

# INFLUENCE OF RADIATION ON REACTIVITY AND CATALYTIC ACTIVITY OF SOLIDS

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## INTRODUCTION

At the last symposium of this series, the fourth, there was for the first time a review of the effects of radiation upon the chemical reactivity of solids<sup>1</sup>. The timing was appropriate, since the field first began to show the effects of serious attention during the period between the third and fourth symposia. There had been some early suggestions and experiments<sup>2</sup>, but, naturally enough, the field lay dormant until radiation chemistry, solid state physics, and practical interest in radiation had reached reasonable stages of development. Now, four years later, there is more than enough material for a brief review, and there are radiation experiments bearing on several kinds of reactivity.

The basic idea in much of this work is that high-energy radiation can be used to introduce defects in a partly controllable way into solids, that these defects may influence various manifestations of reactivity, and that the altered reactivity can therefore be attributed to a specific entity in the solid. This attribution requires, of course, a knowledge of the defects produced, a knowledge sometimes available in advance, but sometimes requiring further experimental study. It would be well to remark here that knowledge of physical radiation damage is not so far ahead of that of reactivity that the flow of helpful information is unidirectional. Particularly with surfaces, conventional techniques do not provide wholly satisfactory information about defects, and we may anticipate mutually helpful interactions between adsorption, catalysis and other surface reactivity on the one hand, and radiation damage on the other.

## RADIATION DAMAGE

The description of the various types of defect produced by radiation seems to be fairly well in hand, although the characterization of specific defects in specific solids is a continuing activity. The largest amount of effort continues to be devoted to seeking quantitative understanding of the mechanisms of defect production. The state of that understanding until recently was such that damage calculated by displacement theory was frequently three- to ten-fold greater than that observed<sup>3</sup>.

Probably the most significant recent advance in this understanding has been the recognition of the influence of the crystal lattice on radiation

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damage, through the phenomena of focusing<sup>4</sup> and channelling<sup>5</sup>. The latter, the deep penetration of particles travelling along open directions in a crystal, has the possibility of resolving most of the remaining disagreement between observed and calculated lattice damage. A particle travelling down a channel loses much of its energy in small interactions, so that fewer displacements are produced than expected. Stochastic calculations<sup>5, 6</sup> like those of Vineyard on focusing<sup>7</sup> described four years ago<sup>1</sup> have been of particular significance, but experimental measurements of ranges<sup>8</sup> and observations of sputtering patterns<sup>9</sup> have helped to reveal the importance of directional properties.

In the characterization of specific point defects, electron spin resonance (ESR) continues to be, where applicable, the most powerful single tool available. The types of solid in which reactivity changes can most easily be studied are frequently suitable for the application of ESR.

Perhaps the greatest recent experimental advance in defect characterization is the increasingly effective use of electron and optical microscopy to observe such many-atom defects as bubbles, fission tracks and dislocations<sup>10</sup>.

### TYPES OF REACTIVITY

The various manifestations of reactivity of irradiated solids are shown schematically in *Figure 1*. The kind of reactivity observed in a given case depends fundamentally on the solid itself, but can be selected to a degree by establishing a particular environment, thermal as well as material, and by sometimes altering the environment appropriately between irradiation and observation.

If a solid is irradiated by itself and examined without any change in environment, then only self-reactivity, changes in the location and bonding of the constituent atoms, can be observed (Type I). If the solid is a metal, valence crystal or purely ionic crystal, changes in location of atoms do not usually represent permanent chemical change, since a displaced atom has the possibility of remaking the same kind of bond as was broken. The macroscopic effects of atomic rearrangements in such crystals are then primarily physical and can be classed as levelling or smoothing (Type IA) and phase transformation (Type IB).

If the solid is partly covalent, a molecular crystal or an ionic crystal with a covalently-bonded ion, then excitation of the bonding electrons (as well as atom displacement) can lead to bond rupture and radiolysis (Type IC). The situation is quite different from that in the previous cases, since the fragments do not find themselves in a position to remake equivalent bonds, but are surrounded by species with which they may react further. Sometimes reactive intermediates can be detected and their reactivity studied. Partly covalent solids are susceptible to thermal decomposition also, and this may be affected by radiation-produced defects, including products of radiolysis (Type ID).

