EFFECT OF IRRADIATION ON THE ADSORPTION AND CATALYTIC PROPERTIES OF SEMICONDUCTORS AND DIELECTRICS

V. G. Baru

I. Introduction 590

II. Radiation effects on semiconductors and dielectrics (general formulation, influence on electronic properties) 590

III. Changes in the adsorption and catalytic properties of semiconductors and dielectrics under the influence of external γ-irradiation 592

IV. Changes in the adsorption and catalytic properties of semiconductors and dielectrics resulting from external corpuscular irradiation 596

V. Changes in the adsorption and catalytic properties of semiconductors and dielectrics resulting from "internal" radioactive radiation 599

I. INTRODUCTION

There have been many recent publications on the effect of various types of radiation on the adsorption and catalytic properties of semiconductors and dielectrics. Increases in adsorption capacity and catalytic activity of up to 3–4 orders of magnitude have been reported. These effects combine obvious scientific interest with great technological potentialities, yet their mechanism is still obscure, and a theoretical interpretation and a unified description of the observed phenomena are still awaited.

The present review aims to give a systematic survey of existing factual material in the hope that it may prove generally informative and that it may stimulate new experimental and theoretical work†.

II. RADIATION EFFECTS ON SEMICONDUCTORS AND DIELECTRICS (GENERAL FORMULATION, INFLUENCE ON ELECTRONIC PROPERTIES)

Energetic electromagnetic radiations and fast particles interact with matter by a complicated cascade process involving, as a rule, ionisation effects and structural changes in the crystal lattice of solids[1]. The primary reaction with the bombarding stream causes many secondary changes in the material. The most important disturbances produced include: (a) non-equilibrium free and localised charge carriers (electrons and holes); (b) lattice defects of the "vacancy" and "interstitial" type, singly or in clusters; (c) chemical impurities produced by nuclear reactions within the solid. The observed radiation effects follow, as a rule, from changes of these types.

Any of the above defects can be induced by various kinds of radiation, but with different efficiencies.

† Experimental and theoretical papers dealing with the effect of light on the adsorption and catalytic properties of semiconductors and dielectrics are excluded.

The most characteristic effect of γ-irradiation is excitation of electrons and ionisation. The resulting non-equilibrium Compton electrons and photoelectrons give rise to phenomena analogous to photoconductivity.

Vavilov and coworkers[2,3] have reported some interesting results of their work on γ-conductivity in silicon and germanium. The mean energy required to generate a hole-electron pair by γ-irradiation was shown to be independent of the quantum energy of the γ-rays, thus establishing a proportionality between the quantum yield and the γ-quantum energy. The γ-conductivity of semiconductors of the CdS group was investigated by Konozenko *et al.*[4] As in the case of photoconductivity the excess concentration of free carriers of a given sign is given by the expression $\Delta n = g\tau$, where g is the rate of generation of carriers (proportional to the intensity of the γ-irradiation) and τ is the average lifetime of non-equilibrium carriers. Since semiconductors have very low τ values, the effect decays very rapidly when irradiation ceases. More lasting effects of ionisation processes are possible only if hole or electron trapping can occur. Particularly effective trapping centres have been shown (in the case of germanium) to be associated with surface states, which can gradually release charge carriers over a period of hours after irradiation has ceased[5].

Direct ionisation processes produce larger effects in insulators than in semiconductors because longer carrier trapping times are possible in these materials. Typical ionisation phenomena in these materials include[1,6,7] the formation of colour centres, luminescence, paramagnetic resonance absorption, etc. Several features of γ-conductivity in various dielectrics (quartz, polyethylene, sulphur, mullite) have been studied experimentally and fully discussed by Vul[8].

Besides ionisation processes, γ-irradiation of semiconductors and dielectrics produces significant structural changes. These defects produce localised energy levels within the forbidden energy band of the crystals which can be detected by measurements of the temperature coefficients of the resistivity and of the Hall effect, and by the spectral characteristics of the photoconductivity and of the recombination processes[9-11].

Defects of this type arise when atoms (or ions) are displaced from their normal sites. In semiconductors, this occurs mainly through the secondary, internal irradiation of the material by fast Compton electrons and photoelectrons produced by the primary γ-irradiation[1]. The number of resulting displacements, N_γ, can be estimated from the formula $N_\gamma = \varphi_\gamma N_0 \sigma_\gamma$, where φ_γ is the intensity of γ-irradiation, N_0 is the number of atoms per unit volume of sample, and σ_γ is the effective displacement cross-section under γ-irradiation. Displacement cross-sections for semiconductors subjected to γ-quanta of normal energies (γ-rays from ^{60}Co, reactor γ-quanta) are not large, as a rule. The measured value for germanium is[12] $\sigma_\gamma \simeq 10^{-26}$ cm^2. Thus, γ-irradiation of semiconductors is less effective than neutron irradiation as a means of generating stable lattice damage.

The effectiveness of γ-irradiation can be much higher in dielectrics, because in these materials γ-quanta can interact with matter by two important additional mechanisms, both of which postulate the conversion of electronic excitation (ionisation) energy into displacement energy. The first mechanism, put forward by Seitz[13], accounts for the formation of lattice displacements by local energy transfer following the annihilation of an exciton (excitons produced

by irradiation are annihilated whenever they encounter a local disturbance of the perfect periodicity of the crystal lattice). The recombination of radiation-induced hole–electron pairs in the vicinity of a lattice defect can also give rise to this effect.

The second mechanism, proposed by Varley[14], applies only to ionic compounds. Varley assumes that a negative lattice ion can undergo multiple ionisation under the influence of irradiation, and develop a positive charge. Such an ion, being surrounded by normal, positive lattice ions, finds itself in a highly unstable environment, and can easily move to an interstitial site before regaining its lost electrons. The postulated multiple ionisation can arise either by direct interaction between a γ-quantum and several outer electrons or in cascade (by the Auger process).

Varley's mechanism presents some fairly stringent requirements: the postulated positive ion must have time to transfer to an interstitial site before its charge is neutralised by recombination with the ejected electrons or by coulombic "repulsion" of the accompanying positive holes.

Some published results suggest[15] that both these mechanisms can, in principle, operate also in semiconductors.

Experimentally observed displacement effects caused by γ-irradiation of dielectrics include the decrease in ionic conductivity of alkali halide crystals under weak γ-irradiation, the decrease in thermal conductivity of artificial sapphire at low temperatures[16], and the appearance of colour centres and paramagnetic resonance absorption in aluminium oxide, quartz, etc.[17]

The irradiation of semiconductors and dielectrics by neutrons and charged particles produces far more significant effects. Electronic excitation and ionisation effects, and displacement of atoms and ions, are produced by the cascade processes initiated by irradiation of this type.

Neutrons interact with matter primarily by elastic collisions‡, leading to displacements. Ionisation effects, if present, are due to secondary processes.

Neutron irradiation can also result in the formation of appreciable quantities of chemical impurities by neutron capture and nuclear reaction if the irradiated material contains atoms of sufficiently large neutron capture cross-section.

Charged particles, whether primary or secondary, of energy $E > E_i$ undergo mainly inelastic collisions, giving rise to electronic excitation and ionisation[18]. Here $E_i = (M_1/m)I$, where M_1 is the mass of the moving particle, m the mass of an electron, and I the threshold excitation energy of an electron (comparable in magnitude with the width of the energy gap of the crystal). When $E < E_i$, elastic collisions (leading to displacements) predominate. It should be noted that ionisation processes can ultimately produce additional displacements by the mechanisms considered in the previous discussion of the effect of γ-irradiation.

Without considering these fast particle mechanisms in detail, we shall merely quote the formula[1] for calculating the total number of resulting displacements: $N_d = \varphi t N_0 \sigma_d \bar{\nu}$, where φ is the intensity of the stream of bombarding particles, t the time of irradiation, N_0 the number of atoms per unit volume of irradiated material, σ_d the cross-section for primary collisions, producing displacements, and $\bar{\nu}$ the average number of displaced atoms resulting from each primary displacement.

The value of σ_d depends on the type of interaction considered[19], but is of the order of 1 barn (1 barn = $= 10^{-24}$ cm^2). The quantity $\bar{\nu}$ is given[20] by the expression

$$\bar{\nu} = 0.5\left[1 + \ln\left(\frac{E_m}{2E_d}\right)\right], \text{ where } E_m = \frac{4M_1M_2}{(M_1 + M_2)^2}E.$$

E_m is the maximum energy which the collision can impart to the target atom; E_d the threshold displacement energy of the atom; E the energy of the bombarding particle; and M_1 and M_2 are the masses of the two atoms undergoing collision.

Estimates of the total number of radiation defects, based on these ideas, are usually found to agree in order of magnitude with the measured values (mostly derived from electrical measurements[1]).

Some changes in properties of semiconductors and dielectrics, resulting from corpuscular irradiation, will now be briefly considered. Irradiation of semiconductors has a strong effect on the free carrier concentration, and therefore on the electrical conductivity of the material. The effect on carrier mobility is much less marked. These effects do not decay, and their sign and magnitude are a function of the initial concentrations of electrons and positive holes. At some well-defined free carrier concentration, which is a characteristic of a given material, these changes become vanishingly small[1,21].

Irradiation of silicon, whether n- or p-type, usually alters the conductivity towards its intrinsic value. Specimens of n-type germanium are invariably converted into p-type as a result of irradiation, but in heavily p-type specimens the conductivity drops. Irradiation effects on InSb are very similar[5].

All these phenomena can be explained on the assumption that irradiation gives rise to donor and acceptor defects of different types, whose localised energy levels are distributed over such a wide band of energies as to produce the observed complexity and multiplicity of effects. In silicon, the induced donor and acceptor levels can be mutually compensating, and the Fermi level of the irradiated specimen is near the middle of the energy gap. In germanium, the acceptor centres are more prominent, and the Fermi level is shifted towards the lower half of the energy gap.

A detailed explanation of the electronic consequences of irradiation effects usually requires an exact knowledge of the energy parameters of the radiation defects involved. The most reliable information is obtained from measurements of the Hall effect as a function of temperature, and from studies of the spectral characteristics and of the transient behaviour of photoconductivity. Except in the case of germanium and silicon[1,5,22–26], our quantitative knowledge of these effects is inadequate.

Measurements of optical and magnetic properties provide the fullest information on the effect of fast particle irradiation of dielectrics. The commonest results of irradiation in these materials are changes in the absorption spectra, colour development, formation of paramagnetic centres, etc. Thus, the absorption spectrum of proton-irradiated NaCl crystals shows additional bands which can

‡ Elastic collisions are defined as processes in which the total kinetic energy of the colliding particles (but not the kinetic energy of the bombarding particle) is conserved.

be assigned to various defects (in particular, to the accumulation of F-centres[27]). Similar phenomena are observed[28] in neutron-irradiated quartz, and the optical spectra can be correlated with EPR measurements[29]. Neutron irradiation of α-Al_2O_3 produces comparable results[1].

A gradual change in properties (not tending, however, to reestablish the original properties) is frequently observed when fast-particle irradiation of specimens is interrupted. This is due to the trapping and reemission of non-equilibrium charge carriers, formed in ionisation processes, which occur at the same time as the time-independent displacement effects. As already remarked, these transient phenomena are most noticeable at the surface, where effective trapping centres are present in large numbers.

