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CURRENT PROBLEMS IN RESEARCH

Radiation Effects on the Reactivity of Solid Surfaces

Defects produced in solids by radiation fields can enter into chemical reactions on the surface.

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When ultraviolet or ionizing radiation interacts with solids, ionizations and excitations are produced. Each ionization results in the formation of a pair of charged species, an electron and a "hole." The electrons and holes migrate through the solid and either become trapped at lattice or surface defects or are lost by interactions (recombinations) which are the reverse of the original ionizations. Electrons, holes, and the species formed by the trapping processes are sometimes capable of interactions on the surface of the solid with molecules which are in the adsorbed phase. Molecules which are physically adsorbed can be converted to more strongly bound forms; chemisorbed molecules can be changed to more weakly bound forms; and adsorbed species can be made more or less active for interaction with molecules in the adjacent liquid or gas phase. Thus, the irradiation can lead to changes in the rate of adsorption and desorption, and in surface reactions such as those which bring about catalysis effects.

Radiation-induced ionizations can affect the surface chemical activity of some systems in another way. In certain cases (especially with ultraviolet irradiation) surface groups or adsorbed molecules are directly decomposed, with the electrons and holes produced in the solid phase playing a more or less unimportant role. Surface species which are active for adsorption or catalysis can be formed in this fashion.

In addition to the ionization effects described, some radiation fields (particularly those carrying "heavy" particles such as neutrons and alpha particles) are capable of causing atomic displacements and dislocations. Atoms or ions are displaced from their normal positions in the lattice or on the surface. The defects formed may be chemically active themselves, or, by introducing new traps, they may alter the roles of some of the charge carriers (*1*).

As might be expected from this complex array of possible fundamental processes, many different radiation effects on surface chemical properties have been observed. It will not be possible in this short space to give an account of even the major topics which have been studied in this field. It is considered that a more effective approach will be to give a fairly detailed account of a few systems which are representative of the theoretical and experimental problems encountered. Three topics have been picked for discussion: (i) radiation-induced adsorption and desorption of oxygen on zinc oxide, (ii) four related radiation-induced adsorption and catalysis effects on silica gel, and (iii) "internal" source effects on the high-temperature exchange between sulfates and a gas phase. The first two topics were chosen because they are better understood than most of those which have been investigated. The last topic was chosen because it is not well known and raises intriguing theoretical and experimental questions (*2*).

Several recent review papers (*3*) may be consulted for a more comprehensive account of the important papers published on other topics in this field.

Adsorption and Desorption of Oxygen on Zinc Oxide

Zinc oxide is an *n*-type semiconductor, the conduction electrons being supplied by ionization of excess, interstitial, zinc (*4*). The amount of excess zinc in a sample depends to a large extent on the sample preparation. Most of the zinc oxide samples used in the experiments described here were powders prepared by decomposing zinc carbonate or zinc oxalate. If the decomposition is carried out *in vacuo*, or if the sample is subsequently heated in hydrogen, the excess concentration of zinc may be higher than if the decomposition is carried out by heating in air.

Chemisorption of gases on zinc oxide has been studied rather thoroughly. The gas of particular interest in this discussion, oxygen, has been found to chemisorb in at least two different forms. One form is stable below about 200°C and was considered by Barry and Stone (*5*) likely to be O^-; the second form, probably O^{--}, is stable above about 300°C.

The zinc-oxide-oxygen system has probably been studied more often in radiation fields than any other system. A number of investigations have been carried out under different conditions of pressure, temperature, irradiation, and sample preparation and pretreatment. The complex pattern of behavior observed is represented in Figs. 1 to 5. It may be seen that both "radioadsorption" and "radiodesorption" were observed, and that one could be converted into the other with adjustment of the experimental conditions.

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Barry, Stone, and others (*5–8*) have developed a mechanism picture which accounts for the behavior shown in Figs. 1 to 5. The fundamental processes assumed to occur are the following.

1) Hole transfer to the surface, followed by hole reactions such as

$$p + O^- \rightarrow O\cdot \qquad (1)$$

$$p + O_2^- \rightarrow O_2\,(\text{adsorbed}) \qquad (2)$$

$$O\cdot + O^- \rightarrow O_2^- \qquad (3)$$

$$O_2^- \rightarrow O_2\,(\text{adsorbed}) + e^- \qquad (4)$$

$$O_2\,(\text{adsorbed}) \rightleftarrows O_2\ (\text{gas}) \qquad (5)$$

(p is positive hole species), which lead to desorption. Hole transfers, since they encounter no potential barrier, have low activation energies.

2) Electron transfer to the surface, followed by electron interactions such as

$$O_2\,(\text{gas}) \rightleftarrows O_2\,(\text{adsorbed}) \qquad (6)$$

$$e^- + O_2\,(\text{adsorbed}) \rightarrow O_2^- \qquad (7)$$

$$O_2^- \rightarrow O\cdot + O^- \qquad (8)$$

$$O\cdot + e^- \rightarrow O^- \qquad (9)$$

$$O_2^- + e^- \rightarrow 2O^- \qquad (10)$$

which lead to adsorption. If oxygen is adsorbed in ionic forms, a negative potential barrier is present and the electron transfer requires an activation energy.

3) Trapping of holes by interstitial zinc and by oxygen adsorbed as O^{--}, the hole-electron recombination rate thus being slowed and the electron concentration increased.