If a solid is irradiated by itself and then exposed to a different environment, it may exhibit a reactivity toward the molecules of the environment, expressed as adsorption, and sometimes proceeding to catalysis or reaction (Type II).

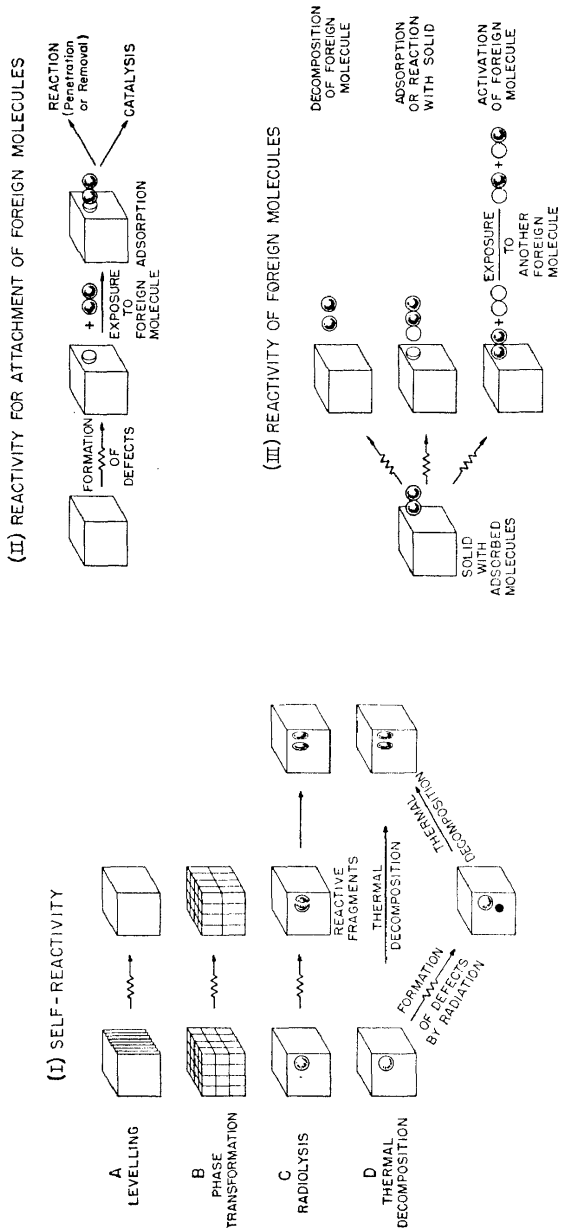


Figure 1. Types of reactivity

If a gaseous (or liquid) environment is present during irradiation of a solid (Type III), not only can shorter-lived reactivity of Type II be observed than if the gas is added afterwards, but the solid with adsorbed molecules may behave differently in its transformation of the radiation energy into reactivity. An adsorbed foreign molecule may be decomposed, in a kind of extension of Type IC; it or the solid may be activated to a stronger adsorption or to reaction; or, the foreign molecule may be activated for subsequent reaction with still another species.

Although the progression from self-reactivity to reactivity toward foreign molecules seems a logical arrangement, the phenomena involving adsorption are probably simpler, and are therefore discussed first.

## REACTIVITY TOWARD FOREIGN MOLECULES

### Adsorption

The simplest manifestation of induced reactivity in a solid is an enhanced adsorption. Naturally, this takes different forms depending on the adsorbate and on the temperature regime chosen, and can range from a small increase in the energy of physical adsorption over almost the whole surface, to a new, strong chemisorption at special sites. Already at the 1960 symposium, Dienes<sup>1</sup> referred to work of Young<sup>11</sup> showing that defects produced by reactor irradiation of alumina increased the site energies for krypton adsorption (originally 2400 to 3400 cal/mol) by 125 to 1500 cal/mol.

Experiments with another system<sup>12</sup>, nitrogen at low coverage on rutile ( $\text{TiO}_2$ ), showed a lowered reactivity following irradiation. A high dose of X-rays appeared to lower the adsorption energy of about 17 per cent of the sites (originally above 3000 cal/mol) by 1000–1500 cal/mol. This lowering of adsorption energy and a concomitant reduction in surface area were explained by a radiation-induced smoothing of the surface, as a consequence of which high-energy sites such as cracks are removed.