The removal ("annealing") of displacement defects can also cause changes in the properties of the specimen after cessation of the irradiation. In many cases, the initial properties of the material can be completely restored by this process. These phenomena have a diffusion mechanism, and are therefore greatly accelerated by a rise in temperature. Under conditions of prolonged irradiation, and therefore of high concentrations of structural defects, annealing effects can occur during the irradiation period, and set an upper limit to the radiation damage.

In conclusion, we may state that the band theory of the solid state offers a reliable description of the effects of irradiation on the electronic properties of semiconductors and dielectrics, provided that the concentrations and the energy parameters of the resulting defects can be evaluated. Modern theories of the interaction of solids with radiation enable us to evaluate (at least approximately) the number of radiation defects, but we are still entirely dependent on experimental information for a knowledge of the energy levels of the defects.

III. CHANGES IN THE ADSORPTION AND CATALYTIC PROPERTIES OF SEMICONDUCTORS AND DIELECTRICS UNDER THE INFLUENCE OF EXTERNAL γ-IRRADIATION

In view of the vast mass of published experimental material, no attempt will be made to include in the present review some of the older papers on the action of energetic electromagnetic radiations (and other forms of radiation) on solid adsorbents and catalysts. These have been adequately described by previous reviewers[30-32], who have also stressed the unreliability of some of the older work.

The effect of γ-radiation on the catalytic properties of zinc oxide, one of the best known and most widely used semiconductor catalysts, has been discussed in a number of papers. Barry and Roberts[33] studied the effect of γ-radiation on the catalytic activity of zinc oxide towards the synthesis of methanol from hydrogen and carbon monoxide. The catalyst, prepared by decomposing zinc carbonate in air at 300°, had n-type conductivity before irradiation. A ^{60}Co source was used to irradiate the material at a dose rate of 2.5×10^{19} eV g^{-1} h^{-1} whilst reaction was proceeding under a pressure of 1 atm. The catalytic activity of ZnO was found to be increased by irradiation, but only for reaction temperatures in the range 175°–250°. The results of three experiments, summarised in Table 1, show that the effect of irradiation is more pronounced at the lower temperatures.

TABLE 1. Synthesis of methanol on non-irradiated and irradiated zinc oxide.

Temp., °C	Rate of production of methanol, ml h^{-1}			Yield of methanol, molecules per 100 eV
	non-irrad.	irrad.	difference	
223	0.18	0.24	0.06	0.58
204	0.103	0.20	0.097	1.93
201	0.036	0.144	0.108	0.04

The authors conclude[33] that the mechanism of catalysis is not affected by the radiation, since the lower temperature limit of the irradiation effect is not very different from that for ordinary thermal catalysis. The observed effects can be ascribed to the free electrons produced by the γ-radiation. The adsorption of both hydrogen[34] and carbon monoxide[35] is known to be ionic over the temperature range of these experiments, a fact which the authors consider very significant[33].

Taylor and Wethington[36] have observed the opposite effect of γ-radiation on the catalytic properties of ZnO. The hydrogenation of ethylene at 0° is appreciably retarded by γ-irradiation of the zinc oxide catalyst. The ZnO specimens were irradiated for various times by γ-quanta from ^{60}Co (6000–10 000 r min^{-1}), in a vacuum and at 15° ± 5°. The specimens had been previously degassed at 0° (in a few cases, at 100°). An irradiation period of 3 months increased the time for 50% conversion in the catalytic reaction by more than a factor of 5. The usual activating procedures (high-temperature treatment and evacuation) were sufficient to restore the initial catalytic activity of the material.

The authors explain this radiation effect in terms of displacements induced by irradiation, but the possibility of catalyst poisoning (by the radiation-induced polymerisation of reactants or products) is not excluded.

On the other hand, zinc oxide irradiated with γ-quanta from ^{60}Co to a dose of 5×10^{18}–10^{19} eV g^{-1} shows a threefold to tenfold increase in catalytic activity towards the hydrogen–deuterium exchange reaction. Poisoning effects associated with oxygen were observed both before and after irradiation of the catalyst[31].

Mishchenko *et al.*[37] have reported very profound changes in the catalytic activity of TiO_2 towards the hydrogen–deuterium isotope exchange reaction as a result of irradiation. The TiO_2 specimens were heated at 500° under a pressure of 10^{-5} mm Hg for several hours, but in the absence of irradiation no catalytic activity could be detected at 0°. A ^{60}Co source (120 r sec^{-1}) was used to irradiate the material in a vacuum at liquid nitrogen temperature (integral dose 1.7×10^7 r). As a result, the catalytic activity of TiO_2 at liquid nitrogen temperature rose by at least 3–4 orders of magnitude.

The effect was found to decay rapidly, the rate constant at 0° decreasing by two powers of ten within an hour of removal from the liquid nitrogen bath. The authors[37] stress their observed correlation between changes in catalytic activity and in magnetic properties of the TiO_2 specimens. Specimens heated to 500° gave no EPR signal before

being irradiated. Irradiated specimens showed paramagnetic resonance absorption at liquid nitrogen temperature, which persisted as long as the material was kept at this temperature. Upon rapid heating to room temperature, the intensity and the shape of the EPR signal changed over a period of about an hour to give a new, stable line. The authors assume that the enhanced catalytic activity and the resonance absorption are due to the same impurity centres, induced by the γ-radiation.

Tsetskhladze and Kalandadze's interesting work[38] on the catalytic activity of γ-irradiated copper oxides calls for detailed discussion. These workers studied the dehydrogenation of ethanol, catalysed by CuO and Cu_2O. The catalysts were degassed in a vacuum at 10^{-5} mm Hg, irradiated with a ^{60}Co source, and used at 275°.

The variation of catalytic activity with dose of γ-radiation, shown in Fig. 1, implies that the catalytic properties of CuO and Cu_2O are affected in opposite senses. This is confirmed by the kinetic curves for irradiated and non-irradiated catalysts (Fig. 2).

In parallel with the measurements of catalytic activity, measurements of the electrical resistance of cold-pressed pellets of the copper oxides were carried out both before and after irradiation. The resistance of CuO was found to be increased, and that of Cu_2O decreased, by the irradiation. Both effects were considerable (at least an order of magnitude), but the authors were not able to establish a clear relationship between the dose and the change in resistance. Nevertheless, the observed correlation is not thought to be fortuitous, and an electronic mechanism to describe the effect of radiation has been put forward.

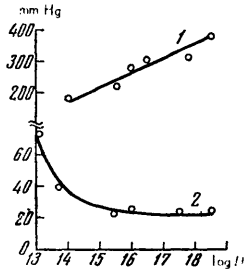


Fig. 1. Influence of irradiation dose (D, röntgens) of CuO (curve 1) and Cu_2O (curve 2) catalysts on hydrogen yield in the dehydrogenation of ethanol. Reaction time: 1 h.

Iron oxide is another oxide system in which γ-irradiation increases the "yield" of catalytic reactions. This oxide, after admixture of potassium carbonate and heating at 1000°–1300° for 4 h, has been used as a Fischer–Tropsch catalyst[39]. Specimens were degassed at room temperature before being irradiated (^{60}Co source). The measurements were made after irradiation.

The reaction kinetics before and after irradiation of the catalyst are illustrated in Fig. 3. Changes in catalytic activity are retained for surprisingly long times at 280°. The dependence on specimen geometry of the effect of irradiation is equally remarkable. The particle size of the catalyst to which Fig. 3 refers did not exceed 100–200 μ. When the particle size was decreased to 0.2–5 μ the percentage conversion was approximately doubled, but with 400–600 μ particles the effect of the same dose of γ-radiation was almost negligible. Pile irradiation (10^{18} neutrons cm^{-2}) was also ineffective under these conditions. There is evidence[31] that in these experiments the conductivity of the specimens was not affected by irradiation.

The authors[39] point out that in the initial stages of the reaction the effect of irradiation is slight (see Fig. 3), and therefore ascribe the observed effects to partial reduction of iron oxide, or formation of iron carbide (either of which can be expected to increase the catalytic activity), at the irradiation stage, rather than to a direct radiation effect such as electronic excitation or the production of structural defects.

Various oxide semiconductors (ZnO, TiO_2, etc.) have a catalytic effect towards certain radiation-induced chemical reactions, resulting from transfer to the reactants of the radiant energy absorbed by the semiconductor. Thus, the decomposition of potassium oxalate in aqueous solution under the influence of γ-radiation is intensified and accelerated[40] by a suspension of the semiconductor ZnO.

Among the dielectrics whose adsorption and catalytic properties are sensitive to γ-radiation, the various modifications of SiO_2 and Al_2O_3 have been most thoroughly investigated.

Kohn and Taylor[41] observed a large increase in the catalytic activity of silica gel towards the hydrogen–deuterium exchange reaction following irradiation. The rate of this

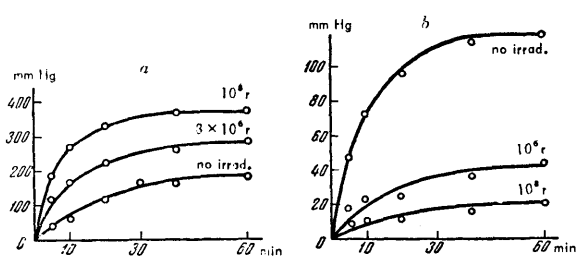


Fig. 2. Hydrogen evolution kinetics (mm Hg) in the dehydrogenation of ethanol on variously irradiated catalysts: (a) CuO, (b) Cu_2O.

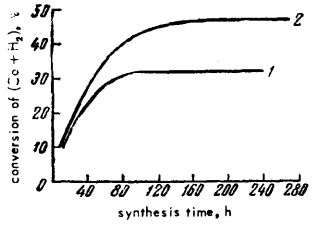


Fig. 3. Influence of γ-irradiation on the kinetics of hydrocarbon synthesis: temp. 280°, pressure 10 atm, irradiation dose 3.6×10^7 r: 1) before irradiation; 2) after irradiation.

reaction is only slightly increased, as a rule, by the presence of silica gel, and the room-temperature "half-life" is of the order of 100–1000 hours. This period was shortened to one hour by γ-irradiation of the silica gel with a dose of 10^{19} eV g^{-1}, which was shown to be vastly superior to conventional pretreatments for catalysts.

The investigation included, besides three specimens of silica gel, other modifications of SiO_2 and also three SiO_2–Al_2O_3 hydrocarbon cracking catalysts. All were degassed at 450°–700° and 10^{-5} mm Hg before being irradiated, at 25°, by γ-quanta from a ^{60}Co source (dose rate 1.2×10^{17} eV g^{-1} min^{-1}). The initial impurity content (Mg, Al, Fe, Mo) was in every case less than 10^{-1}–10^{-2}%.

The activation energy of the process before and after irradiation was deduced from measurements over a range of temperatures. Irradiation was found to lower the activation energy from 9 to 2 kcal $mole^{-1}$, which the authors interpret as evidence that a new path has been made available to the catalytic reaction. Since the activation energy is now small, a large number of active sites on the surface is no longer required. The results are set out in Table 2.