4) Migration of interstitial zinc toward the surface, due to forces presented by negative adsorbed oxygen species.

Thus, in general, an increase in the bulk or surface concentration of interstitial zinc increases the electron concentration in irradiated zinc oxide samples and contributes to radioadsorption effects through reactions such as reactions 6 to 10. The bulk interstitial zinc concentration may, for example, be increased by direct reduction or by vacuum preparation. The surface concentration may be increased by adsorbing ionic oxygen species.

In terms of these postulated processes, the variety of effects shown in Figs. 1 to 5 can be explained, as described briefly in Table 1.

Since the photoinduced desorption is accompanied by increases in conductivity (*9*, *10*), it apparently involves hole reactions such as reaction 2, or direct ionizations such as reaction 4. The gamma-induced desorption seems to be more complicated, however. Barry and Klier (*7*) found that desorption in a

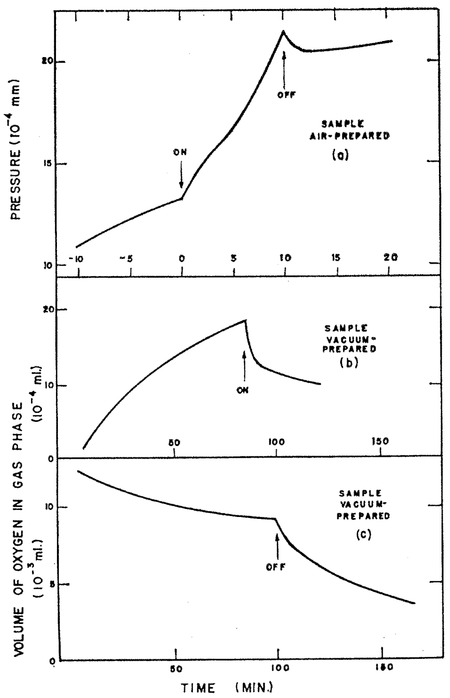


Fig. 1. Photo-induced oxygen adsorption and desorption effects on air-prepared and vacuum-prepared zinc oxide samples. Temperatures: (*a*) 25°C; (*b*) and (*c*) 22°C. Pressure ranges: (*b*) 10^{-4} to 10^{-3} mm-Hg; (*c*) 10^{-3} to 10^{-2} mm-Hg. "On" and "off" refer to the ultraviolet radiation source. [Barry and Stone (*5*)]

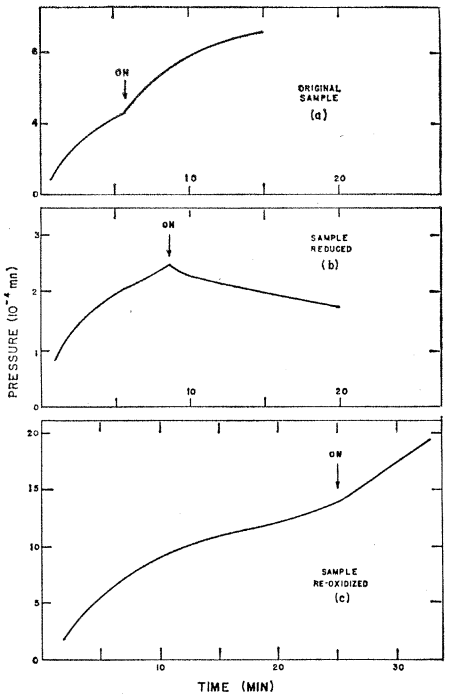


Fig. 2. Photoinduced oxygen adsorption and desorption effects on oxidized and reduced zinc oxide samples. (*a*) Air-prepared sample; (*b*) sample heated in hydrogen at 520°C; (*c*) sample heated in an oxidizing atmosphere at 520°C. "On" refers to the ultraviolet radiation source. [Barry and Stone (*5*)]

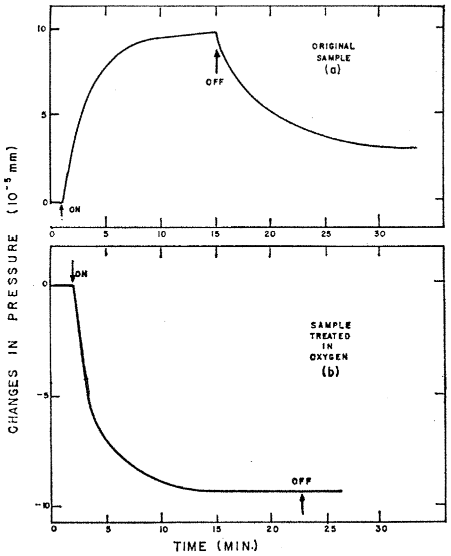


Fig. 3. Photoinduced oxygen adsorption and desorption effects. (*a*) Original sample; (*b*) same sample after treatment in oxygen at a pressure of 0.1 mm-Hg for 1 hour at 300°C. "On" and "off" refer to the ultraviolet radiation source. [Solonitzin (*32*), Fujita and Kwan (*33*)]

