagnetic centres. Fig. 1 shows the dependence of the total number of such centres on the specific radioactivity of strontium sulphate over the range 0.1–50 mc $g^{-1}$. In all cases the specimens were kept for 55 days, since the concentration of paramagnetic centres reaches its maximum value in this time. A similar variation is observed in all the radioactive sulphates investigated.

A characteristic feature of radioactive crystalline sulphates containing a "soft" $\beta$-emitter (sulphur-35) is that

the value of $G_{pmc}$ in them is higher than in irradiated non-radioactive salts (Table), and the maximum concentration $C^*$ of paramagnetic centres usually exceeds the corresponding values for externally irradiated materials (Fig. 2).

Parameters of the radiation stability of sulphates.

| Sulphate | Crystal system | Radius of cation, Å | Ionicity of $SO_4^{2-}$ | Lattice energy, kcal mole$^{-1}$ | Free vol. of unit cell, Å$^3$ | Self-irradiation at 25°C: initial specific radioactivity ($^{35}S$), mc g$^{-1}$ | Self-irradiation at 25°C: $G_{pmc}$ | External γ-irradiation at 30°C: $G^*_{pmc}$ | External γ-irradiation at 30°C: $(SO_3^- + SO_4^-)$ |
|---|---|---|---|---|---|---|---|---|---|
| $BaSO_4$ | rhombic | 1.43 | 0.46 | 589 | 88 | 20 | 0.7 | 0.5±0.18 | (4±2.0)·10$^{-2}$ |
| $SrSO_4$ | rhombic | 1.23 | 0.56 | 612 | 67 | 50 | 2.5 | 0.3±0.15 | (2±0.7)·10$^{-2}$ |
| $CaSO_4$ | rhombic | 1.09 | 0.71 | 647 | 76 | 50 | — | (4±1.6)·10$^{-2}$ | (7±3)·10$^{-3}$ |
| $CaSO_4 \cdot 2H_2O$ | mono-clinic | 1.09 | 0.46 | 635 | 165 | 50 | 0.2 | — | — |
| $K_2SO_4$ | rhombic | 1.32 | 0.5 | 432 | 136 | — | — | 5±1·10$^{-3}$** | 1·10$^{-4}$ |

*$G_{pmc}$ applies to the total paramagnetic centres formed on irradiation, but since $SO_4^- > SO_3^- + SO_2^-$ groups, it corresponds mainly to the primary products of radiolysis, which are $SO_4^-$ radical-ions.
**Determinations made at −196°C.

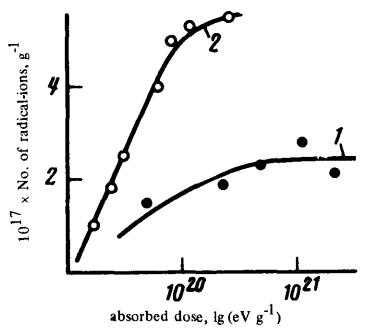



**Figure 2.** Accumulation of paramagnetic centres in barium sulphate at room temperature: 1) γ-irradiated salt; 2) radioactive $BaS^*O_4$ (20 mc g$^{-1}$).

Such relations between $C_{irrad}$ and $C_{radioact}$ are characteristic of all the specimens studied, especially with small doses absorbed. This is probably because the radiation-chemical yield in radioactive salts corresponds to the number of paramagnetic centres in the zone of continuous irradiation. Hence, at any instant while self-irradiation is occurring, $C^*_{radioact}$ should exceed $C_{irrad}$ by an amount corresponding to the number of paramagnetic centres that recombine rapidly after exposure has ceased (doses and dosage rates are assumed to be the same in comparable specimens). Experiment shows in fact that in radioactive sulphates $C^*_{radioact} \simeq (2-10)C_{irrad}$. Therefore the yields of paramagnetic centres are higher in radioactive salts than in externally irradiated specimens.