The authors believe that displacements induced in SiO_2 by the γ-radiation are responsible for these radiation effects. From data on the total number of displacements in SiO_2, deduced from EPR measurements and from calculations of the Compton scattering of γ-rays, they conclude that only about one displaced atom in a thousand gives rise to a catalytically active centre. "Yields" of catalytically active centres were calculated by dividing the measured rate constants K by the rate constants for a single active centre, which were evaluated by assuming an area of $\sim 16 \times 10^{-16}$ cm^2 per active centre, an activation energy of ~ 1 kcal $mole^{-1}$, and an average velocity of 1.5×10^5 cm $\times$ $\times$ sec^{-1} for a gas molecule at 25°.

In two subsequent papers[42,43], Kohn discusses the formation of colour centres and paramagnetic centres in irradiated silica gel. Colourless SiO_2 reddens on irradiation by X-rays or γ-rays and the colour does not disappear on heating to 250°. Hydrogen has an instantaneous bleaching effect, but the rate of bleaching decreases at low temperatures. Before irradiation, hydrogen was only weakly and slowly adsorbed, but after irradiation the extent and the rate of hydrogen adsorption increased. This was only a temporary effect, however, and hydrogen adsorption ceased as soon as the last trace of colour had disappeared. Starting from the dose of radiation and the amount of hydrogen adsorbed on the irradiated specimen, Kohn estimates that $\sim 3 \times 10^{18}$ colour centres were formed per gramme, each colour centre requiring the absorption of 100 eV of energy.

Ethylene, water vapour, and ammonia were also found to have a bleaching action, but oxygen had no effect. The colour centres were identified with holes, bound to excess oxygen in SiO_2. Bleaching results from the interaction of these holes with electrons donated by the gas. EPR studies of γ-irradiated silica gel showed that the paramagnetic centres are not related to the colour centres. A sample of SiO_2 irradiated at 50° gave an EPR signal which was stable at room temperature but not in the presence of ultraviolet radiation, oxygen, mercury vapour, or water vapour. The yield of these centres was 0.1 per 100 eV of energy absorbed. "Annealing" set in at 250°. The author ascribed this signal to electrons trapped in oxygen vacancies. The effect of oxygen suggests that we are dealing with a surface rather than a bulk phenomenon. Irradiation at -196° produced a new signal, insensitive to oxygen.

In an earlier paper[44], Taylor and Kohn had established that the catalytic activity of γ-Al_2O_3 towards the hydrogen–deuterium exchange reaction is strongly affected by γ-radiation.

The specimens, which were saturated with water when prepared, were degassed at high temperatures (~400°) for several hours, and irradiated *in vacuo* for 30 min at a dose rate of 2×10^{17} eV g^{-1} min^{-1}, using a cobalt source. Measurements of the rate of hydrogen–deuterium exchange at -78° showed a sevenfold increase in activity as a result of irradiation. The effect disappeared after storage for 2–4 h at room temperature, but could again be induced by repeating the irradiation. Specimens not previously degassed (and which were therefore catalytically inactive) showed an increase in activity of three orders of magnitude after irradiation, but the effect did not survive a few hours' storage, even at -78°. No significantly different results were obtained when irradiation was carried out during the course of the reaction, thus showing that fast-decaying processes do not play a major part. The authors explain these effects in terms of possible electron or hole trapping processes in the γ-Al_2O_3 lattice.

The study of this system was continued in a subsequent paper by the same authors[45]. Specimen pretreatment consisted, as in the previous work[44], in degassing at 200°–650°. In the absence of this treatment, the samples were catalytically less active, but more sensitive to irradiation. A study was made of the influence of degassing temperature on the radiation effect, and also of the effect of possible catalyst poisons (H_2O, H_2, C_2H_2). High degassing temperatures produced smaller radiation effects, and it was found that the sign as well as the magnitude of the effect could be influenced by the pretreatment, leading in some cases to loss of catalytic activity.

Poisoned specimens were shown to be more sensitive to radiation, and to regain their initial characteristics more rapidly. The authors suggest that radiolysis of the poison may be responsible for this, through either direct removal of the poison or the formation of compounds able to promote the reaction. They think it more likely, however, that electrons or holes trapped at unidentified localised states are responsible for the radiation effect. This view is supported by the effect of irradiation temperature on the increase in rate constant[45]. Specimens were irradiated at progressively decreasing

TABLE 2. Effect of γ-irradiation on SiO_2 and SiO_2–Al_2O_3 catalysts.

Catalyst	Degassing temp., °C	Rate constant at 25° before irradiation, min^{-1} m^{-2}	Radiation dose per unit surface area, eV m^{-2}	K after irradiation, min^{-1} m^{-2}	Yield of active sites per 100 eV	Yield of active sites per displacement
				25°		
Gel 1	450	$1.0 \cdot 10^{-8}$	$8.0 \cdot 10^{16}$	$2.4 \cdot 10^{-5}$	$1.3 \cdot 10^{-8}$	$1.3 \cdot 10^{-3}$
Gel 2	485	$1.4 \cdot 10^{-8}$	$3.6 \cdot 10^{16}$	$1.1 \cdot 10^{-5}$	$1.4 \cdot 10^{-8}$	$1.4 \cdot 10^{-3}$
Gel 3	525	$4.9 \cdot 10^{-9}$	$8.0 \cdot 10^{16}$	$5.5 \cdot 10^{-7}$	$3.1 \cdot 10^{-10}$	$3.1 \cdot 10^{-5}$
Quartz	500	$1.2 \cdot 10^{-4}$	$6.4 \cdot 10^{17}$	$>2.1 \cdot 10^{-3}$	$>1.6 \cdot 10^{-8}$	$>1.6 \cdot 10^{-3}$
Glass	500	$4.6 \cdot 10^{-4}$	$4.6 \cdot 10^{17}$	$>9.8 \cdot 10^{-3}$	$>9.4 \cdot 10^{-8}$	$>9.4 \cdot 10^{-3}$
Cristobalite	550	$8.1 \cdot 10^{-6}$	$4.7 \cdot 10^{18}$	$7.1 \cdot 10^{-3}$	$6.7 \cdot 10^{-9}$	$6.7 \cdot 10^{-4}$
"Cab-O-Sil"*	625	$1.1 \cdot 10^{-6}$	$2.5 \cdot 10^{17}$	$1.9 \cdot 10^{-5}$	$3.4 \cdot 10^{-10}$	$3.4 \cdot 10^{-5}$
		—78°		—196°		
SiO_2 – Al_2O_3	450	$8.8 \cdot 10^{-5}$	$3.8 \cdot 10^{17}$	$7.3 \cdot 10^{-5}$	$2.1 \cdot 10^{-7}$	$2.1 \cdot 10^{-2}$
SiO_2 – Al_2O_3	450	$2.2 \cdot 10^{-4}$	$8.3 \cdot 10^{17}$	$1.4 \cdot 10^{-4}$	$1.8 \cdot 10^{-7}$	$1.8 \cdot 10^{-2}$
SiO_2 – Al_2O_3	510	$1.7 \cdot 10^{-4}$	$2.7 \cdot 10^{18}$	$1.6 \cdot 10^{-5}$	$6.0 \cdot 10^{-9}$	$6.0 \cdot 10^{-4}$

* Anhydrous, particulate, colloidal silica made by Cabot Corp., USA. (Ed. of Translation).

temperatures (from 25° to -78°), and their catalytic activity was measured at -78° after each exposure. A plot of the logarithm of the rate constant for the exchange reaction against the reciprocal of the irradiation temperature is shown in Fig. 4. This graph defines the temperature dependence of the decay rate of the effect induced by irradiation. The corresponding activation energy (3 kcal × × mole^{-1}) is stated to be in tolerably good agreement with the depth of a typical trapping level for electrons or holes.

Kazanskii and Pecherskaya's report[46] that γ-irradiation of γ-Al_2O_3 at liquid nitrogen temperature induces paramagnetic resonance absorption at -196° is of relevance to Taylor and Kohn's results[44,45]. After two days at room temperature, the EPR signal had decreased tenfold. The Soviet workers point out that the symbathic relationship between the decrease in EPR signal and the loss of catalytic activity[45] of the γ-Al_2O_3 specimens allowed to reach room temperature is not fortuitous, and they suggest that both sets of phenomena are due to centres of a single type.

The influence of γ-irradiation on the catalytic properties of semiconductors and dielectrics is abundantly demonstrated by the work reviewed above. There have also been a number of publications on the effect of γ-irradiation on adsorption properties.

A paper by Starodubtsev *et al.*[47] discusses the adsorption properties of γ-irradiated silica gel. Changes in adsorption behaviour were observed by noting the pressure of a gas in a bulb containing the silica gel before and after irradiation. The silica gel specimens had previously been carefully heat-treated. Radiation was obtained from a ^{60}Co source of intensity 15×10^4–35×10^4 r h^{-1}, to give integral doses of 1.5×10^6–2×10^6 r.

A significant increase in the equilibrium adsorption capacity of silica gel towards various gases (H_2, N_2, C_2H_4, NH_3, CO, CO_2) was observed. Heating to 100° almost completely restored the initial adsorption properties of the silica gel, but annealing did not take place at room temperature (a hydrogen-filled bulb was stored for five months without significant change in hydrogen pressure). The authors ascribe the effect of irradiation to removal of hydroxyl groups with formation of free radicals on the surface of the adsorbent, and also to ionisation in the gas phase.

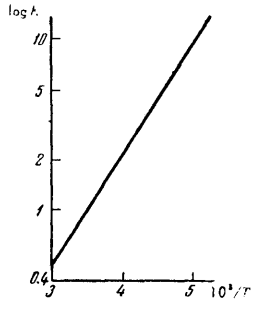


Fig. 4. Effect of irradiation temperature of a γ-Al_2O_3 catalyst on the rate constant (K, h^{-1} g^{-1}) of H_2–D_2 exchange at -78°.

Tagieva and Kiselev[48] studied the changes in adsorption properties of other modifications of SiO_2 (highly dispersed quartz and aerosil). The specimens were degassed at 200° under a pressure of 5×10^{-5} mm Hg; γ-irradiation from a ^{60}Co source was carried out at room temperature over a period of 24 h (integral dose 12×10^6 r).

The measured adsorption isotherms showed that the adsorption properties of SiO_2 towards water vapour had been reduced by the irradiation. The more highly hydrated specimen (quartz) was found to be more sensitive to radiation.

A decrease in surface hydration following γ-irradiation is also suggested by independent measurements of the structural water content of irradiated and non-irradiated specimens. Greatly increased (hundredfold) oxygen adsorption at room temperature following γ-irradiation, as compared with ultraviolet irradiation, is also reported in the same paper[48].

These authors[48] stress the appearance of a greyish colour on irradiation, which supports their theory that the observed effects are due to bond breaking in the adsorbed molecules or in the silanol groups. According to Molin and Voevodskii[49], this should produce paramagnetism in the irradiated specimens.