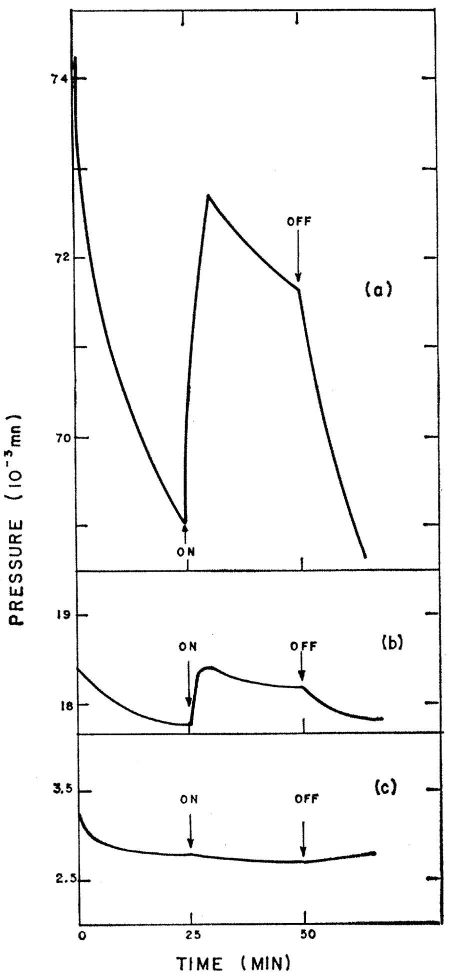


Fig. 4 (right). Photo-induced oxygen adsorption and desorption effects on air-prepared zinc oxide samples at room temperature. The effect of varying the oxygen pressure is shown. "On" and "off" refer to the ultraviolet radiation source. [Romero-Rossi and Stone (*8*)] gamma field on reduced samples at 0°C occurred only above a certain critical coverage, and that it was not accompanied by a change in conductivity. Also, above the critical coverage an appreciable fraction of the adsorbed material was found to be reversibly adsorbed. One postulate which explains these results assumes that more than one adsorbed species is involved, relatively weakly adsorbed nonionic species being connected with the radiation-induced desorption and the reversible adsorption (*7*).

Space does not permit discussion of the numerous other radiation-induced surface chemical effects which have been observed on zinc oxide. For a listing of most of the other pertinent papers, see bibliographical note 1.

Several Effects on Silica Gel

A number of different radiation-induced surface chemical effects have been observed on silica gel. Among the best known of these are the following: (i) enhancement of catalytic activity for the hydrogen-deuterium intermolecular exchange reaction, (ii) increase in the oxygen adsorption capacity, and (iii) increase in the hydrogen adsorption capacity. A fourth effect, the formation of various centers which give optical absorption, is not a surface chemical effect but will be shown to be closely related to the other three effects.

The experimental evidence seems to lead to several approximate propositions concerning these four phenomena. It is implied that the first and second effects are connected, that the third and fourth effects are connected, and that, to a large extent, the first and second are independent of the third and fourth. Brief descriptions of the evidence for various statements of these propositions are given in Table 2.

Other aspects of these phenomena have been observed by Kohn and Taylor (*11–13*). It was found that the observed properties decayed slowly with time elapsed after the irradiation; half-times of the order of days were usually observed. The effects described began to be important when threshold doses of 10^{18} to 10^{19} electron volts per gram were reached.

The simplest model to explain this pattern of behavior postulates only two categories of active sites: one category which can be identified with the radiation-enhanced hydrogen-deuterium exchange activity and the induced oxygen adsorption capacity, and another category which can be identified with the enhanced hydrogen adsorption capacity and the induced coloration. It is very likely that more detailed experimental investigations will require a more refined model involving a number of special types of active sites. But the simple classification provided here should form a basis for a more complex model. To simplify the description, the first category of sites will be called the *A* sites and the second category will be called the *B* sites.

We may now provide rather limited speculations on the fundamental nature of the *A* and *B* sites. Terenin and Solonitzin (*14*) have postulated that the sites responsible for the enhanced oxygen adsorption, activated either by ultraviolet illumination or by high-temperature degassing, are free valences formed when silanol groups decompose. Although little can be said concerning the exact nature of the interaction, it is implied that the sites leading to catalysis of the hydrogen-deuterium exchange are in some manner closely connected with these surface sites.