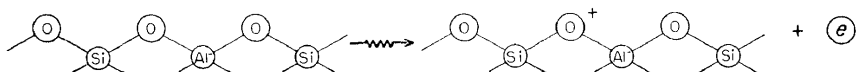
Altogether, what is known about radiation and physical adsorption shows two opposed trends. Enhanced diffusion resulting from radiation-produced point defects produces a smoothing of the solid surface<sup>13, 14</sup> and a loss of specially reactive sites associated with many-atom defects (cracks, ridges, peaks) (see also "Self-Reactivity", p. 417). On the other hand, some of the point defects produced by irradiation may persist, and these may have special reactivity even towards indifferent substrates. Either of these effects may predominate, as illustrated by the different behaviour of alumina and rutile, and one of the determining factors is no doubt the initial degree of perfection of the solid.

Behaviour nearer to conventional chemical reactivity can be observed by using a molecule capable of chemisorption, and several examples of modification of chemisorptive behaviour of solids by radiation are now available. A striking picture of such reactivity is presented by irradiated silica gel and hydrogen<sup>15</sup>. If ordinary silica gel is evacuated at 500° it is colourless and shows essentially no adsorption of hydrogen at room temperature. If it is irradiated with gamma rays at room temperature, still in vacuum, it acquires a pale magenta colour. If, now, excess hydrogen is

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admitted, the colour bleaches instantly, and some of the hydrogen is adsorbed. If, instead, the hydrogen is admitted in small doses, the pressure from each dose falls quickly to zero (on a thermistor gauge), and the colour bleaches little by little with each successive dose. When a dose finally removes the last of the colour, it (or the next dose) leaves a residual pressure, signalling the completion of the adsorption. Clearly, the colour centres participate directly in the adsorption, and probably are themselves the adsorption sites. This is a nearly ideal example of the use of radiation to understand a particular kind of reactivity. If one can identify the colour centre (and the colour makes it easy to follow), one will have a specific picture of the reactive entity in the solid.

The magenta centre has recently been shown<sup>16a</sup> by electron spin resonance and optical spectroscopy to be analogous to the purple colour centre in crystalline quartz. The latter is attributed<sup>16b</sup> to a positive hole trapped at an oxygen bound to an aluminium impurity (*Figure 2*). The centre in



*Figure 2. Radiation-produced colour centre in quartz  
(Reproduced after M. C. M. O'Brien and M. H. L. Pryce, ref. 16b)*

the gel probably differs only through the inherent disorder present in that form.

Very convincing evidence linking reactivity for adsorption to a different type of radiation-produced defect is given in the recent publication of Nelson and Tench<sup>17</sup> extending earlier work by Charman and Dell<sup>18</sup>. For nickel oxide and magnesium oxide, the latter showed that oxygen and hydrogen adsorption after neutron bombardment occurred at discrete sites that were probably vacancies and interstitials produced by the bombardment. The tentative identification with the defects themselves was based on the approximate equality of the induced fast chemisorption and the calculated number of defects produced. Since the results were nearly identical in substances of such different electronic properties, it appeared that such atomic defects as vacancies and interstitials were probably sufficient by themselves for chemisorption, regardless of the electronic nature of the matrix in which they were produced.

Nelson and Tench<sup>17</sup> combined observations of electronic spin resonance and of colour with adsorption of oxygen to make a closer assignment of the reactivity to a specific defect. They found that neutron irradiation of magnesium oxide in vacuum produced two types of centre. One (F) was shown by ESR to be identical with the previously identified centre<sup>19</sup> consisting of an electron in an oxygen-ion vacancy, analogous to the classical F-centres in alkali halides. The other (S, for "surface") gave a different ESR signal and a reddish-blue colour. This centre reacted with oxygen faster than oxygen diffused into the sample, as shown by a sharp line of colour demarcation when insufficient oxygen for total bleaching was

admitted. Excess oxygen (in air) bleached the colour and destroyed the S-resonance in a few seconds. This suggests a surface centre, perhaps an anion vacancy containing a trapped electron. The bleached portion of a sample still showed the F-centre resonance.

