THE SZILARD-CHALMERS REACTION IN SOLIDS[1]

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I. Introduction

The chemical effect of a nuclear transformation was observed by Szilard and Chalmers (*78*) in 1934. They irradiated liquid ethyl iodide with neutrons and found that radioactive iodine could be extracted into water. The effect was attributed to the rupture of the carbon-iodine bond by the mechanical recoil imparted to the iodine nucleus by the incident neutron. Subsequently Fermi *et al.* (*1*) showed that the recoil energy given to the nucleus by the emission of gamma rays following thermal neutron capture was sufficient to break the bonds holding the capturing atom to the remainder of the molecule.

The chemical behavior of atoms which have undergone nuclear transformations is as yet imperfectly understood. Numerous investigations have shown that the radioisotope produced by thermal neutron irradiation of a compound in dilute solution or in the gas phase is usually obtained in a chemical form other than that of the capturing molecule. The mechanical recoil (*45*) imparted to the nucleus by the capture gamma rays, or the molecular excitation resulting from the internal conversion of the capture radiation must therefore be large enough to ensure the disruption of the chemical bonds holding the capturing atom to the remainder of the molecule in practically all neutron captures. However, when pure liquids or solids are irradiated, an appreciable fraction of the total activity is found in the parent compound. This activity presumably arises from a secondary reentry process.

The various theories proposed to explain the reentry process will be briefly considered.

A. ELASTIC-COLLISION OR BILLIARD-BALL MODEL

An elastic-collision model was proposed by Libby (*45*) and extended by Miller, Gryder, and Dodson (*57*). The essential feature of this model is that the recoil atom loses its energy predominantly in "billiard-ball" collisions with the atoms of the surrounding molecules. If sufficient energy is transferred to an atom in a given collision, the molecule containing the struck atom will dissociate into free radicals. If the recoil atom has a kinetic energy less than a critical amount after a collision, it will be trapped in a "reaction cage" and react with a radical trapped with it; otherwise it will escape from the cage. It is assumed that such processes return the radioactive atom to a nonseparable form.

While this model can qualitatively explain the retention[3] as the parent compound in the alkyl halides it cannot account for the formation of relatively large yields of radioactive products resulting from hydrogen substitution and carbon-carbon bond rupture. For if the recoil halogen atom can impart sufficient energy to a hydrogen atom to break the carbon-hydrogen bond in an elastic collision, the halogen atom should be left with sufficient energy after the collision to enable it to escape from the reaction cage. These considerations led Libby to modify the elastic-collision model.

B. ELASTIC-INELASTIC COLLISION MODEL

In the modification of the elastic-collision model Libby (*29*) still maintained that retention as the parent alkyl halide results from the replacement of an inactive halogen atom by the recoiling atom in an elastic collision as described above. This process occurs while the recoil atom is still moving with about 100 ev of kinetic energy and is called a "hot reaction." However, Libby now proposed that in a lower energy region the recoil atom can undergo inelastic collisions with the alkyl halide molecule as a whole, and this can lead to carbon-hydrogen and carbon-carbon bond rupture. Such inelastic processes are supposed to lead to the formation of products corresponding to hydrogen-substitution and synthesis. These processes are probable in the 10-ev energy region and are designated "epithermal reactions."

This model is unable to account for the distribution of radioactive products resulting from the reactions of recoil halogens in liquid hydrocarbon media (*56*). In these systems it is found that reactions leading to retention as the parent compound occur in an energy region below that leading to hydrogen substitution.

C. EPITHERMAL-REACTION MODEL

In order to explain the behavior of recoil chlorine atoms in liquid hydrocarbon media, Miller and Dodson (*56*) proposed that every recoil atom forms an excited intermediate complex with the hydrocarbon diluent, and that this complex then decomposes by a number of different paths, leading to the various radioactive products. They also showed that the concept of elastic atom-atom collisions could be entirely relinquished

[3] "Retention" is a term widely used in the literature to denote either qualitatively, the appearance of radioactive atoms in a particular molecular species, or quantitatively, the percentage of the radioactive atoms in such a species, or loosely, the sum total of all such combinations. Thus one speaks of "retention of iodine as ethyl iodide" or "organic retention of iodine in irradiated ethyl iodide." The latter means the sum of all the organic species containing iodine such as ethyl and methyl iodide, methylene iodide, etc.

in interpreting their results and instead they suggested a more familiar chemical approach. On this model the distribution of products is determined by competing chemical reactions in the epithermal region.

D. BRUSH-HEAP OR RANDOM-FRAGMENTATION MODEL

Willard (*82*) has also questioned the validity of the elastic-collision model. He points out that since the molecules in a condensed phase are not isolated, the assumption of elastic atom-atom collisions is not justified. On the random-fragmentation model (*82*) the recoil atom loses its energy by inelastic collisions with the surrounding molecules and breaks bonds in rather indiscriminate fashion. When its energy has been reduced below bond-breaking energies, it may combine either with the radicals in its immediate vicinity, or with radicals it encounters in the course of its diffusion in thermal equilibrium with the medium. While the appearance of a wide variety of radioactive products, as found in the alkyl halides (*28, 29, 43, 48, 68, 72*), lends support to this model, their distribution is generally not that expected from a random fragmentation of bonds.