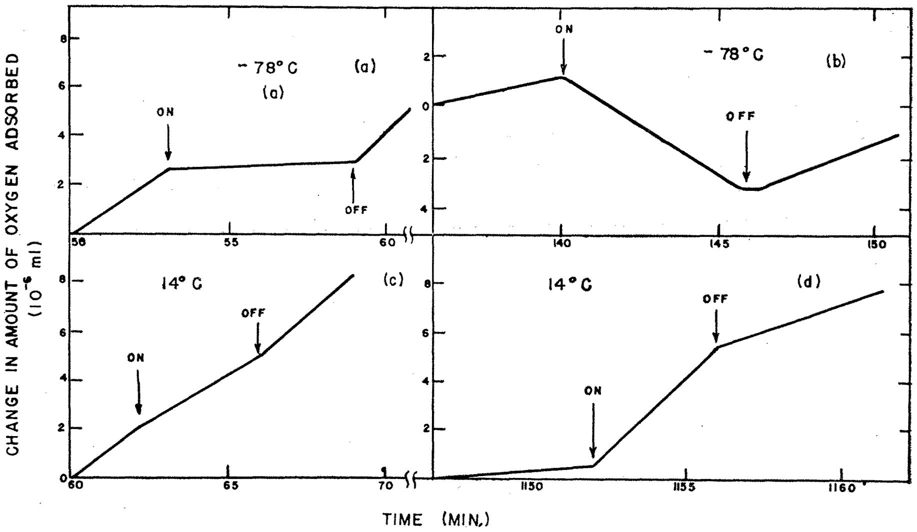


Fig. 5. Gamma-induced oxygen adsorption and desorption on vacuum-prepared zinc oxide samples. Pressures: 1.5 to 1.7 × 10^{-2} mm-Hq. Total volumes adsorbed: (*a*) 0.98 × 10^{-3} milliliters; (*b*) 1.04 × 10^{-3} milliliters; (*c*) 1.19 × 10^{-3} milliliters; (*d*) 1.38 × 10^{-3} milliliters. "On" and "off" designate the placing of the sample in and out of the gamma radiation field. [Barry (*6*)]

Table 1. Explanation of the effects shown in Figs. 1 to 5 (see text).

Observed effect	Explanation
Photoadsorption on vacuum-prepared samples; photodesorption on air-prepared samples (Fig. 1).	Vacuum-prepared samples have higher interstitial zinc concentration than air-prepared samples. Electron concentrations in irradiated vacuum-prepared samples are higher, and reactions 6 to 10 are favored (*5*).
Photoadsorption on a reduced sample and photodesorption on the same sample oxidized at 520°C (Fig. 2).	Reduction gives high interstitial zinc concentrations; oxidation at high temperatures removes interstitial zinc. Radiation-induced electron concentration in reduced samples is higher, and reactions 6 to 10 are favored (*5*).
Photodesorption on a sample and photoadsorption on the same sample after treatment in oxygen at 300°C (Fig. 3).	Treatment in oxygen at 300°C causes adsorption of ionic oxygen forms and concentration of interstitial zinc near the surface. Electron concentration in irradiated oxygen-treated samples is higher, and reactions 6 to 10 are favored (*5*).
Photoadsorption and desorption in the same experiment; decrease in photodesorption with decreasing oxygen pressure (Fig. 4).	Hole reactions leading to photodesorption decrease in importance as the oxygen coverage decreases (*8*).
Gamma-induced desorption at −78°C; at 14°C, small radiodesorption at low coverages, definite radioadsorption at higher coverages (Fig. 5).	Hole transfers leading to radiodesorption are favored at low temperatures, due to the low activation energy; radioadsorption is favored at higher temperatures and higher oxygen coverages, the latter giving rise to surface interstitial zinc (*6*).

Table 2. Brief descriptions of the evidence for propositions concerning four effects of radiation on silica gel (see text).

Conclusion	Evidence
The H_2–D_2 exchange and O_2 adsorption on irradiated silica gel are dependent.	(i) O_2 adsorption poisons the radiation-induced exchange activity (*11*). (ii) Both the O_2 adsorption (*30*) and the exchange (*31*) can be activated by high-temperature degassing. (iii) Both the O_2 adsorption (*14, 32*) and the exchange (*11*) are enhanced by ultraviolet illumination (whereas the H_2 adsorption and coloration are destroyed).
The H_2–D_2 exchange and O_2 adsorption on irradiated silica gel are independent of the radiation-induced coloration and H_2 absorption capacity.	Ultraviolet illumination enhances the exchange activity (*11*) and the O_2 adsorption capacity (*14*) but *destroys* the enhanced H_2 adsorption capacity and the induced coloration (*11*).
The radiation-induced H_2 adsorption capacity and coloration are dependent.	(i) Hydrogen adsorption bleaches the radiation-induced coloration (*11, 12*). (ii) Ultraviolet illumination destroys both the induced coloration and the enhanced H_2 adsorption capacity (*11*) (but enhances the exchange activity and O_2 adsorption capacity).
The radiation-induced O_2 adsorption capacity and induced coloration are independent.	Adsorption of O_2 on irradiated silica gel does not bleach the induced coloration (*11*).
The H_2–D_2 exchange on irradiated silica gel is independent of the radiation-induced coloration.	(i) Bleaching of the induced coloration by H_2 adsorption does not remove the induced exchange activity (*11*). (ii) Bleaching of the induced coloration by ultraviolet illumination does not remove the induced exchange activity (*11*).
H_2 adsorption and O_2 adsorption on irradiated silica gel are independent.	O_2 adsorbs on irradiated silica gel to which H_2 has been added, and vice versa (*11*).

Kazansky, Pariisky, and Voevodsky (*15*) have observed from gamma-irradiated silica gel a complex electron spin resonance (ESR) signal at room temperature which had a splitting factor (*g* factor) identical with that of diphenylpicrylhydrazyl, and interacted with oxygen to form what was evidently a peroxide radical. Kazansky *et al.* suggested that this surface radical might also have been the one responsible for the enhanced exchange activity. It is also possible that such sites could be formed in heat and ultraviolet treatments, and could be responsible for the radiation-enhanced oxygen adsorption.