Kolbanovskii *et al.*[50] studied the effect of hydrocarbon adsorption (n-heptane, n-heptene, cyclohexane, benzene) on the EPR spectra of aluminium oxide before and after γ-irradiation. Commercial chromatographic alumina, and variously prepared mixtures of Al_2O_3 with Mo, Co, and Cr oxides, were used as adsorbents. The proportion of added oxides was normally kept below 10%. Doses of γ-radiation (^{60}Co source) between 6 and 120 Mr were applied at temperatures of -20°, -78°, and -196°. EPR spectra were recorded at different temperatures before and after irradiation. Irradiation produced profound changes in some of the EPR spectra. In some cases, signals due to radicals formed by homogeneous radiolysis were observed. The effect of temperature on the concentration of carriers with unpaired spins indicated the presence of activation energy barriers.

Special mention is due to the interesting results of Haissinsky and Siejka[51,52], who studied the effect of γ-radiation on the surface adsorption of various ions from aqueous solution: $^{144}Ce^{3+}$, $^{137}Cs^{+}$, $^{131}I^{-}$. In most experiments the adsorbent consisted of thin strips of platinum ($2 \times 1 \times 0.001$ cm^3) or stainless steel ($2 \times 1 \times 0.04$ cm^3), and the presence of a semiconducting film of oxide on the metal surface was found to be essential. Some measurements were also made on gold ($2 \times 1 \times 0.001$ cm^3) and poly(vinyl chloride) ($2 \times 1 \times 0.06$ cm^3) strips. The extent of adsorption was measured (in counts per minute) by monitoring the radioactivity of the adsorbent surface, since the cerium, caesium, and iodine isotopes used in the investigation were all radioactive.

Measurements before irradiation showed that cations and anions are adsorbed by different mechanisms. These results and the work of Balashova[53], led the authors to conclude that cation adsorption in their systems was mainly electrostatic, but iodine was chemisorbed.

The specimens were irradiated from a 650 c cobalt source during 7 days at temperatures between -1° and -2°. This was sufficient to saturate the radiation effect. Doses of 1.5×10^{19} eV and 36×10^{19} eV were absorbed by the platinum and the steel specimens respectively.

Irradiation increased the equilibrium adsorption of cations, and had a powerful effect on the adsorption kinetics and on the temperature coefficient. Kinetic curves for the adsorption of Ce^{3+} on platinum before and after irradiation are shown in Fig. 5.

The corresponding curves for the adsorption of I^- (Fig. 6) show a decrease in adsorption after irradiation, and vastly different adsorption kinetics. The activation energy of the process was unaffected by irradiation.

A special study was made of the effect on adsorption of degassing the adsorbents (500°) and the solution. The oxide film on platinum is partly dissociated at this temperature, whereas the oxide film formed by steel remains unchanged. This work (both irradiation and adsorption) was done in a vacuum.

After 30 min, cerium adsorption at ordinary temperatures was 2–3 times higher on the degassed (but not irradiated) specimens than on the initial specimens. Iodine adsorption decreased 80–100-fold on platinum, but not on steel. Irradiation of the degassed substrates lowered the adsorption of Ce^{3+} on platinum by a factor of 2 or 3, but produced a twofold increase in the adsorption of this ion on steel. The adsorption of I^- on platinum rose by a factor of 20, whereas the adsorption of I^- on steel was practically unaffected.

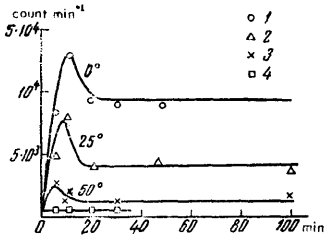


Fig. 5. Adsorption kinetics of Ce^{3+} on Pt: 1), 2), and 3) irradiated adsorbent; 4) adsorbent not irradiated.

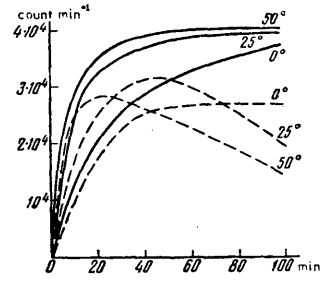


Fig. 6. Adsorption kinetics of I^- on Pt. Continous lines: adsorbent not irradiated; broken lines: irradiated adsorbent.

Haissinsky and Siejka interpret these observations by postulating that cation adsorption is mainly electrostatic, whereas iodine is chemisorbed. The results are consistent with the electronic theory of chemisorption and with the theory of the electrical double layer at a metal–solution interface.

IV. CHANGES IN THE ADSORPTION AND CATALYTIC PROPERTIES OF SEMICONDUCTORS AND DIELECTRICS RESULTING FROM EXTERNAL CORPUSCULAR IRRADIATION

The effect of neutron and charged particle bombardment on solid non-metallic adsorbents and catalysts has been investigated far less thoroughly than the effect of γ-radiation. Only two of the commoner catalysts, SiO_2 and Al_2O_3, have been studied in detail.

Weiss and Swegler[54] reported an increase in the catalytic activity of neutron-irradiated silica gel towards the isomerisation reaction of the double bond in hex-1-ene. The silica gel specimens, previously heated at 550° for 16 h, were irradiated in a reactor by a fast neutron flux of 7.5×10^{18} cm^{-2} (and approximately the same number of slow neutrons). The surface area of the specimens was not altered by irradiation.

The average percentage conversion of hex-1-ene on a catalyst which had not been irradiated, and on catalysts irradiated with 1.8×10^{18} and 7.5×10^{18} neutrons cm^{-2}, was 3.3, 4.6, and 9.4% respectively. The effect is ascribed to atomic displacements which, according to the authors' calculation, can amount to 1% of the total number of lattice atoms. Nuclear reactions are entirely negligible ($< 10^{-6}$%) because of the very small cross-sections involved ($\sim 10^{-27}$ cm^2). The authors also point out that neutron irradiation does not affect the catalytic activity of silica gel towards the cracking reaction of isopropylbenzene.

Lucchesi and coworkers[55,56] have reported a decrease in the rate of isomerisation of alkenes on an alumina–silica catalyst following irradiation. A study of the catalytic activity of SiO_2–Al_2O_3 catalysts towards isomerisation of the double bond in but-1-ene under pile irradiation conditions was carried out.

The catalyst contained 87 wt.% SiO_2. It was given a preliminary heat-treatment at ~540° for 16 h followed by 3 h at 675°.

Pile irradiation was applied as follows: fast neutrons (>0.5 MeV), 6.9×10^{18} neutrons cm^{-2}; thermal neutrons 6.1×10^{18} neutrons cm^{-2}; dose of γ-radiation, 1.2×10^{10} r. The induced radioactivity consisted of 2 MeV β-radiation (90%) and 0.5–2.6 MeV γ-radiation (10%).

Catalytic measurements, carried out at 65° during the 30 days following irradiation, showed that the activity of the catalyst had decreased as a result of irradiation (Fig. 7). The authors point out that atoms of Al, P, F, Mg, and Na may be formed in the lattice by nuclear reactions. Their concentration, however, is so small ($< 10^{-5}$–10^{-7}%) that they can hardly explain the observed effect. The number of displacements (a few hundreds per primary impact) is much larger, and an acceptable interpretation must involve these entities. Lastly, the effect of radiation on water, which is known to promote this catalyst, may also be important.

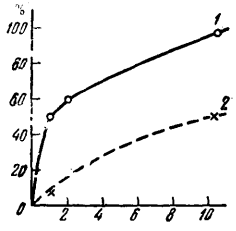


Fig. 7. Variation of percentage conversion of but-1-ene with reciprocal rate of admission in g h^{-1}. SiO_2–Al_2O_3 catalyst, not irradiated (curve 1) and irradiated (curve 2).

Kohn and Taylor's work[41], discussed in the previous section, had shown that the activity of silica gels in the hydrogen–deuterium exchange reaction and of SiO_2–Al_2O_3 catalysts in hydrocarbon cracking reactions was greatly increased by γ-irradiation. The effect of neutron irradiation on these systems was found to be even more striking. The impurity contents, and the pretreatment procedures adopted for the catalysts, are listed in Section III.

The specimens were irradiated in the pile with doses between 2.5×10^{15} and 2.2×10^{18} neutrons cm^{-2}. The catalytic activity rose to such an extent that the measurements had to be made at -196°. Table 3 lists the results, and also the authors' estimates for the numbers of displaced atoms and nuclear transformations, and for the yield of "catalytically active sites" per displaced atom. The rate constants observed before irradiation of the specimens are set out in Table 2.

It can be seen that neutron irradiation leads to calculated "yields" of active centres per displaced atom which are 100–1000 times smaller than in the case of γ-irradiation. This is interpreted by the authors as "aging" of the neutron-irradiated specimens, or as a demonstration of the greater effectiveness of the simple defects induced by γ-radiation, such as an isolated "vacancy–interstitial" pair, as compared with the more complex defects generated by neutron irradiation.

Kohn and Taylor[45] have studied the effect of neutron irradiation of γ-Al_2O_3 on the catalytic activity of the material in hydrogen–deuterium exchange reactions. The experiments on the effect of γ-radiation, and details of specimen purity, were summarised in the previous section.

The main conclusion of this work was that the reaction is significantly accelerated by neutron irradiation of the γ-Al_2O_3 catalyst.

Spitsyn *et al.*[57] have reported an interesting study of the effect of various types of radiation (including radiation from nuclear reactors) on the catalytic dehydration of n-decanol on Al_2O_3. The alumina used for this work contained 0.11% Fe_2O_3 and traces of SiO_2. The pile radiation had a neutron flux of $\sim 0.8 \times 10^{13}$ neutrons cm^{-2} sec^{-1}. The time of irradiation was varied between 1 and 10 days. The catalytic activity of the irradiated specimens was measured, in the temperature range 250°–400°, three days after irradiation. Typical results (for a temperature of 340°) are set out in Table 4.

It is interesting to note that the sign of the effect changes with the time of irradiation, and therefore with the integral dose of radiation: the catalytic activity is decreased by a brief irradiation, but increases on prolonged irradiation.

Measurements of temperature effects showed that storage during 49 days at 280° had practically no effect, whereas the same length of storage at 390° considerably decreased the effect of irradiation. The weak induced radioactivity (mostly due to the isotopes ^{24}Na and ^{59}Fe) cannot possibly account for the observed effects. However, irradiation with slow neutrons produces the short-lived radioactive isotopes ^{28}Al and ^{19}O of half-life 2.3 min and 29.5 sec respectively, which emit radiation of very high energy. The authors thus ascribe the observed effects to two opposing factors: on the one hand, to the appearance of lattice defects and production of electrical charges by radioactive decay, and on the other hand, to a decrease in the number of active sites at the surface due to the "polishing" effect of the radiation.

The loss of catalytic activity towards dehydration of n-decanol[58] induced by pile irradiation of the Al_2O_3 catalyst is given a similar explanation. The largest negative effect was observed with a specimen which had been kept for a long time (270 days) after 30 days' pile irradiation.

Yang[59] has reported enhanced physical adsorption of krypton on γ-Al_2O_3 as a result of fast neutron irradiation

TABLE 3. Effect of neutron irradiation on SiO_2 and SiO_2–Al_2O_3 catalysts.