These bleaching (of spin and colour) experiments suggest that the fast, irreversible chemisorption of Charman and Dell is indeed occurring on the S-centres. The identification is made still stronger by the observation that the amount of oxygen necessary to bleach the centres is very close to that measured previously<sup>18</sup> as being chemisorbed in the fast process.

It was found also<sup>17</sup> that oxygen in excess of that required by the S-centres slowly destroyed the ESR signal of the F-centres, suggesting that the slower adsorption found by Charman and Dell<sup>18</sup> probably involved these. The slowness of the destruction and adsorption suggests that the defects are in the interior rather than on the surface, and that the limiting process is the transfer of an electron from a centre to an oxygen at the surface.

It was also found<sup>17</sup> that gamma rays produce S-centres but no F-centres in magnesium oxide. Hence oxygen ion vacancies do not exist in appreciable concentration in the bulk, but have to be produced by displacement. The production of S-centres means either that oxygen ion vacancies are initially present on the surface, or that displacement is enough easier on the surface (with one side of the atom not enclosed by neighbours) for the rather inefficient production of recoil by gammas to lead to detectable effects. It was noted that the slow chemisorption did not occur on the gamma-irradiated samples, in agreement with the absence of F-centres.

Experiments in which surface reactivity of irradiated solids is explored by measuring adsorption lead to the following general picture. Much of it has previously been drawn from other kinds of experiment, but in many cases the evidence from radiation experiments is more direct. The rather non-specific reactivity of solids toward inert molecules varies from place to place on a given solid as various structural features allow different numbers of surface atoms to interact with a visiting molecule. The presence of trapped charges alters the interaction, whether the visitor is on a perfect portion of the surface or at a defect. Whether radiation weakens physical adsorption by smoothing out gross defects, or whether it strengthens it by creation of point defects is a balance between processes, and depends strongly on the nature of the solid and its original degree of imperfection.

Reactivity toward less inert molecules can frequently be attributed to specific defects, such as surface vacancies, or impurities, and the electronic state of the defect may have a determining effect upon the adsorption reaction. Defects in the bulk solid may affect adsorptive reactivity by taking part in charge transfer with molecules at the surface. Some slow adsorptions may be limited in rate by this charge transfer, and the reversibility of adsorption may depend on whether the adsorbate can actually reach the atomic defect and annihilate it in the process of reaction (irreversible) or whether the defect is protected by being in the interior and able only to exchange electrons with the adsorbed molecule (reversible).

### Catalysis

There are also examples in which radiation-induced catalytic activity has

been tied to more or less well-identified sites. These include H<sub>2</sub>-D<sub>2</sub> exchange on MgO at V-centres by Lunsford and Leland<sup>20</sup>, formic acid decomposition at dislocations in silver by Sosnovsky<sup>21</sup>, and the hydrogenation of ethylene at Cu-H or Ni-H centres on copper and nickel by Schwab, Sizmann, Ritz and Todo<sup>22</sup>. However, since the most clear-cut examples available have been used in discussing adsorption, it may give a better perspective to discuss under catalysis some examples for which the interpretation is considerably more speculative.

An interesting observation that has been made with zinc oxide is the opposite effect of radiation upon two different but related reactions. For the hydrogenation of ethylene, radiation has a deleterious effect<sup>23</sup>; for H<sub>2</sub>-D<sub>2</sub> exchange it has the enhancing effect noted with most oxides<sup>24</sup>. This behaviour is a characteristic of the catalyst rather than of these two reactions in general, since both reactions are promoted by radiation on silica gel<sup>25</sup>. Evidence for the independent course of two reactions on one catalyst is of course not new or unusual, but it may ultimately prove valuable to have such an example in an area where assignment of activity to particular structural features is a good possibility. The enhancement for the isotopic exchange is easy to understand in general; one of the radiation-produced defects, perhaps one analogous to a V-centre, could be capable of binding H<sub>2</sub> in a suitably reactive way. Another possibility would be that a previously existing site (even an ordinary, non-defective one) would be so affected by the electronic readjustment to new trapping levels as to become suitable for the chemisorption and activation of H<sub>2</sub>. The difficult feature to explain is the decrease in activity for the hydrogenation. This can hardly be ascribed to an effect on the hydrogen; it is difficult to imagine an activation of H<sub>2</sub> for exchange that would not also activate it for hydrogenation, and even if this were somehow true, the effects are introduced at quite different rates. Deactivation of ZnO for hydrogenation takes days in a typical gamma source, while activation for exchange requires only hours. The logical assumption from this difference is that the two reactions take place at quite different sites, the exchange-activating one being produced relatively efficiently and the hydrogenation-spoiling one being introduced relatively inefficiently. The latter can hardly be the reaction site itself, but must affect it indirectly. The relative rates of destruction of hydrogenation activity by electromagnetic<sup>23</sup> and by heavy-particle radiation<sup>26</sup> give a clue to the kind of site involved. The low rate with gamma rays almost rules out a simple electronic defect, and the greater rate per unit dose with neutrons is only understandable if atomic displacement is involved.