Radiation-induced color center formation in quartz and other silica forms is well known and has been extensively studied (*16*). One particular optical absorption which is connected with the hydrogen adsorption centers gives a "magenta" color and appears to be similar to the broad band which has been observed at 500 to 600 millimicrons (*12*). Since such color centers are believed to be connected with electronic defects, a similar origin is suggested for the hydrogen adsorption sites. This conclusion is also suggested by the fact that the hydrogen adsorption can be annealed by ultraviolet illumination, a property commonly associated with color centers. Kohn and Taylor (*11, 12*) have pointed out the possibility that trapped holes form the magenta color centers and that the hydrogen adsorption occurs when these trapped holes interact with hydrogen on the surface. Consistent with this postulate is the observation by Kohn and Taylor (*11*) that radiation-induced hydrogen adsorption was enhanced by incorporating small amounts of aluminum, which probably acts as a hole trap (*17*), into the silica gel.

Room-temperature ESR signals which are indirectly related to the color-hydrogen-adsorption centers have been observed by Kohn (*18*) and by Kazansky, Pariisky, and Voevodsky (*15*). Kohn observed a signal from irradiated silica gel which (i) had a splitting factor $g = 2.0005 \pm 0.0005$; (ii) did not increase in intensity when the samples were doped with aluminum; (iii) had properties similar to a signal observed by Weeks and Nelson (*19*) and considered by them to be due to an electron trapped at an oxygen vacancy; (iv) was destroyed by ultraviolet illumination; (v) was destroyed when oxygen was admitted to the samples; (vi) was not destroyed when hydrogen bleached the color centers; and (vii) did not develop unless the samples were degassed at 500°C or higher temperature. Kohn's data suggest that the trapped electron species which gives this ESR signal is distinct from the visible color centers and hydrogen adsorption centers, possibly because the latter are due to trapped holes instead of trapped electrons. Consistent with this picture are the facts that the signal did not increase in intensity with aluminum doping and that it was not destroyed when the color centers were bleached by hydrogen adsorption. The high-temperature degassing appears to be necessary to develop the oxygen-deficiency defects which act as electron traps. In Kohn's experiments these defects may have been formed near the surface, since the addition of oxygen removed the signal. Kazansky *et al.* (*15*) have observed what seems to be the same signal (splitting factor $g = 2.0006 \pm 0.0004$), but they found that it was stable in the presence of oxygen. Possibly in the latter work bulk oxygen-deficiency defects were formed.

Thus, the general picture emerges—that radiation induces certain centers (the *A* sites) which are active for oxygen adsorption and catalysis of the hydrogen-deuterium exchange, and certain distinctly different centers (the *B* sites) which cause optical absorption and hydrogen adsorption. The centers responsible for the ESR signal at $g = 2.0005$ seem to be closely related to the *B* sites. The *A* sites may possibly be formed by radiolysis of surface silanol groups, and the *B* sites may be the result of trapping of radiation-produced holes.

Hydrogen has interactions with both *A* and *B* sites—with the *A* sites leading to catalysis of the hydrogen-deuterium exchange, and with the *B* sites leading to most of the hydrogen adsorption. In fact, Kohn and Taylor (*11*) observed that a small amount of the hydrogen adsorption appeared to be weaker than the rest, and they considered the possibility that two different sites might have been involved. They also found that when deuterium was placed on irradiated silica gel, a small portion of it was exchangeable with gas phase hydrogen; the exchange rate may have been high enough to explain the intermolecular exchange catalysis. The fraction of the adsorbed hydrogen which exchanged was roughly of the same magnitude as the fraction which was weakly adsorbed.

The nature of the interaction between the hydrogen and the *A* sites is not clear—we merely recognize that it is different from the oxygen interaction—but it seems possible that some of the hydrogen involved may initially be adsorbed on the *B* sites. This would explain the otherwise unexpected observation that aluminum doping increases the exchange activity of both irradiated and unirradiated silica gel (*11*).

Once again space limitations require the omission of a complete account of relevant papers. For a listing of most of the further work which has been done on the surface chemical properties of irradiated silica gel, see bibliographical note 2.

Effects of "Internal" Radiation Sources

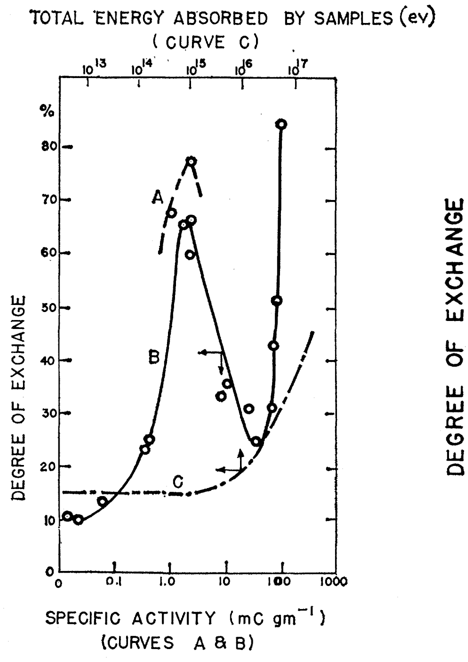
Work reported recently from the Soviet Union has indicated some extraordinary effects on the surfaces of solids containing radioactive isotopes. A variety of physical and chemical effects due to this "internal" radiation field has been reported, but the most remarkable results have been observed in certain high-temperature gas-solid exchange reactions and certain catalysis reactions.