Catalyst	Dose per m^2, *nvt*	No. of displaced atoms per m^2	No. of nuclear transmutations per m^2	k after irradiation at −196°, min^{-1} m^{-2}	Yield of active sites per displaced atom
SiO_2, gel 4*	$3.4 \cdot 10^{15}$	$1 \cdot 10^{16}$	$2.8 \cdot 10^{11}$	$1.2 \cdot 10^{-4}$	$1.2 \cdot 10^{-7}$
SiO_2, gel 2	$6.1 \cdot 10^{13}$	$1.8 \cdot 10^{14}$	$5 \cdot 10^{9}$	$9.3 \cdot 10^{-6}$	$5.4 \cdot 10^{-7}$
SiO_2, gel 3	$3.8 \cdot 10^{12}$	$1.2 \cdot 10^{13}$	$3.1 \cdot 10^{8}$	$2.5 \cdot 10^{-6}$	$2.3 \cdot 10^{-6}$
SiO_2 – Al_2O_3	$1.6 \cdot 10^{15}$	$4.9 \cdot 10^{15}$	$1.2 \cdot 10^{12}$	$>1.1 \cdot 10^{-3}$	$>2.4 \cdot 10^{-6}$
SiO_2 – Al_2O_3	$3.6 \cdot 10^{15}$	$1.1 \cdot 10^{16}$	$2.6 \cdot 10^{12}$	$>2.4 \cdot 10^{-3}$	$>2.3 \cdot 10^{-6}$
SiO_2 – Al_2O_3	$1.2 \cdot 10^{16}$	$3.5 \cdot 10^{16}$	$8.5 \cdot 10^{12}$	$3.6 \cdot 10^{-3}$	$1.1 \cdot 10^{-6}$

* K on SiO_2 (gel 4) before irradiation had the value $9.3 \times 10^{-9} \times \times min^{-1}$ m^{-2} at 25°.

TABLE 4. Effect of neutron irradiation on the catalytic activity of Al_2O_3 towards dehydration of n-decanol.

Irradiation time, days	Radioactivity, mc g^{-1}	Yield of unsaturated hydrocarbons at 340°, %	Change in conversion relative to non-irradiated specimen, %
—	—	45	—
1	0.09	28	−38
1 (stored 49 days)	0.0002	37	−18
5	0.13	42	−7
10	0.14	51	+13

(2×10^{18} neutrons cm^{-2}), and has attributed the effect to radiation defects in the crystal lattice of the adsorbent.

Very little has been published on the irradiation of solid non-metallic catalysts by charged particles. In the case of heavy charged particles, the lack of data is almost complete.

Kohn and Taylor's paper[45] on the effect of γ- and neutron irradiation on the catalytic properties of γ-Al_2O_3 towards the hydrogen–deuterium exchange reaction deals also with the effect of α-particles, which is found to be appreciable. Irradiation by the α-particles emitted by an Rn source (150 mc) adsorbed on the specimen was allowed to proceed for 102 days.

Gromov and Spitsyn[60] studied the sorption of dyestuff ions from solution on to barium sulphate as a function of electron and proton irradiation. Before irradiation, the barium sulphate was heated in a vacuum (10^{-3} mm Hg) at 300°–350°, and stored under nitrogen at 5 atm. Electron irradiation was carried out in a nitrogen atmosphere. An electron energy of 800 keV was used throughout, but the rate and total dose were varied. Irradiation with 1.5 MeV protons was carried out in a vacuum (10^{-5}–10^{-6} mm Hg); in this case the dose was 0.4×10^{21} eV g^{-1}. The specimens were heated to 100°–150° during irradiation; no induced radioactivity was detected. The specific surface of the specimens was practically unaffected by the irradiation. The sorption capacity of $BaSO_4$ decreased with increasing dose of electron irradiation, irrespective of the nature of the dyestuff. The sorption inhibition was more marked (for a fixed total dose and electron energy) at the lower dose rates.

Proton irradiation decreased the sorption of Acid Orange more markedly than electron irradiation. It was noticed that the colour of the specimens changed from white to light brown after irradiation. After a week at room temperature they lost their brown tint (both in air and in nitrogen), but did not recover their initial sorption capacity. 1 h at 200°–250° removed the colour, and also partly restored the original sorption capacity.

The authors consider that the external irradiation decreases the number of active sites on the surface ("polishing effect"), but they do not exclude the possibility of radiation defects in the $BaSO_4$ lattice.

Significant changes in the adsorption of sulphur trioxide on potassium sulphate were observed in a study[61] of the effect of electron irradiation on the isotope exchange of sulphur in the K_2SO_4–SO_3 system. The solid was irradiated during 10 min in a 5 MeV electron beam. Measurements at 840° showed that above a critical dose of the order of 10^{16}–10^{17} eV the rate of exchange increases in direct proportion to the dose absorbed by the substrate.

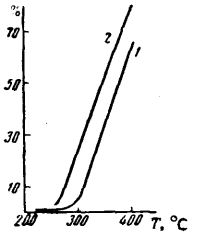


Fig. 8. Dehydration of n-decanol on Al_2O_3: 1) specimen not irradiated; 2) radiation dose 10^{20} eV g^{-1}.

Comparable doses of internal electron irradiation (produced by introducing a source of β-radiation into the bulk of the K_2SO_4) have a much more marked effect on the rate of exchange. This work is discussed in greater detail in the following section. The authors ascribe the effects to excitation of surface SO_4^{2-} ions under the influence of electron bombardment. The influence of electron bombardment on the gaseous SO_3 is significant, but much weaker.

The paper by Spitsyn *et al.*[57] on the dehydration of n-decanol on Al_2O_3 mentions the effect of electron irradiation on the activity of the catalyst. The catalyst and the alcohol vapour were irradiated for 10 min, during the reaction, with 760 keV electrons, to give a dose of 10^{20} eV $\times$ $\times$ g^{-1}. A significant increase in the rate of conversion of the decanol was observed, particularly at 250°–300°. The effect of temperature on the percentage conversion before and after irradiation is illustrated in Fig. 8. At 280° the yield of unsaturated hydrocarbons is increased by a factor of 10, but at higher temperatures the effect is less marked, due, no doubt, to "annealing" of the radiation defects. The authors describe the observed effects in terms of electron interactions with the Al_2O_3 lattice and excitation of the alcohol molecules.

Excitation and ionisation of atoms adsorbed on the Al_2O_3 surface are also invoked to explain the increased activity of an Al_2O_3 + 19.4% $CaCl_2$ catalyst towards dehydration of n-dodecanol[58] after electron irradiation (10^{20} eV g^{-1}).

We conclude this section with a discussion of an interesting paper by Roginskii, Zhabrova, and their coworkers[62] on the influence of electron bombardment on the topochemical processes involved in the decomposition of copper oxalate ($CuC_2O_4.\frac{1}{2}H_2O$) and nickel oxalate ($NiC_2O_4.2H_2O$).

The specimens were irradiated in air with different doses of electron (electron energy 0.6–2 MeV); the specimen thickness was of the same order as the depth of penetration of electrons of this energy. The heat thus generated did not raise the specimen temperature above 100°–150°.

Thermal decomposition of copper oxalate before irradiation begins at 225° *in vacuo* (to give Cu and Cu_2O) and at 250° in air (to give CuO). Non-irradiated nickel oxalate begins to decompose at 240° *in vacuo*, giving Ni, and at 300° in air, giving NiO.

Under the influence of radiation, the oxalates decompose in air some 200°–250° below the normal temperature of thermal decomposition, giving the same products as thermal decomposition in a vacuum. The depth of the effect increases with the dose of radiation. The radiation-chemical yield was found to be of the order of several tenths of a molecule per 100 eV.

Previous irradiation has a very marked effect on the decomposition kinetics of the oxalates (Fig. 9). Non-irradiated copper oxalate gives typically autocatalytic kinetic curves, with a long induction period which decreases with increase in temperature. Irradiation speeds up the reaction and shortens the induction period even at low temperatures. Really large doses (10^9 rad) can mask the autocatalytic effect.

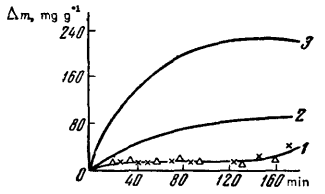


Fig. 9. Effect of previous irradiation on the decomposition kinetics of copper oxalate *in vacuo* at 225°: 1) non-irradiated specimen (Δ) and specimen irradiated with a dose of 2.2×10^8 rad (×); 2) specimen irradiated with 6×10^8 rad; 3) specimen irradiated with 1.1×10^9 rad.

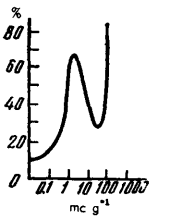


Fig. 10. Variation of percentage exchange with specific activity of $K_2S^*O_4$.

The authors[62] describe their observations in terms of excess electrons and holes, formed as a result of irradiation. The shortening of the induction period is ascribed to aggregation of the metal atoms formed by irradiation, giving crystallites (or nuclei) of a new phase.

V. CHANGES IN THE ADSORPTION AND CATALYTIC PROPERTIES OF SEMICONDUCTORS AND DIELECTRICS RESULTING FROM "INTERNAL" RADIOACTIVE RADIATION

The present section is devoted to the numerous papers on the control of the adsorption and catalytic properties of various solid catalysts by radioactive emitters of positive or negative particles, incorporated into the bulk of the catalyst (see Spitsyn's reviews[63,64]).

An effect of internal β-radiation on surface properties was first observed by Spitsyn and Mikhailenko, in their study[65] of the isotopic exchange of sulphur in the $K_2S^*O_4$–SO_3 system. These workers reported that the level of radioactivity of their preparations had an influence on the rate of isotopic exchange. The $K_2S^*O_4$ specimens were prepared by introducing a small amount (0.04–3%) of sulphur-labelled sodium sulphate into a solution of potassium sulphate, evaporating to dryness, and heating the residue to 800°. The exchange reaction was brought about by heating at 840° for 10 min. The rate of exchange was shown to be unaffected by inactive Na_2SO_4.

Within the limits of activity used in that investigation (0.02–19.2 mc g^{-1}), the extent of exchange was found to rise to a maximum at 2–2.3 mc g^{-1}, and then fall off again. The system was reinvestigated by the same workers[66] in greater detail and over a wider range of activities (up to 130 mc g^{-1}), with the results shown in Fig. 10. The formation of Cl^- ions by radioactive decay is not thought to affect the degree of exchange: an experiment in which 0.12% of KCl was added to a K_2SO_4 preparation of activity 0.06 mc g^{-1} gave 11.6% exchange, *i.e.* practically the same as in the control experiment.