Another kind of experiment with zinc oxide has to do with the H<sub>2</sub>-D<sub>2</sub> exchange activity<sup>24</sup>. Pure ZnO was 8 to 20 times as active (different for different preparations) after  $3 \times 10^{20}$  eV/g of gamma rays as before, while samples doped with 1 mol per cent of Na<sup>+</sup>, Cd<sup>2+</sup>, Al<sup>3+</sup> or Ga<sup>3+</sup> showed essentially no enhancement, the ratios of activity after irradiation to that before ranging only from 0.8 to 1.3. As a function of concentration of impurity (Al<sup>3+</sup>), the ratios were 10 for 0 mol per cent, 10 for 10<sup>-6</sup> per cent, 5 for 10<sup>-4</sup> per cent, 3.5 for 10<sup>-2</sup> per cent and 1.4 for 1 per cent.

A simple explanation of this unidirectional effect is that reasonable levels of impurities always outweigh radiation-produced species. The degree of

filling of electron or hole traps will be set preponderantly by the donor or acceptor properties of the impurities rather than by the production and differential trapping of holes and electrons during irradiation. Thus, even though the catalytic activity may be determined by the electronic state of a particular kind of atomic defect, the buffer action of the impurity may prevent a detectable radiation effect.

### Reaction with foreign molecules

Under suitable conditions, a foreign molecule adsorbed on a solid may not simply leave without change or with change only to itself, but it may either take with it part of the solid, as in the oxidation of carbon, or remain as part of a new solid phase, as in the oxidation of a metal. Either of these processes may be affected by prior irradiation, and, since such effects have practical implications for reactor materials, they have received considerable attention.

Graphite is markedly affected by reactor irradiation, not only in dimensions and other physical properties, but in chemical reactivity as well<sup>27</sup>. Recent electron-microscopical observations<sup>28</sup> of ultra-thin sections have shown conclusively that irradiation leads to a pitting attack by oxygen over the entire surface, in contrast to the behaviour of unirradiated samples which are attacked almost exclusively at grain boundaries. The radiation-induced pitting is believed to start at vacancies, because the edges of the lattice planes are more reactive than the surfaces, and a vacancy gives access to an edge. The oxidation proceeds across the layer from the vacancy until a vacancy in the second layer allows it to be attacked in the same way.

Similar phenomena can be shown where the attack on the solid is by an aqueous solution. Using a dislocation etchant and copper of low dislocation density, Young<sup>29</sup> showed that almost the whole surface of a neutron-irradiated copper crystal was pitted by the etchant, whereas, before irradiation, the only attack was at the relatively few dislocations. The reactive sites on the irradiated samples were attributed to small dislocation loops which form by coalescence of vacancies in irradiated copper<sup>30</sup>.

Radiation-produced defects may well enhance the other type of reaction, in which the foreign molecule is incorporated into a new solid phase, but it is not likely that the effect will be large except possibly in the initial stages of the process. When the new phase is established and moving into the solid, the movement of the phase boundary will be accompanied by a large concentration of defects which will usually swamp out the effects of radiation-produced ones.

### Activation of adsorbed molecules

The presence of an adsorbed layer during irradiation (Type III) may have a directing effect on the absorbed energy in one of the following ways: (i) highly efficient radiolysis of the adsorbate, in which energy absorbed by the solid is channelled to decomposition of the foreign molecules<sup>31</sup>; (ii) chemisorption or reaction with the solid<sup>32</sup>; or (iii) activation of the adsorbate for subsequent reaction with another species<sup>33</sup>. Because the short-lived reactivity involved in the first two of these is more in the province of radiation



chemistry than of solid reactivity, it will not be discussed further here, except to point out that the various kinds of reactivity have certain aspects in common, and that understanding of these short-lived kinds of reactivity may be advanced by findings with other types. There is too little information about the third possibility to discuss it now.