In a series of papers beginning in 1956 (*20–25*) Spitsyn, Mikhailenko, Finikov, and others described a number of experiments in which it was shown that addition of the radioisotope sulfur-35 to alkali sulfates could greatly affect the high-temperature (600° to 1000°C) isotopic exchange rate between the solid sulfate and sulfur trioxide or oxygen in the gas phase. The relationship between the specific activity of sulfur-35 and the degree of exchange obtained (in 10 minutes in the case of sulfur exchange and in 7 hours in the case of oxygen exchange) is shown in Figs. 6 and 7. The most noteworthy features of these results are (i) that effects were obtained with very small specific activities and (ii) that the effect showed a maximum-minimum behavior with increasing dose. The behavior of the activation energies for the two types of exchange with increasing specific activity is shown in Fig. 8, the sulfur exchange showing a gradual decrease with increasing specific activity and the oxygen exchange showing a peculiar sharp minimum.

To determine whether the observed effects were due to direct radiolysis, Spitsyn *et al.* (*23*) carried out the sulfur exchange experiments in the electron beam of a betatron with a sulfate sample of low activity. Dose rates for the solid phase were adjusted so that they were comparable to the effective dose rates for samples containing sulfur-35. It was assumed that a specific activity of 2.3 millicuries per gram deposited 3.4×10^{15} electron volts in a 0.4-gram gas sample in 10 minutes (*26*). It may be seen from Fig. 6 that the external and the internal irradiations gave quite different results.

Several interesting facets of these phenomena can be developed if *G*-yields, or the number of reactions induced per 100 electron volts absorbed, are calculated. Since the samples with internal radiation sources absorbed energy from the time of their preparation, it is difficult to calculate precise *G*-yields, but in any case the ratio $\Delta W/y$, where ΔW is the radiation-induced change in the degree of exchange and y is the specific activity, should be proportional to the *G*-yield for the effect. Figure 9 shows $\Delta W/y$ plotted against y for the data of Mikhailenko and Spitsyn (*25*) on the sulfur exchange. It may be seen that $\Delta W/y$ changes rather abruptly from a higher value to a lower value in the specific activity range 1 to 5 millicuries per gram, and that the maximum-minimum behavior of the plot of $\Delta W/y$ against y used by Spitsyn *et al.* does not appear.

A range of possible magnitudes for the *G*-yields can be calculated on the assumption that all of the energy carried by the emitted beta particles is absorbed, and that the effective "irradiation time" lies between several hours (the time between sample preparation



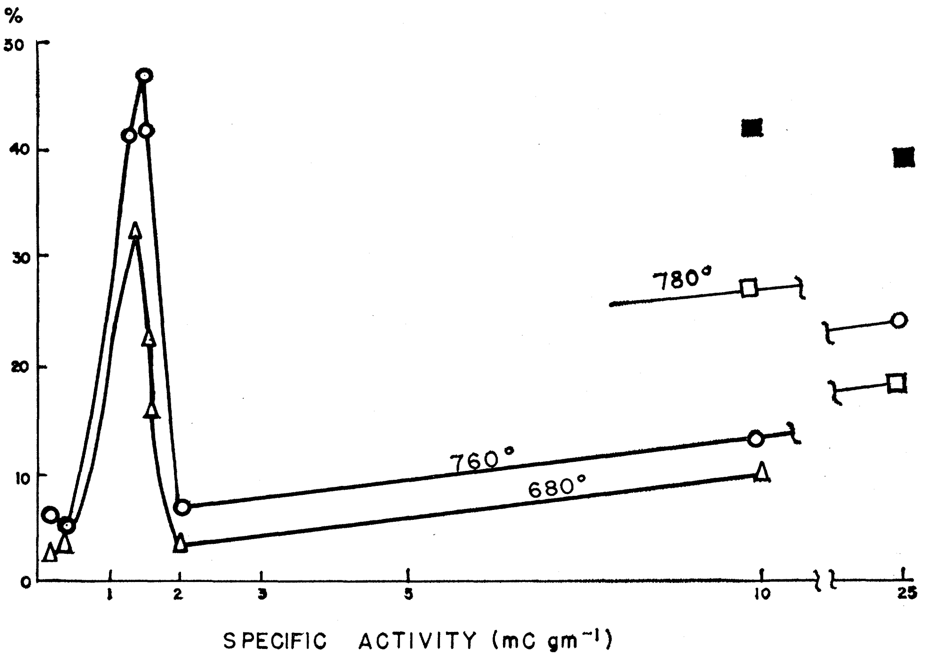
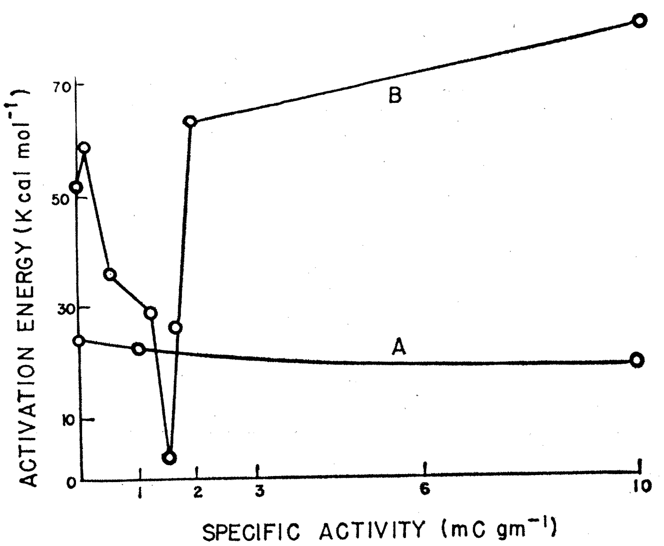