The appearance of a maximum in the time dependence of the concentration $C$ of paramagnetic centres and the permanence of the relation $C^* > C_{irrad}$ can be explained [13] by an exponential decay in the intensity of self-irradiation with time, on the assumptions that radiation disturbances are reversible and are annealed both by direct recombination and under the influence of the emission itself (radiation anneal). The generation and destruction of radicals by a mechanism of "removal and addition" of electrons on exposure, which is characteristic e.g. of radioactive sulphates when the $SO_4^-$ radical-ion is formed, satisfies these conditions. With the above limitations, and bearing in mind that [37,38] the annealing and production of defects have first-order kinetics, we obtain the formula [13]

$$\overset{*}{C}_t = a\exp\left[\frac{b}{\lambda}\exp(-\lambda t) - \alpha t\right]\int_0^t \exp\left[(\alpha-\lambda)t - \frac{b}{\lambda}\exp(-\lambda t)\right]dt \qquad (5)$$

where $a$, $b$, and $\alpha$ are coefficients depending on the probabilities of formation and disappearance of defects and on the initial intensity of irradiation, with $a > b$. Introduction of the dimensionless variable $\tau = \lambda t$ (in which $\lambda$ is the disintegration constant and $t$ the time), expansion of the integrand as a series, and integration yield

$$\overset{*}{C}_\tau = \exp(a e^{-\tau} - \sigma\tau)\sum_{n=0}^{\infty}\frac{(-\alpha)^n}{n!(n+\gamma)}\{1 - \exp[-(\alpha-\lambda)t]\} \qquad (6)$$

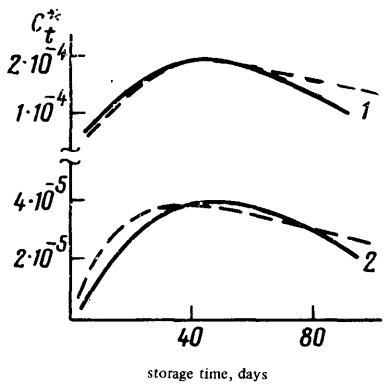



**Figure 3.** Variation in relative quantity of radicals in strontium and barium sulphates containing radioactive sulphur (20 mc g$^{-1}$):[13] 1) $SrS^*O_4$; 2) $BaS^*O_4$. Here $C^*_t$ is the total number of paramagnetic centres divided by the number of irradiated molecules in 1 g.

Depending on the relation between the parameters $\alpha$ and $\sigma$ the plots of the number of radiation defects $C^*_\tau$ against the reduced time $\tau$ pass through a maximum, whose height and position are determined by the values of these constants.

Fig. 3 illustrates experimental and calculated ratios (to ±10%) of the number of radicals to the number of molecules irradiated in 1 g of $BaS^*O_4$ and $SrS^*O_4$. During storage of the radioactive material (the radioactive isotope disintegrates in conformity with the law $I = I_0\exp(-\lambda t)$,

where $I$ is the emission intensity) a maximum occurs in $C_t^*$, and Eqn. (6) describes quite accurately the curves for the accumulation of radicals in radioactive materials. From the derivation of formulae (5) and (6) it follows that the maximum in the $C_t^*$–$t$ curves is due to the fact that the spontaneous annealing of defects becomes of decisive importance with decrease in the emission intensity.

When the intensity of the emitter remains practically unchanged—i.e. $\lambda \simeq 0$ and $I = I_0 = \text{const}$—no maximum is observed. In this case the variation in $Ct$ with time is represented by the formula

$$C_t = \bar{C}\{1 - \exp[-(b + \alpha)t]\}, \quad (7)$$

where the equilibrium concentration of defects is

$$\bar{C} = nAIP_1/(AP_1I + AP_2I + BP_3);$$

$n$ is the number of irradiated molecules, $P_1$, $P_2$, and $P_3$ are the probabilities of the formation and disappearance of defects under the influence of irradiation and of their recombination, $I$ is the dosage rate of the emission, and $A$ and $B$ are constants depending on the properties of the specimen and the conditions of irradiation.

Equations (6) and (7) show that an equilibrium number of defects may accumulate in the irradiated materials, their concentration at a given temperature depending solely on the properties of the medium and the intensity of self-irradiation[35,36,38].

It follows from Eqn. (7) that, with a constant intensity of irradiation, the number of radiation defects reaches $\bar{C}$ more rapidly the larger are $P_1$–$P_3$. Furthermore, $Ct$ tends to $nP_1(P_1 + P_2)$ with increase in the dosage rate $I$ (since $IAP_1 + IAP_2$ becomes $> BP_3$: i.e. spontaneous recombination of defects is small). Thus the equilibrium concentration of defects should be greater at higher values of $I$ with the same dose absorbed. With decrease in the intensity of the emitter, Ct tends to $nIAP_1/BP_3$ (in this case $AP_1I + AP_2I > BP_3$). When $I = 0$, the formulae are devoid of physical meaning.