In some cases, induced catalytic activity (belonging to Type II) may be too short-lived to be observed after irradiation. However, if the solid is irradiated in the presence of the substrate, the short-lived enhancement may be observable. For example, certain samples of thoria showed no radiation-enhancement of  $H_2$ - $D_2$  exchange when tested after gamma irradiation<sup>24</sup>. The same samples showed a marked increase in activity if the test exchange was run during the irradiation. That this increase represented an enhanced catalytic exchange (Type II) rather than an enhanced radiolytic exchange (Type III) was indicated by experiments with more active examples which could be tested at  $-78^\circ$ , and which retained the enhancement so that it could be observed after the irradiation.

### SELF-REACTIVITY

There remain to be considered the kinds of reactivity that result from the irradiation and observation of a solid in chemical isolation. Typical chemical changes can occur with some solids (covalently-bound sub-units in an ionic or molecular lattice), but even with metals and valence crystals there is a kind of reactivity that, under irradiation, produces macroscopic changes. Real solids have a potential reactivity that results from imperfections. Point defects in excess of equilibrium are an obvious example, but the atoms of gross defects also have excess chemical potential. Many solids have alternative ways of binding the same atoms, and the tendency to transform into the stable phase represents a related kind of reactivity.

Several good examples now exist of a smoothing of macroscopic furrows, peaks and pits by radiation-induced transport of atoms. At the 1960 symposium, Riehl, Marth and Sizmann<sup>13</sup> showed electron micrographs of surface replicas of copper before and after heavy bombardment with alpha particles. These and later work<sup>34</sup> exhibited a marked levelling of the furrows (*ca.* 2000 Å deep) originally present. A similar effect revealed by a 20 to 50 per cent decrease in surface area was found for copper bombarded with 350 MeV protons<sup>14</sup>. In both cases, the transport of the requisite number of atoms could be explained by the enhancement of diffusion during the recombination of the large numbers of vacancies and interstitials produced near the surface.

Reduction in surface area on bombardment seems to be the rule with non-metals as well, since it has been observed for carbon<sup>35</sup>, silica and silica-alumina<sup>36</sup>, and titania<sup>12</sup>.

For phase transformation, diffusion is not always required, since only small rearrangements of atoms are necessary. However, in this case too, radiation can bring to realization the potential reactivity, as demonstrated so clearly in the transformation of white to grey tin<sup>37</sup>. The function of the radiation is thought to be the production of nuclei of the new phase from which the transformation can proceed.

A very short-lived reactivity toward phase transformation might be exhibited in thermal spikes, the small regions of very high temperature thought to be produced near the ends of the tracks of massive particles. Such minute, hot regions might nucleate a high-temperature phase of the material under study. A failure to observe such an effect<sup>38</sup> was already noted four years ago<sup>1</sup> in the case of the reverse transformation of tin, grey to white. More recently, a graphic example of the operation of such reactivity has been given in the transformation of a synthetic mica to forsterite, observed by electron microscopy<sup>39</sup>. Though more complicated than a transformation in an element, it seems to show directly the possibility of nucleation of a high-temperature phase by radiation. Straight, thin tracks from fission fragments could be seen in mica which had been irradiated with neutrons while in contact with a sputtered uranium film. When the mica was then annealed at about 780°, each track developed a rounded blob at each end. With further annealing, the blobs grew until they could be identified by electron diffraction as forsterite,  $Mg_2SiO_4$ , which is a normal high-temperature transformation product of the fluorphlogopite mica. With unirradiated material, no transformation could be detected below 890°.

With a solid consisting of some covalently-bonded molecules or ions in either a molecular or an ionic lattice, both high-energy radiation and thermal energy can produce chemical change. The reactivity exhibited by solids undergoing radiolysis is perhaps too short-lived to discuss here, but some reference should be made to it<sup>40</sup>, because it is possible in some cases to freeze-in radiation-produced reactivity and obtain a solid whose reactivity can be studied at leisure. Furthermore, the products of radiolysis may have an effect upon subsequent thermal decomposition of a solid, and a knowledge of their identities and concentrations is needed for understanding such an effect.