Fig. 6 (left). Relation between specific activity and the degree of exchange in the $K_2S^{35}O_4$–SO_3 system. Temperature, 840°C. (Curve *A*) Data taken after 93 to 270 days of aging; (curve *B*) data taken in normal runs; (curve *C*) data taken in external irradiations. [Spitsyn *et al.* (*23*, *25*)] Fig. 7 (right). Relation between specific activity and the degree of exchange in the $Na_2SO_4^{16}$–O_2^{18} system. (Open points) Data taken in normal runs; (closed points) data taken after 6 to 15 days of aging. [Spitsyn and Finikov (*22*)]



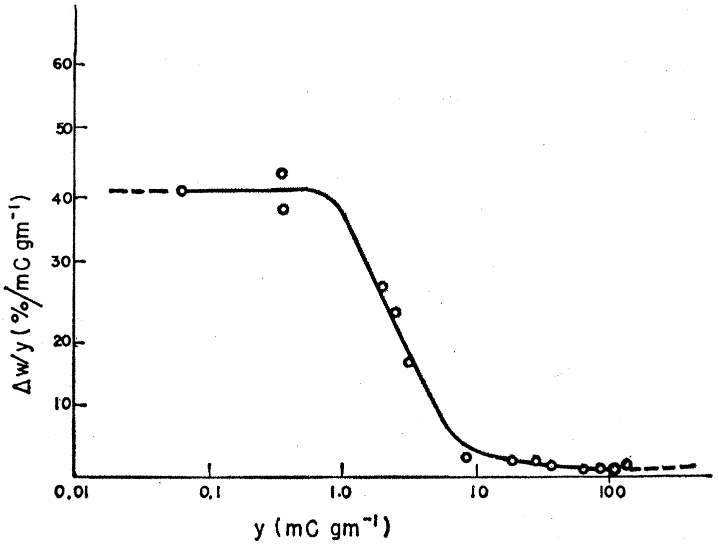


Fig. 8 (left). Relation between specific activity and activation energy in the system $Na_2S^{35}O_4$–SO_3 (curve *A*) and in the system $Na_2SO_4^{16}$–O_2^{18} (curve *B*). [Spitsyn *et al.* (*22, 25*)] Fig. 9 (right). Relation between $\Delta W/y$ (radiation-induced increase in specific activity) and y (specific activity) for data (*25*) on the system $K_2S^{35}O_4$–SO_3.

and the exchange measurement) and 10 minutes (the time of the exchange runs). For the samples with activity of 2.3 millicuries per gram, which gave 67 percent exchange (*25*), values in the range 10^6 to 10^8 per 100 electron volts absorbed are obtained. Since only about 1 to 10 primary-radiation-induced events are likely to occur for each 100 electron volts absorbed, these *G*-yields are extraordinarily high.

Thus, the effects observed by Spitsyn and his co-workers are marked by several peculiarities. Of particular interest are the differences between external and internal irradiations, and the very high *G*-yields.

The latter aspect can be crudely explained by assuming that the irradiation forms sites which are active for the exchange, and that these remain active for a large number of reactions of the normal thermal variety. Formally this mechanism could be treated in a manner somewhat similar to that used to describe the well-known chain mechanisms in homogeneous systems.

The difference between the external and internal irradiations implied by the data of Spitsyn *et al.* is not easily explained. Evidently, with specific activities below about 10 millicuries per gram, defects were induced by the internal sulfur-35 sources which could not be formed by the external betatron radiation source. Radiation-induced defects which would be formed in the former case but not in the latter can be described, but no likely candidate for the observed effect can be found among them. The more evident of the possibilities, together with the arguments which make it improbable that they are effective, are given below.

1) *Chlorine-35 impurities formed when sulfur-35 decays.* Impurity defects formed in this manner would occur in extremely low concentrations. A sample of activity 1 millicurie per gram would accumulate a chlorine concentration of only 3×10^{11} per gram in 2 hours of decay time. This is probably far below the level of other impurities. Mikhailenko and Spitsyn (*25*) have reported experiments in which 0.12 percent of potassium chloride was added to sulfate samples; no effect on the exchange rate was observed. When the chlorine-35 nucleus recoils after the decay it carries a maximum energy of only about 3 electron volts. Thus, the recoil nucleus could not cause much additional damage.

2) *Accumulation of positive surface charge when the emitted beta particles escape.* This possibility has been mentioned by Spitsyn (*21*). Here also the concentrations would be small. If all of the beta particles emitted by a sample of activity 1 millicurie per gram escaped, a surface charge of less than 2×10^7 per square centimeter would accumulate in 2 hours, if surface areas were greater than 1 square meter per gram. Surface charge concentrations required to affect such processes as adsorption are usually larger than 10^{12} per square centimeter. One charge per atom on the surface would give a concentration of the order of 10^{15} per square centimeter.