A variation in the extent of exchange with specific activity of the solid of the type shown in Fig. 10 was observed also for the system $Na_2S^*O_4$–SO_3. The authors suggest that in both systems isotopic exchange of sulphur involves a reaction between SO_3 and SO_4^{2-} ions on the surface, with formation of the ionic intermediate $S_2O_7^{2-}$. The initial increase in the degree of exchange (see Fig. 10) is ascribed to the appearance of positive surface charge as a result of the continuous emission of β-particles; the subsequent drop can be explained by neutralisation of the positive charges setting in above a certain rate of electron emission. Lastly, the third, sharply rising portion of the curve is thought to be largely controlled by "activation" of the crystal lattice of the solid sulphate and of the SO_3 molecules under the influence of β-particles. The point was confirmed by comparing the results of Fig. 10 with those obtained in a parallel investigation[61]: the doses of external radiation required[61] to influence the amount of exchange in K_2SO_4 are effectively the same as the doses of internal electronic radiation experienced by the $K_2S^*O_4$ preparation whose specific activity corresponds to the beginning of the third section of the curve of Fig. 10. This is clear evidence that the two phenomena must be related.

The authors' suggestion of a change in mechanism for the sulphur isotope exchange reaction at different levels of radioactivity of the substrate has been confirmed by measurements of the rate constant for the exchange reaction in the $Na_2S^*O_4$–SO_3 system in the temperature range 700°–800°, leading to the activation energies of the process: 23–24 kcal $mole^{-1}$ and 18–19 kcal $mole^{-1}$, respectively, for specific activities of 0.02–1 mc g^{-1} and 10–25 mc g^{-1}.

Spitsyn and Finikov[67] reported very similar effects in their study of the oxygen isotope exchange in the $Na_2S^{*16}O_4$–$^{18}O_2$ system between 600° and 800°. By working over a range of temperatures, they were able to show that the activation energy of the process is a function of the specific activity of the sample. An energy minimum of 4 kcal $mole^{-1}$ was observed for activities of 1–2 mc g^{-1}, but at high specific activities the activation energy was even higher than the 54 kcal $mole^{-1}$ which characterise the process in the absence of radiation effects.

These workers noticed a "build-up" of the radiation effect with time, as shown in Table 5. These results confirm that the main effect of radiation takes place in the solid rather than in the gas phase, since the effect increases with time elapsed after irradiation as well as with the initial radioactivity. The specimens became greyish violet and the intensity of the colour increased with specific activity and with storage time. The colour was bleached by heating the solid to 600°.

Spitsyn and his coworkers studied the direct influence of internal radiation on adsorption properties[68–70]. We have already discussed their work[60] on the adsorption from

TABLE 5. Isotopic exchange of oxygen in the $Na_2{}^{*16}O_4$–$^{18}O_2$ system.

Temp., °C	Specific activity, mc g^{-1}	Storage time, days	Amount of exchange in 8 h, %	
			before storage	after storage
786	0.5	4	5.6	6.3
782	10.0	15	26.8	—
785			—	40.6
780	25.0	8	18.5	38.6
760		6	24.8*	29.6

* Specimen kept for 2 days before the first measurement.

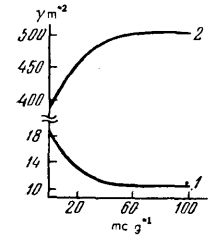


Fig. 12. Effect of initial radioactivity of BaS^*O_4 on dye sorption: 1) Methylene Blue; 2) Acid Orange.

solutions of ions of the dyestuffs Acid Orange and Methylene Blue, using barium sulphate adsorbents subjected to external electron and proton irradiation. The same workers investigated the influence of "internal" β- and α-radiation on the system[68] by coprecipitation of the isotopes ^{35}S and ^{226}Ra with the barium sulphate.

The equilibrium sorption curves (Fig. 11) show that sorption of the coloured cations of Methylene Blue decreases with increasing β-activity of the BaS^*O_4, whilst sorption of the coloured anion of Acid Orange increases under the same conditions. Internal α-radiation produces even stronger effects, but in the opposite sense.

Another basic dye, Brilliant Green, showed the same behaviour as Methylene Blue.

The measured sorption capacity of BaS^*O_4 is plotted in Fig. 12 against specific β-activity. The authors interpret these curves by invoking the accumulation of electrical charge on the $BaSO_4$ surface, the surface charge being positive for β-radiation and negative for α-radiation. The difference in behaviour between basic and acidic dyestuffs is, of course, consistent with this model. Gromov and Spitsyn's results[60] suggest that different mechanisms are involved in the interaction of external electronic and of proton radiation with a given system.

The same school has investigated[69,70] the effect of internal β-radiation on the adsorption capacity of potassium and barium sulphates towards various gases. The adsorption

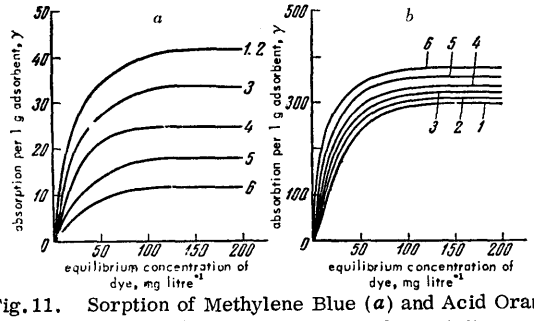


Fig. 11. Sorption of Methylene Blue (*a*) and Acid Orange (*b*) by precipitated BaS^*O_4 of varying specific activity: 1) inactive; 2) 0.01 mc g^{-1}; 3) 0.1 mc g^{-1}; 4) 1 mc g^{-1}; 5) 4 mc g^{-1}; 6) 10 mc g^{-1}.

of methanol on a $K_2S^*O_4$ specimen of specific activity 17.2 mc g^{-1} is 20% higher than on an inactive specimen. A $K_2S^*O_4$ specimen of specific activity 0.08 mc g^{-1}, which had been allowed to decay during 473 days, had an adsorption capacity 40% higher than an inactive sample.

Radioactive BaS^*O_4 was found[70] to have a much higher adsorption capacity towards n-hexane, benzene, and other vapours, than inactive specimens. The BaS^*O_4 was prepared by precipitation from solutions of $BaCl_2$ and $Na_2S^*O_4$, the latter containing varying proportions of ^{35}S. Specimens having an initial specific activity of ~85–100 mc g^{-1} were obtained. These were stored for various times, and degassed at 200°, before the adsorption measurements.

The main outcome of this work was the failure to observe a "build-up" effect, repeatedly detected in previous work. The adsorption measurements could be duplicated exactly after storage of the adsorbent for two months.

These effects are ascribed to the formation of a non-uniformly active adsorbing surface by incorporation of $Na_2S^*O_4$ during preparation of the BaS^*O_4, rather than to modification of the specimen surface by the subsequent radioactive decay.

Balandin, Spitsyn, and their coworkers[71–74] first observed an effect due to "internal" radioactive radiation on the catalytic properties of solids when studying the dehydration of cyclohexanol on MgS^*O_4. Atoms of ^{35}S and ^{45}Ca, introduced as $Na_2S^*O_4$ and Ca^*Cl_2 respectively during preparation of the material, were used as sources of internal β-radiation. Control specimens were prepared with identical admixtures of inactive Na_2SO_4 and $CaCl_2$. The reaction was studied between 350° and 420°, the percentage dehydration of cyclohexanol being used as a measure of the catalytic activity.

Pure $MgSO_4$ was found to have the highest catalytic activity (significantly decreased by additions of inactive Na_2SO_4 or $CaCl_2$). Radioactive $Na_2S^*O_4$ and Ca^*Cl_2 do not themselves catalyse the reaction, but appreciably increase the extent of dehydration when added to $MgSO_4$. Clearly, the action of radiation on the $MgSO_4$ has an important effect on the catalytic process.

Apparent activation energies were calculated, and found to be somewhat lower for the radioactive specimens.

The authors' curves for the increase in percentage conversion of cyclohexanol, Δ, as a function of the specific activity and of the dose rate of self-irradiation of the

MgS^*O_4 (Fig. 13) have some interesting features. Curve *2* of Fig. 13*a* is reversible: the spontaneous decay of radioactivity upon storage is accompanied by a proportional fall in Δ. It follows that "build-up" of the catalytic effect of radiation does not occur in this system.

The difference between curves *1* and *2* of Fig. 13 is thought to arise from the difference in β-energy of ^{35}S (E_{max} = = 0.167 MeV) and ^{45}Ca (E_{max} = 0.254 MeV), and hence to involve secondary radiation effects on the catalyst.

Irradiation of the catalyst, during the reaction, with a beam of 800 keV electrons had no effect whatever on the extent of conversion.

A paper by Krohn and Smith[75] should be considered in conjunction with the work just discussed[71–74]. These workers studied the effect of X-rays on the dehydration of cyclohexanol (catalysed by $MgSO_4$ and $MgSO_4$–4% Na_2SO_4) using dose rates of 113 and 123 rad min^{-1}, but failed to observe any changes in catalytic properties.

Krohn and Smith point out that X-radiation produces high-energy electrons in the bulk of the material, and should therefore be equivalent to radiation from previously incorporated ^{35}S atoms. They calculate that their X-ray treatment should produce an effect at least equal to that of a specific radioactivity of 14 mc g^{-1}. Yet, this level of activity in MgS^*O_4 catalysts had been found[74] almost to double the rate of reaction, whereas X-rays had no effect on the catalytic properties of $MgSO_4$. Krohn and Smith conclude that the effects reported by the Soviet workers[74] are due to the conversion of ^{35}S into ^{35}Cl, and not to electron emission.

It should be noted that Spitsyn *et al.* have themselves published some results[57] which contradict their other findings[73]: the isotope ^{144}Ce, when introduced into Al_2O_3, had practically no effect on its catalytic activity towards the dehydration of n-decanol, whereas external electron irradiation had given a large positive effect. On the other hand, the isotope ^{45}Ca had sharply increased[58] the catalytic activity of Al_2O_3 with respect to the dehydration of n-dodecanol, the effect being suppressed by electron irradiation (energy 800 keV, dose 10^{20} eV g^{-1}) during the reaction. Thus, the effect of internal radioactive radiation on the surface properties of solids is seen to be highly specific.

A paper by Spitsyn *et al.*[76] should be mentioned in this context. These workers made a special electron-microscopic study of the effect of radioactive radiation on the surface structure of various solids, including $K_2S^*O_4$, MgS^*O_4, BaS^*O_4, and Mo^*O_3. The solids were examined in the inactive condition, as well as at various levels of specific activity. Inactive specimens had a much less developed surface than the radioactive ones, even when the latter were examined immediately after preparation. This confirms the authors' conclusion[70] reached independently that radioactive radiation affects the formation of the surface during specimen preparation by crystallisation. The subsequent effect of radiation on the crystal lattice of the solid must, of course, also be considered. The authors point out that this conclusion is confirmed by measurements on inactive K_2SO_4, irradiated by an external electron beam: in spite of a higher dose of radiation, the surface development in this material was less than in the radioactive specimens.

We conclude this section by discussing two interesting papers[77,78] on the effect of internal radioactive radiation upon semiconductor catalysts. The isotopes introduced into the specimens in this work (^6Li and ^{10}B) were not themselves radioactive, but they gave α emitters when irradiated by thermal neutrons because they present a very large cross-section to the (n, α) reaction.