Low-temperature radiolysis is most often employed to obtain samples of intermediates for identification by ESR or optical spectroscopy, with the ultimate goal of explaining the ordinary radiolysis. In addition, however, such experiments serve a more general purpose, because they provide samples of reactive solids in which the reactivity can be associated with specific entities. In some cases, these reactive species cannot be obtained in other ways, and the trapping technique provides a unique opportunity to study the reactivity of a particular radical. More generally, such reactive entities can be used as probes to study the influence of the solid state upon the diffusion and reaction of a reactive species.

An example of this type is the work on atomic and molecular hydrogen yields in frozen acids by Livingston and Weinberger<sup>41</sup>. They measured the yield of atomic hydrogen by spin resonance at 77°K and the resulting molecular hydrogen yield by melting and gas analysis. The reactivity of the trapped hydrogen atoms was studied as a function of solid structure for sulphuric acid, of which two kinds, glassy and crystalline, could be obtained over a wide range of composition. With crystalline samples, the molecular yield was very close to the atomic yield, implying a high-efficiency, like-radical recombination, but with glassy samples the two were markedly different (*Figure 3*). Although the yields of hydrogen atoms (before melting) were different for the two types of sample, a circumstance which may reflect a difference in suitable trapping sites, the point of interest here is that a large

difference could be observed in the recombination reaction depending upon the nature of the solid. The wider study of solids with such radiation-introduced reactive probes should give useful information about the transport aspects of solid reactivity.

The covalent bonds which permit the radiolysis just considered can, of course, be broken by thermal activation, and the resulting decompositions

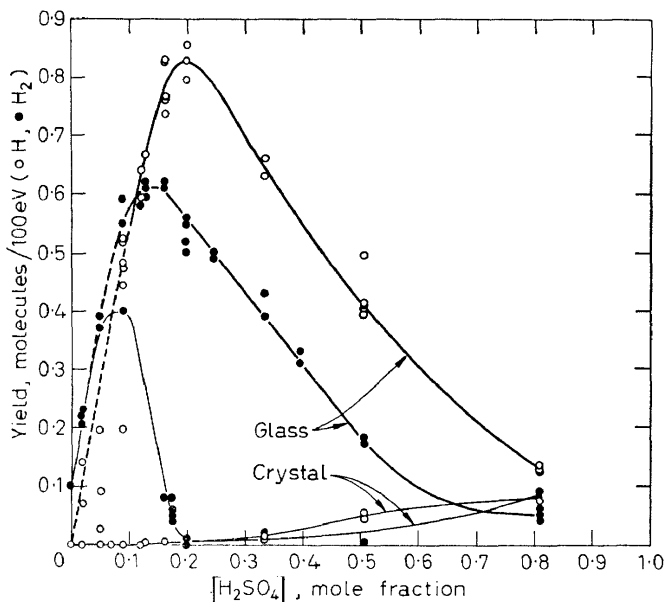


Figure 3. Effect of type of solid on recombination of hydrogen atoms in frozen H<sub>2</sub>SO<sub>4</sub>  
(Reproduced by courtesy of R. Livingston and A. J. Weinberger, ref. 41)

provide a significant fraction of the literature on solid reactivity. Among the factors which influence thermal decomposition is the presence of other species, which, viewed broadly, may include lattice defects as well as ordinary chemical substances. It is therefore to be expected that irradiation of a solid before measuring thermal decomposition might alter the decomposition, and that the introduction in this way of known defects or substances might help to clarify the thermal mechanism.

About as simple a process as may be imagined is the dehydration of a solid hydrate, in that the decomposition product is present in the starting material as a molecular entity. The usual course of such a reaction is nucleation at a surface, coalescence of nuclei to form islands of the new phase, and penetration of the interface into the crystal. Reactor irradiation was shown to affect even this simple process in manganous oxalate dihydrate as shown in Figure 4<sup>42</sup>. The almost immediate onset of decomposition at a constant rate is attributed to rapid establishment on heating of a constant-area interface from the many nuclei formed in the irradiation. The greater rate of penetration is thought to be the result of radiation damage in the interior.