A possible reason why the number of radicals in materials containing radioactive isotopes is larger than in the externally irradiated non-radioactive compounds, under otherwise similar conditions[11–13], is that spontaneous annealing continues (rapidly at first, and then more slowly) after the termination of exposure, and by the time defects are recorded some of them have inevitably disappeared. Radioactive materials are under continuous irradiation, and therefore a higher concentration of defects is maintained in them. If the annealing of defects is negligible (e.g. at low temperatures), the same number of radiation disturbances accumulate in the two cases (external irradiation and self-irradiation). The formulae obtained for the accumulation of radiation defects in radioactive salts reflect only one aspect—the variation in the intensity of self-irradiation with time—of this complicated process. This effect is unable, of course, to explain all the features of radiation-chemical phenomena in radioactive crystals. As already mentioned, the accumulation of impurity atoms and specific aspects of the ionisation of electron shells in radioactive disintegration are of great significance here. Unfortunately, the influence of these factors has still not been adequately studied.

The above rules for the accumulation of paramagnetic centres apply only with identical or almost identical linear energy transfers in comparable specimens. Furthermore, if the transfer is large, a smaller quantity of disturbances may even accumulate in radioactive materials than in irradiated samples. In frozen water containing tritium (1 c $ml^{-1}$), for example, the yield of atomic hydrogen is about one-half of the yield in $\gamma$-irradiated ice with the same doses absorbed[24,25]. This is explained by intense recombination of radicals in the tracks. However, experiments with radioactive crystals of barium, strontium, and calcium sulphates revealed no variation in $G$(pmc) with the content of the radioactive isotope up to specific radioactivities of $\sim 150$ mc $g^{-1}$.

## III. SELF-RADIOLYSIS OF RADIOACTIVE MATERIALS

Radioactive compounds may undergo considerable changes as a result of radiation-chemical processes. The radiolysis products gradually accumulate in them, and change the physicochemical properties of the radioactive specimens. Even the low-energy $\beta$-radiation emitted by carbon-14 affects the kinetics of the thermal decomposition of certain radioactive carbonates[17–21,39–41]. Thus the temperature of the vacuum decomposition ($10^{-4}$–$10^{-5}$ mmHg) of $CdC^*O_3$ and $NaHC^*O_3$ of specific radioactivity up to 120 mc $g^{-1}$ is about 60% [sic] lower than that of the non-radioactive salt. The form of the decomposition curves also changes: radioactive cadmium carbonate and radioactive sodium bicarbonate in a vacuum or in an atmosphere of nitrogen exhibit a maximum (sometimes even two maxima) on the rate curves (especially well defined with cadmium carbonate), whereas the non-radioactive salts show a minimum[40,41]. The composition of the gaseous products did not depend on the action of radiation.

These effects are explained[39] by increase in the reactivity of the radioactive carbonates due to the accumulation of radiation disturbances under the influence of the $\beta$-disintegration of carbon-14 (recoil atoms, the appearance of impurity centres—nitrogen atoms—rupture and distortion of chemical bonds, and the establishment of a local charge).

Cadmium carbonate was more sensitive to radiation than sodium bicarbonate. Thus $CdC^*O_3$ even of specific radioactivity 0.5 mc $g^{-1}$ possesses enhanced reactivity, whereas $NaHC^*O_3$ of 95–120 mc $g^{-1}$ (with respect to carbon-14) differs little in rate of thermal decomposition from the non-radioactive salt. Radioactive disintegration is assumed to facilitate the generation of a reaction centre but to have no appreciable effect on its migration inside the crystal. The second stage, almost unaffected by self-irradiation, is evidently the most important in the case of sodium bicarbonate. It is probable that not only different structure-sensitive properties of a solid but also various kinetic characteristics of a chemical reaction involving it will have different sensitivities to radioactive disintegration. This view is supported also by a kinetic investigation of the thermal decomposition of radioactive mercuric oxide (specific radioactivity ($^{203}Hg$) $\sim 50$ mc $g^{-1}$), whose kinetic parameters were identical with those of the non-radioactive analogue[42].