The paper by Sayto *et al.*[77] describes the decomposition of nitric oxide on NiO, SnO_2, and Al_2O_3. The SnO_2 and Al_2O_3 catalysts contained additions of B_2O_3 (10%) and Li_2O (10%); the NiO contained 10% B_2O_3 and 1% Li_2O. The preparations were heated for 2.5 h at 750° and exposed to a neutron flux of 10^{11} neutrons cm^{-2} sec^{-1} during 3 h. The catalytic measurements were made one month after irradiation.

Apparent activation energies and relative values of the frequency factor (Table 6) were calculated from the temperature dependence of the percentage decomposition of nitric oxide.

The slight negative effect (decrease in catalytic activity) observed with NiO, a *p*-type semiconductor, is thought to be due to a decrease in hole concentration, resulting from the removal of excess oxygen ions from their equilibrium sites under the influence of α-radiation. SnO_2, an *n*-type semiconductor, shows a fairly large positive effect, which is also explained by an increase in the number of donor levels of the oxygen vacancy type as a result of irradiation, leading to a higher concentration of electrons in the material. Lastly, the behaviour of Al_2O_3 is ascribed to the dielectric properties of this compound.

Braun and Maxim[78] studied the effect of pile irradiation on the catalytic activity of NiO doped with Li_2O (2.5 mole %) towards the oxidation of CO. The specimens were heated for 3 h at 850° and exposed to pile radiation (2×10^{11} thermal neutrons and 7×10^9 fast neutrons cm^{-2} sec^{-1}). However, the time of irradiation (over 150 h) was much longer

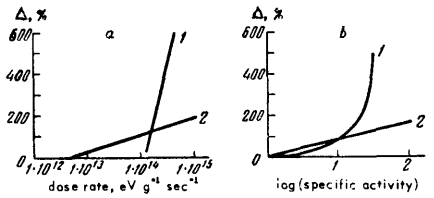


Fig. 13. Increase in the degree of conversion (Δ) of cyclohexanol with dose rate experienced by the catalyst (*a*) and with specific activity (mc g^{-1}) achieved (*b*): 1) $MgSO_4$ + + Ca^*Cl_2; 2) $MgSO_4$ + $Na_2S^*O_4$.

TABLE 6. Catalytic properties of NiO, SnO_2, and Al_2O_3, before and after irradiation, towards the decomposition of nitric oxide.

Catalyst	NiO				SnO_2				Al_2O_3			
	Li_2O		B_2O_3		Li_2O		B_2O_3		Li_2O		B_2O_3	
	before	after	before	after	before	after	before	after	before	after	before	after
Relative values of the frequency factor	1.7	1	1.1	1	1	2.9	1	2.5	1.6	1	1	2.5
Apparent activation energy, kcal $mole^{-1}$	22	23	19	19	21	20	43	20	23	23	23	24

than in the previous work[77], so that the effect of the reaction $^6Li(n, \alpha)^3H$ was to some extent masked by the normal effect of external neutron irradiation. An increase in the catalytic activity of NiO towards the oxidation of CO was observed (Fig. 14).

---o0o---

In spite of the wealth and diversity of our fund of factual information concerning the influence of irradiation upon the adsorption and catalytic properties of non-metallic solids, a unified description and a quantitative interpretation of these phenomena are still awaited. This is not surprising, in view of the complexity of adsorption and catalytic systems, and of the inadequacy of our understanding of radiation defects.

However, the experimental papers discussed here (and also in recent review articles[30-32,79,80]) give the impression that most workers prefer to rely on electronic concepts to explain the observed effects§. The electronic nature of these phenomena is most strikingly demonstrated by the correlation between changes in adsorption and catalytic properties, on the one hand, and electrical, optical, magnetic, and other solid state properties on the other. Thus, a successful interpretation of these phenomena must, in all probability, involve a synthesis of modern theoretical concepts on the effects of radiation on solids[1] and of the electronic theory of chemisorption and catalysis[81].

Vol'kenshtein[82] has taken the first step in this direction by formulating the problem of radiation effects on the adsorption and catalytic properties of semiconductors in terms of the electronic theory of solids, and giving a possible mechanism for the effect.

The electronic theory teaches that surface electrons and holes, either free or localised on surface defects, are responsible for the adsorption and catalytic properties of solids. The equilibrium concentrations of these charge carriers are defined by the position of the Fermi level at the surface, which itself depends on the position of the bulk Fermi level. Clearly, any radiation effect which alters the position of the Fermi level in the specimen can influence the adsorption and catalytic properties. As already stated, the main effects of radiation are ionisation, displacement of atoms (or ions), and nuclear transmutations in the crystal lattice of the solid.

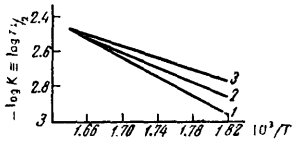


Fig. 14. Arrhenius plots for the catalytic oxidation of CO on (NiO + 2.5% Li_2O): 1) before irradiation; 2) 80 h pile irradiation; 3) a further 80 h irradiation.

Ionisation processes destroy the electronic equilibrium in the crystal and create non-equilibrium charge carriers both in the bulk and at the surface, thus significantly affecting the adsorption capacity and the catalytic activity of the material. Basically, this mechanism is the same as the photoadsorption and photocatalytic mechanism quantitatively analysed by Vol'kenshtein[82]. Changes in adsorption capacity, adsorption kinetics, and rate of catalytic reaction under the influence of ionising radiation are correlated, and it is shown that if the irradiation conditions are fixed, the magnitude and sign of the effect are a function of temperature and of the original position of the Fermi level. We should stress that the ionisation effect decays rapidly because of the short lifetimes of non-equilibrium charge carriers: in the absence of electron or hole trapping processes, the effect should be observable only during the irradiation period. This suggests an experimental test for distinguishing between this and other, more stable, effects.

The various lattice defects formed at the surface or in the bulk as a result of atomic or ionic displacements behave as electron donors or acceptors, and therefore cause the Fermi level to move in the appropriate direction, with a consequent effect on the surface properties of the crystal. Depending on what determined the initial adsorption capacity and catalytic activity of the crystal, the major effect could be due either to changes in the free carrier concentrations or to changes in the population of localised surface states. This mechanism accounts for more persistent changes in surface properties. "Annealing" of the defects involves diffusion and can only occur at high enough temperatures.

Nuclear transmutations produce chemically foreign species, which affect the surface properties by much the same mechanism. The only difference is that these changes are irreversible, and do not respond to "annealing".

Irradiation can produce electronic effects even when the bulk and the surface Fermi levels remain almost unaffected. This situation will arise in the presence of large concentrations of free carriers, as a result of mutual compensation of radiation defects, and for other reasons. When these defects reach the surface, however, they can give rise to new active sites from the point of view of adsorption and catalytis. The electron (or hole) occupancy of these states, and therefore also the efficiency of the mechanism, are determined by the original position of the Fermi level.

The efficiency of any mechanism involving lattice defects, it should be noted, depends on the concentration of defects produced and on the position of their energy levels in the energy band diagram of the semiconductor or dielectric. It is highly desirable, therefore, that adsorption and catalytic measurements should be accompanied by observations of the influence of radiation on other solid state properties, so as to characterise the resulting defects.

We have considered some general mechanisms which can be deduced directly from the effect of radiation on solids and from the electronic theory of adsorption and catalysis. Other effects of a more specialised nature can also be very important: charging of the specimen during

§ Some new experimental papers in general agreement with the views presented here have been published after the manuscript had passed the editorial stage. We shall not mention these individually, but refer the reader to the authoritative review by R. Covkelbergs, A. Cruck, and A. Frennet, Advances in Catalysis, 13, 55 (1962).

self-irradiation or external irradiation, for example, in which charge "leakage" is a significant factor.

Charge accumulation in the specimen can affect its adsorption and catalytic properties in various ways. One likely effect of charge accumulation is a shift in the Fermi level of the specimen, which then leads to the observed phenomena. Processes in which the solid acts as an energy moderator between the radiation and the reactant molecules in the gas phase or in solution can also be of importance.

Lastly, phenomena such as radiolysis of surface promoters or poisons, radiation polymerisation of organic substances, radiochemical reactions in the gas phase or in solution, etc., must be kept in mind, even though their influence has proved decisive only in a few concrete instances. As a rule, they play a secondary part, and tend to mask the major effects.