Similar effects of irradiation and a generally similar interpretation are

found<sup>43</sup> in the decomposition of nickel oxalate to nickel and CO<sub>2</sub>, although the decomposition is obviously somewhat more complex.

After the stage of nucleation, one would not expect prior irradiation to have a large effect upon reactivity, because of the self-generation of defects during the movement of the phase boundary. Only when an appreciable fraction of the solid is damaged, enough essentially to change its bulk properties, would one expect to observe an altered reactivity in the post-nucleation stages. This is borne out for the nickel oxalate<sup>43</sup>, where irradiation

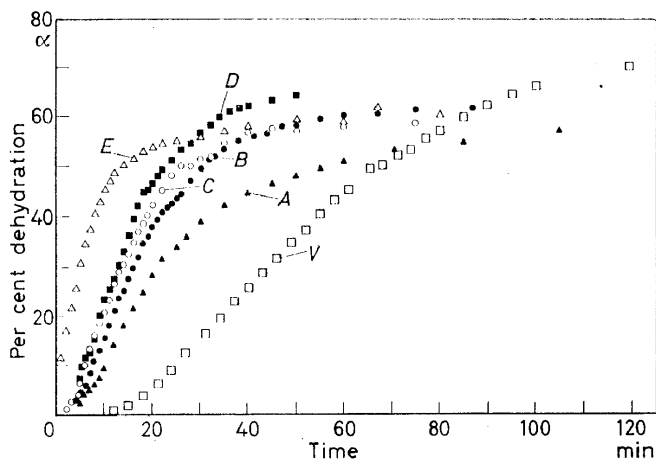


Figure 4. Effect of reactor-irradiation upon the dehydration of manganous oxalate dihydrate (75°, 0.15 mm helium): *V*: virgin sample; *A*:  $2.2 \times 10^8$  n cm<sup>-2</sup>; *B*:  $4.6 \times 10^8$  n cm<sup>-2</sup>; *C*:  $5.2 \times 10^8$  n cm<sup>-2</sup>; *D*:  $6.0 \times 10^8$  n cm<sup>-2</sup> (irradiated in air); *E*:  $9.8 \times 10^8$  n cm<sup>-2</sup> (Reproduced by courtesy of T. B. Flanagan and C. H. Kim, ref. 42)

tion has no effect on the maximum rate of decomposition. On the other hand, the maximum rate is greater for the irradiated material in the dehydration of manganous oxalate<sup>42</sup>; this may reflect greater damage in this case, arising from the large neutron capture cross section of manganese. With heavily damaged lead azide (20 per cent decomposed by radiation) the maximum rate was also greater than for unirradiated material<sup>44</sup>.

The interpretation of thermal decomposition reactions and the effect of radiation on them is complicated by the additional possibilities introduced by the decomposition products. A case in point is the decomposition of the alkali (and other) permanganates. Prout suggested<sup>45</sup> that the observed radiation-enhancement of the thermal decomposition of the potassium, barium and silver salts resulted from displacement of the cation. But a comparative study of the alkali permanganates (Li, K, Rb, Cs) by Boldyrev and Oblivantsev<sup>46</sup> showed that the effect of prior irradiation on the rate of thermal decomposition increased from lithium through caesium, in the reverse order of the sensitivity to cation displacement. For lithium, which, being lightest, should be most easily displaced, no effect of irradiation on the thermal rate was observed. These authors suggest that the important factor is catalysis of the thermal decomposition by radiolysis products, presumably

the manganese oxides, rather than by physical damage such as cation displacement.

## CONCLUSION

A number of kinds of reactivity are exhibited by irradiated solids, and in several cases the induced or altered reactivity has been attributed to a specific, radiation-produced defect. The use of radiation in this way to improve our knowledge of various kinds of reactivity is likely to be most successful for reactivity toward a foreign molecule, because in that case the defects can be studied under the simplest conditions. The solids of interest are usually simpler than those susceptible to radiolysis, and the production and characterization of the defects are done in the absence of foreign molecules. It is perhaps an exception to the usual perversity of nature that adsorption and catalysis, two of the types of reactivity in this class, are probably those of greatest general interest.

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