3) *Accumulation of charge by the trapping of carriers on the surface.* This might involve a charge displacement similar to that observed in irradiated insulators (see, for example, *27*). However, it may be deduced from the analysis of Proctor (*27*) that the field produced by radiation-induced charge displacement reaches a steady-state value rapidly unless the conductivity is very low. At the temperatures of the experiments described (600° to 1000°C), very low conductivities do not seem likely for ionic solids such as sulfates. Thus, the same electric field should be developed in the 10 minutes of external irradiation as in the longer periods of internal irradiation, and no difference between the two would be expected.

A more reasonable possible explanation is that the difference between the external and internal irradiations described by Spitsyn *et al.* was due to the fact that, although the two irradiations were carried out under equivalent dose rate conditions, *dose* conditions were not the same. Since the time elapsed between sample preparation and the exchange measurement (several hours) was effectively "irradiation time" in the internal irradiation, the time during which energy was absorbed was considerably greater than the 10-minute period of external exposure. Then, if the mechanism at low dose rates (or low specific activities) simply involves accumulation of a reactive species with increasing dose (for example, by direct radiolysis), the accumulated dose from the external source may have been insufficient to have given an observable effect. If it is further assumed that at higher dose rates the mechanism involves the removal, in addition to the formation, of the reactive species, the decrease in effective *G*-yield reflected in Fig. 9 is explained. This assumption also leads to the conclusion that at higher dose rates a steady-state concentration of reactive species, dependent mainly on the dose rate (or specific activity), will ultimately develop. That dose accumulation in the internal irradiations has an effect and that the dose rate is not the only important parameter are indicated by the fact that when the radioactive samples were aged the exchange enhancement increased (see Figs. 6 and 7), even though the specific activity decreased.

Perhaps similar mechanisms are involved in certain catalysis reactions. Balandin, Spitsyn, and others (*24*, *28*) have observed that sulfur-35 and calcium-45 activity in sulfates and phosphorus-32 activity in phosphates increased the catalytic activity of these compounds for certain reactions, and that in the former case external irradiations had no effect. The external irradiation has been carried out under more controlled conditions by Krohn and Smith (*29*), with the same result.

A number of other effects of internal sources have been observed by Spitsyn and his co-workers. For pertinent papers, see bibliographical note 3.

Bibliographical Notes

1. A brief listing of other papers on the surface chemical activity of irradiated zinc oxide is given here. In addition to the work described, Melnick (*10*), Medved (*9*), Terenin (*14*, *34*), and Solonitzin (*14*, *35*) have also investigated photoeffects on the zinc-oxide-oxygen system. Other gases studied include hydrogen (*7*, *14*) and carbon monoxide (*14*). A number of workers have reported "radiocatalysis" effects on zinc oxide. The catalytic activity of irradiated zinc oxide was found to be changed for the following reactions: ethylene hydrogenation (*29*, *31*, *36*), hydrogen-deuterium exchange (*31*), carbon monoxide oxidation (*8*), methanol synthesis (*37*), methanol decomposition (*38*), the O_2-36-O_2-32 intermolecular exchange (*5*), oxidation of water to H_2O_2 (*39*), the polymerization of isobutene (*40*), and the oxidation of isopropyl alcohol (*41*).
2. The following additional radiation-induced surface chemical effects on silica gel have been reported and studied: (i) enhancement of the rate of exchange between deuterium in the adsorbed phase and hydrogen in the gas phase (*11*); (ii) enhancement of the rate of exchange between deuterium in the solid phase (in silanol groups) and hydrogen in the gas phase (*42*); (iii) appearance of oxidizing and reducing properties on the surface (*11*); (iv) enhancement of the catalytic activity toward a number of reactions other than the hydrogen-deuterium exchange, including ethylene hydrogenation (*11*), the *o-p* hydrogen conversion (*43*), hexene double bond isomerization (*44*), butene-1 double bond isomerization (*45*), formic acid decomposition (*46*), and cyclohexene hydrogenation (*47*); (v) dynamic measurement of the radiation-induced enhancement of chemisorption of hydrogen and other gases (*48*); appearance of carbonium ions derived from adsorbed organic compounds (*49*).
3. In addition to the exchange and catalysis effects mentioned, a number of other effects on sulfates carrying S^{35} have been observed. Spitsyn, Torchenkova, and Glazkova (*50*) investigated the effect of S^{35} activity on the solubility and dissolution kinetics of $BaS^{35}O_4$. Spitsyn and Gromov (*51*) studied the effect of internal irradiation on the adsorption of organic dyes of $BaSO_4$ samples labeled with S^{35}. This work also included observation of the effect of an external pre-irradiation (*24*). The effect of CE^{144} activity on the solubility of $Ce_2 (C_2O_4)_3 \cdot 10\ H_2O$ was investigated by Spitsyn and Moshchanskaya (*52*). Spitsyn, Mikhailenko, Kisselev, and Belyakova (*53*) found that $K_2S^{35}O_4$ samples having specific activities around 20 millicuries per gram adsorbed appreciably more methanol vapor than nonradioactive samples.

References and Notes

1. Since the emphasis is on the solid phase, no consideration is given here to processes due to active species formed outside the solid—that is, in the surrounding liquid or gas phase.
2. I acknowledge with gratitude the support of the Atomic Energy Commission [contract AT(30–1)–2791]. I also thank the Royal Society for permission to reproduce Figs. 1 and 2, the Chemical Society of Japan for permission to reproduce Fig. 3, and Editions Technip for permission to reproduce Figs. 4 and 5.
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