Detailed investigations have been made[43–47] of the spontaneous decomposition of plutonium and americium oxalates. At room temperature the simple and double oxalates of tervalent, quadrivalent, and sexivalent plutonium undergo vigorous decomposition with the evolution of gas under the influence of their own $\alpha$-radiation[43–45]. After storage for 18 months the double ammonium, sodium, and potassium plutonium(IV) oxalates yielded a mixture of $PuOCO_3$ and $(Na, K)_2CO_3$. Pure plutonium(IV) oxalate gave a product corresponding in composition to plutonium oxide carbonate[44,45].

The decomposition of americium oxalate occurs so rapidly that the almost pure carbonate remains after

twenty days (Fig. 4). The efficiency of decomposition is 1.3 mol. per 100 eV of absorbed energy. The oxalate is converted into the carbonate, and carbon dioxide and monoxide are evolved. It is significant that the composition of the evolved gases and the final compound in the thermal decomposition of americium oxalate closely resemble the products of its radiolytic decomposition [46,48].

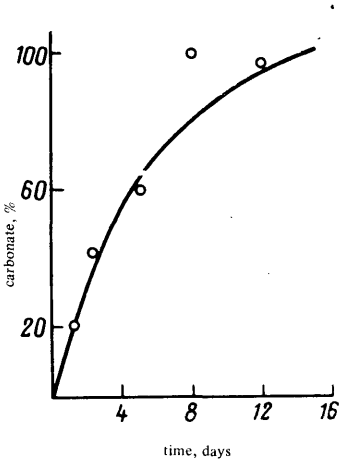



**Figure 4.** Variation with time in the carbonate content of americium oxalate crystals [47].

The addition of cobalt-60 to cobalt formate in amounts of 1.42 mc $g^{-1}$ shortens the half-period of the topochemical decomposition of the radioactive salt to less than one-quarter. A gas comprising hydrogen and carbon dioxide is evolved. The effect of self-irradiation on the kinetics of the radiolysis of cobalt formate depends on the length of storage of the radioactive material, which involves the accumulation of radiation defects in the crystal lattice.

The contamination of silver azide with cadmium atoms by the disintegration of silver-110 (initial radioactivity $\sim 3.5$ mc $g^{-1}$) increases the detonation velocity of the azide by 50%. The accumulation of cadmium for 270 days changes the crystals from almost colourless to brown [49]. It is supposed that cadmium atoms and radiation defects ($F$-centres, displaced atoms) accelerated the decomposition of silver azide.

Insufficient data have been published on the self-radiolysis of radioactive materials for definite generalisations to be made. Barium, strontium, calcium, and potassium sulphates are exceptional in this respect.

An important parameter of the radiation properties of any system is the primary yield of products determined when the recombination of the disturbances can be neglected. Values of $G_{pmc}$ for crystalline specimens are usually found from the initial linear portion of the curves representing the accumulation of paramagnetic centres at low temperatures. Values obtained with the irradiated salt at a high temperature, although different from the primary yields, can also characterise the radiation-chemical stability of solids (Table).

The Table shows that the yield of primary products of radiolysis of the sulphates, as well as of $SO_3$ groups + $SO_2$, which are formed mainly in secondary processes, decreases with increase in the lattice energy of the irradiated salts. Many workers have observed such a relation in series of compounds of the same type [50-52]. Hence the radiation stability of the crystalline anhydrous sulphates of the alkaline-earth metals conforms to the general rules of radiolysis established for other compounds. The ionicity† of the anion in the series of sulphates—barium, strontium, and calcium—has no appreciable effect on radiolysis (Table), the lattice energy being of decisive importance.

The radiolysis of radioactive sulphates under the influence of their own radiation supports the principle [51,53-55] that the radiation stability in the irradiated zone is greater in solids of smaller lattice energy: i.e. values of $G_{decomp}$ are lower in crystals having smaller lattice energies (see "self-irradiation" column in Table). This is a characteristic feature of the self-radiolysis of radioactive salts, in addition to those noted previously—high values of $G$, rise in temperature, appearance of impurities and recoil atoms, and in some cases a maximum in the time dependence of the concentration of paramagnetic centres resulting from the exponential loss in intensity of self-irradiation.

The above experimental results are also a convincing demonstration that processes occurring in radioactive materials cannot always be simulated by external irradiation. The possible effects of self-irradiation must be thoroughly analysed in each specific case, and their role in the system carefully assessed.

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†The Russian text has "electronic fraction" (Ed. of Translation).

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