1. G. J. Diennes and G. H. Vineyard, "Radiation Effects in Solids" (Translated into Russian), Inostr. Lit., Moscow, 1960.
2. V. S. Vavilov, Uspekhi Fiz. Nauk, 75, 263 (1961).
3. M. V. Chukichev and V. S. Vavilov, Fiz. Tverdogo Tela, 3, 935 (1961).
4. I. D. Konozenko, V. I. Ust'yanov, and A. P. Galushka, Ukrain. Fiz. Zhur., 5, 276 (1960); Fiz. Tverdogo Tela, 3, 2629 (1961).
5. K. Lark-Horovitz, J. J. Harwood, H. H. Hausner, J. G. Morse and W. G. Rauch (Eds.) in "Effects of Radiation on Materials", New York, Reinhold, 1958 (Translated into Russian), Leningrad, 1961.
6. M. N. Haissinsky, "Yadernaya Khim" (Nuclear Chemistry), 1961.
7. "Tezisy Dokladov II Vsesoyuznogo Soveshchaniya po Radiatsionnoi Khimii" (Summaries of Papers Presented at the 2nd All-Union Conference on Radiation Chemistry), 1961.
8. B. M. Vul, Fiz. Tverdogo Tela, 3, 2264 (1961).
9. G. N. Galkin, Fiz. Tverdogo Tela, 3, 630 (1961).
10. N. A. Vitovskii, S. M. Ryvkin, T. V. Mashovets, and V. P. Sondievskii, Fiz. Tverdogo Tela, 3, 998 (1961).
11. S. M. Ryvkin and R. Yu. Khansevarov, Fiz. Tverdogo Tela, 3, 3219 (1961).
12. J. W. Clealand, J. H. Crawford, and D. K. Holmes, Bull. Amer. Phys. Soc., 11, 135 (1956).
13. F. Seitz, Rev. Mod. Phys., 26, 1 (1954).
14. J. H. O. Varley, Nature, 174, 886 (1954).
15. T. Ya. Sëra, V. V. Serdyuk, and I. M. Shevchenko, Fiz. Tverdogo Tela, 3, 3537 (1961).
16. J. W. Glenn, Uspekhi Fiz. Nauk, 60, 446 (1956) [Translated from Adv. Phys., 4, 381 (1955).
17. P. W. Levy, J. Chem. Phys., 23, 764 (1955); Phys. Rev., 123, 1226 (1961).
18. F. Seitz, in "The Effect of Radiation on Semiconductors and Insulators" (Translated into Russian), Inostr. Lit., Moscow, 1954.
19. H. A. Bethe and J. Ashkin (Editors), "Experimental Nuclear Physics" (Translated into Russian), Vol. 1, Inostr. Lit., Moscow, 1955.
20. G. H. Kinchin and R. S. Pease, Uspekhi Fiz. Nauk, 60, 590 (1956) [Translated from Reports Progr. Phys.], 18, 1 (1955).
21. G. Fan and K. Lark-Horovitz, "Problemy Sovremennoi Fiziki" (Problems in Modern Physics), Vol. 8, 1957, p. 156.
22. V. S. Vavilov, A. S. Smirnov, *et al.*, Zhur. Tekh. Fiz., 26, 1865 (1956).
23. M. V. Chukichev and V. S. Vavilov, Fiz. Tverdogo Tela, 3, 1522 (1961).
24. V. S. Vavilov and A. F. Plotnikov, Fiz. Tverdogo Tela, 3, 2455 (1961).
25. A. F. Plotnikov, V. S. Vavilov, and L. S. Smirnov, Fiz. Tverdogo Tela, 3, 3253 (1961).
26. B. M. Konokalenko, S. M. Ryvkun, and I. D. Yaroshetskii, Fiz. Tverdogo Tela, 4, 379 (1962).
27. R. Smoluchowski in "The Effects of Radiation on Materials", New York, 1958 (Translated into Russian), Leningrad, 1961.
28. E. W. Mitchell and E. G. S. Paige, Phil. Mag., 1, 1805 (1956).
29. R. A. Weeks, J. Appl. Phys., 27, 1376 (1956).
30. E. H. Taylor, J. Chem. Educ., 36, 396 (1959).
31. E. Taylor, H. Kohn, and G. E. Moore, in "Large Radiation Sources in Industry: Proceedings of a Conference on the Application of Large Radiation Sources in Industry and Especially to Chemical Processes, Warsaw, Sept. 8–12, 1959", Vol. 2, International Atomic Energy Authority, Vienna, 1960, p. 119.
32. M. N. Haissinsky, Jaderna energie, 7, 73 (1961).
33. T. J. Barry and R. Roberts, Nature, 184, 1061 (1959).
34. J. Gubokawa and O. Toyama, J. Phys. Chem., 60, 883 (1956).
35. N. P. Keier and G. I. Chizhikova, Dokl. Akad. Nauk SSSR, 120, 830 (1958).
36. E. H. Taylor and J. A. Wethington, J. Amer. Chem. Soc., 76, 971 (1954).
37. Yu. A. Mishchenko, G. K. Boreskov, V. B. Kazanskii, and G. B. Pariiskii, Kinetika i Kataliz, 2, 296 (1961).
38. T. V. Tsetskhladze and G. Sh. Kalandadze, Trudy Inst. Fiz. Gruzin. SSR, 6, 61 (1958–1959).
39. E. J. Gibson and R. W. Clarke, Nature, 180, 140 (1957).
40. D. M. Shub, V. P. Belokopytov, and V. I. Veselovskii, in "Tezisy Dokladov II Vsesoyuznogo Soveshchaniya po Radiatsionnoi Khimii" (Summaries of Papers Presented at the 2nd All-Union Conference on Radiation Chemistry), 1960.
41. H. W. Kohn and E. H. Taylor, J. Phys. Chem., 63, 966 (1959).
42. H. W. Kohn, Nature, 184, 630 (1959).
43. H. W. Kohn, J. Chem. Phys., 33, 1588 (1960).
44. E. H. Taylor and H. W. Kohn, J. Amer. Chem. Soc., 79, 252 (1957).
45. H. W. Kohn and E. H. Taylor, J. Phys. Chem., 63, 500 (1959).
46. V. B. Kazanskii and Yu. I. Pecherskaya, Zhur. Fiz. Khim., 34, 477 (1960) [Russ. J. Phys. Chem., 225 (1960)].
47. S. V. Starodubtsev, Sh. A. Ablyaev, and S. E. Ermatov, Dokl. Akad. Nauk SSSR, 129, 72 (1959).
48. M. M. Tagieva and V. F. Kiselev, Zhur. Fiz. Khim., 35, 1381 (1961) [Russ. J. Phys. Chem., 680 (1961)].
49. Yu. N. Molin and V. V. Voevodskii, Zhur. Tekh. Fiz., 28, 143 (1958).
50. Yu. A. Kolbanovskii, I. M. Kustanovich, L. S. Polak, and A. S. Shcherbakova, Dokl. Akad. Nauk SSSR, 129, 145 (1959).
51. M. Haissinsky and J. Siejka, J. Chim. phys., 56, 702 (1959).
52. J. Siejka and M. Haissinsky, J. Chim. phys., 57, 1090 (1960).
53. N. A. Balashova, Zhur. Fiz. Khim., 32, 10 (1958).
54. P. Weiss and E. Swegler, J. Chem. Phys., 23, 1568 (1955).
55. P. J. Lucchesi, D. L. Baeder, J. P. Longwell, and M. C. Schroeder, J. Chem. Phys., 31, 558 (1959).
56. P. J. Lucchesi, D. L. Baeder, and J. P. Longwell, J. Amer. Chem. Soc., 81, 3235 (1959).
57. V. I. Spitsyn, Ion Madsim [J. Maxim ?], G. N. Pirogova, I. E. Mikhailenko, and P. N. Kodochigov, Dokl. Akad. Nauk SSSR, 141, 1145 (1961).
58. V. I. Spitsyn, I. E. Mikhailenko, and G. N. Pirogova, Dokl. Akad. Nauk SSSR, 143, 1152 (1962).
59. D. Yang, Phys. and Chem. Solids, 15, 119 (1960).
60. V. V. Gromov and V. I. Spitsyn, Dokl. Akad. Nauk SSSR, 141, 891 (1961).
61. V. I. Spitsyn, I. E. Mikhailenko, I. V. Vereshchinskii, and P. Ya. Glazunov, Dokl. Akad. Nauk SSSR, 31, 360 (1960).
62. V. A. Gordeeva, E. V. Egorov, G. M. Zhabrova, B. M. Kadenatsi, M. Ya. Kushnerev, and S. Z. Roginskii, Dokl. Akad. Nauk SSSR, 136, 1364 (1961).

63. V.I. Spitsyn, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1296 (1958).
64. V.I. Spitsyn, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1325 (1960).
65. V.I. Spitsyn and I.E. Mikhailenko, Dokl. Akad. Nauk SSSR, 121, 319 (1958); Atomnaya Energiya, 5, 463 (1958).
66. V.I. Spitsyn and I.E. Mikhailenko, Dokl. Akad. Nauk SSSR, 131, 129 (1960).
67. V.I. Spitsyn and V.G. Finikov, Dokl. Akad. Nauk SSSR, 133, 1381 (1960).
68. V.I. Spitsyn and V.V. Gromov, Dokl. Akad. Nauk SSSR, 123, 722 (1958).
69. V.I. Spitsyn, I.E. Mikhailenko, A.V. Kiselev, and L.D. Belyakova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1311 (1960).
70. L.D. Belyakova, V.V. Gromov, A.V. Kiselev, and V.I. Spitsyn, Dokl. Akad. Nauk SSSR, 138, 1139 (1961).
71. A.A. Balandin, V.I. Spitsyn, N.P. Dobrosel'skaya, and I.E. Mikhailenko, Dokl. Akad. Nauk SSSR, 121, 495 (1958).
72. A.A. Balandin, V.I. Spitsyn, N.P. Dobrosel'skaya, and I.E. Mikhailenko, Dokl. Akad. Nauk SSSR, 137, 628 (1961).
73. A.A. Balandin, V.I. Spitsyn, N.P. Dobrosel'skaya, I.E. Mikhailenko, I.V. Vereshchinskii, and P.Ya. Glazunov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 565 (1961).
74. A.A. Balandin, V.I. Spitsyn, N.P. Dobrosel'skaya, I.V. Vereshchinskii, and P.Ya. Glazunov, Paper Presented at the 2nd International Congress on Catalysis, Paris, 1960.
75. N.A. Krohn and H.A. Smith, J. Phys. Chem., 65, 1919 (1961).
76. V.I. Spitsyn, L.I. Zemlyanova, I.E. Mikhailenko, V.V. Gromov, and I.E. Zimakov, Dokl. Akad. Nauk SSSR, 139, 1163 (1961).
77. Y. Sayto, Y. Yoneda, and S. Makishima, Nature, 183, 388 (1959).
78. T. Braun and J. Maxim, Nature, 192, 548 (1961).
79. M.N. Haissinsky, 2nd International Congress on Catalysis, Paris, 1960.
80. E.H. Taylor, Nucleonics, 20, 53 (1962).
81. F.F. Vol'kenshtein, "Elektronnaya Teoriya Kataliza na Poluprovodnikakh" (Electronic Theory of Catalysis on Semiconductors), 1960.
82. F.F. Vol'kenshtein, Kinetika i Kataliz, 2, 481 (1961); Discuss. Faraday Soc., 31, 209 (1961).

Institute of Physical Chemistry,
Academy of Sciences of the USSR

CHEMICAL CHANGES DURING β-DECAY PROCESSES

V. D. Nefedov, V. M. Zaitsev,
and M. A. Toropova

CONTENTS

I. Introduction 604

II. Factors determining the state of daughter atoms 605
1. Recoil during β-decay 605
2. Excitation and ionisation of an atom during β-decay 606
3. The emission of γ-quanta by the excited nuclei of daughter atoms and the phenomenon of internal conversion during β-decay 607

III. Processes developing in molecular systems during β-decay 608

IV. Experimental methods of studying chemical changes during β-decay processes 610

V. Review of experimental work 611
1. Inorganic systems 611
2. Organic systems 612
3. Organoelemental systems 614

I. INTRODUCTION

The study of the chemical consequences of nuclear transformations is one of the most interesting and at the same time one of the most complex fields of radiochemistry; it has been called the chemistry of hot and excited atoms[1-11]. Studies in this field are of considerable theoretical and practical interest for both radiochemistry and chemistry in general, since they make it possible to obtain important information on the characteristic features of the behaviour of atoms of elements existing in particular energy and charged states and in completely new and unusual experimental conditions. From the practical view point, the study of the behaviour of atoms produced in different kinds of nuclear process is of considerable importance for the concentration of radioactive isotopes, the separation of nuclear isomers, and the preparation of various labelled compounds.

The study of the chemical changes during β-decay processes has revealed new possibilities in studies of this type. The processes of the electron- and positron-decay of atoms have provided a new method of exciting and ionising molecules and an original source of positive and negative molecular ions of any degree of complexity and with different initial localisation of the charge and excitation. Such ions may be generated both in highly rarified (gaseous) and in condensed (liquid and solid) phases. This makes it possible to examine how their behaviour is influenced by effects associated with the possibility of transfer of excitation energy to the surrounding medium, reaction with this medium, and other processes. Comparison of the consequences of excitation produced by the β-decay of atoms with other forms of molecular excitation (electron collision, photoionisation) makes it possible to observe the characteristic features of the redistribution of the energy of the nuclear transformation between the emitted β-particle and the molecular system and also to study the ways in which the excitation energy is redistributed in the molecular ion.

Methods making use of the chemical effects accompanying β-transformations and based on the processes of stabilisation and breakdown of molecular ions make it possible to prepare compounds of the daughter element with the highest possible specific activity, extremely difficult to prepare by ordinary methods. These new methods may be particularly important for the preparation of compounds of typical radioactive elements such as polonium, francium, and astatine. Moreover, in recent years extremely simple and elegant methods have been developed for the separation of radioactive isotopes by making use of the phenomenon of chemical-bond rupture during β-decay.