E. HOT-ZONE MODEL

A model based upon the "displacement spike" concept of radiation damage in solids has recently been proposed by the authors (*37*). An essential feature of this model is that the energy of the recoil atom is dissipated in producing displaced atoms and in heating a small region of the crystal (the "displacement spike"). This hot zone eventually comprises about 1000 atoms which remain above the melting temperature of the crystal for about 10^{-11} sec; during this time chemical reactions have a reasonable chance of occurring. Such reactions probably do not have sufficient time to go to completion but are quenched by the cooling of the hot zone. Subsequent heating ("annealing") of the irradiated crystals may give these reactions an opportunity to proceed further, and these effects are generally termed "thermal-annealing reactions."

The main respects in which the hot-zone model differs from the other models previously described will be considered next.

The distance between successive collisions of the recoil atom on the hot-zone model depends upon the energy of the recoil atom. On the other hand the mean free path of the recoil atom on the billiard-ball model is independent of the recoil energy, and is of the order of atomic radii. Thus at 1000 ev the mean free path calculated on the hot-zone model is about ten times larger than that given by the billiard-ball model. The latter model accordingly gives a relatively higher temperature and longer relaxation time of the hot zone than that given by the authors' model. It has been pointed out (*89*) that the hot zone would reach such high temperatures on the billiard-ball model that extensive decomposition of polyatomic species would result.

The hot-zone model differs from the random-fragmentation model in an important respect. The random-fragmentation model is based upon free radical recombinations. The authors' model suggests that in view of the relatively low concentration of free radicals present in the hot zone, chemical reactions with the parent species may also play an important part. The picture may be further complicated by ion-molecule reactions (*71*).

The concept of chemical reactions during the lifetime of the hot zone, which is an important feature of the authors' model, is similar to the epithermal-reaction concept proposed for liquid systems by Miller and Dodson. However, the latter authors did not attempt to estimate such parameters as the size, temperature, and lifetime of the hot zone.

In the next section we will consider some recent results of Szilard-Chalmers studies against the background of the various models and in the third section we will treat annealing phenomena in some detail.

II. Chemical Effects of Nuclear Recoil

A. DIFFICULTIES IN THE INTERPRETATION OF EXPERIMENTS

Although hot-atom effects have been observed in many systems, most of these appear in isolated experiments, frequently for the sole purpose of preparing isotopes of high specific activity. Some few systems have, however, been rather more extensively investigated with a view to understanding the fundamental processes involved. For the purposes of this discussion, we shall consider two broad classes: ionic crystals and molecular crystals. The application of any model to predict accurately the hot-atom chemistry of a particular compound would require a detailed knowledge of such factors as capture gamma-ray spectra, internal conversion coefficients, bond energies, intermolecular forces, crystal structure, orientation and mobility of molecules, thermal diffusion coefficients, energy transfer mechanisms, activation energies and entropies, and will not be attempted here.

In interpreting the experimental results, a major difficulty arises. This is the question of the possible alteration of the original distribution of radioactive atoms among the various species present in the crystals by the particular method of analysis employed. This difficulty may be illustrated by considering potassium chromate. If chromium recoil leads to species such as $CrO_4^{=}$, CrO_3, CrO_2^{2+}, CrO^{4+}, and Cr^{6+} in the crystal (*31*), dissolution of the sample in water will result in the production of chromate by all but the last two, at least, since chromic anhydride and chromyl ion are known to hydrolyze to chromate (or dichromate) under all conditions of pH. However, one can only guess at the reactions of CrO^{4+} and Cr^{6+} in water. Similar problems of interpretation arise in the other oxyanions.

Attempts have been made by several investigators to limit these difficulties. In the arsenic (*52*) and antimony triphenyls (*33*), chromatographic separations were employed; in the cobaltic trisethylenediamine (*91*) experiments alternative fractionation methods were used, while in the cobalticyanide (*66*) and chloriridate (*22*) cases paper electrophoresis was found useful in separating a number of species produced by dissolution in various media. In the organic halides (*48*) and organic (carbon-14) compounds (*70*) carriers for many possible products were added and then fractionated. The same technique has recently been applied in studies of potassium periodate (*5*), in which iodide, iodate, and periodate fractions were separated. However, it is difficult to develop completely reliable analytical procedures; and, in general, inferences as to the original distribution of the radioactive species are drawn from the observed data and the assumed reactions during analysis of hypothetical entities present in the solid.

B. Ionic Crystals

If we consider under this classification the broad group of oxyanions, we find that there are certain general trends in the data (Table I). Although there are seen to be substantial differences among various metallic salts of a given anion (for example $KMnO_4$ and $NaMnO_4$), it appears that there is an inherent tendency of permanganate retentions to fall around 10%, chromates about 70-80%, iodates roughly the same, bromates about 10%, chlorates the same or lower, phosphates about 50-60%, perrhenate 100%, and arsenates fairly high. Where lower oxidation states of the same elements have been studied, it has been found that phosphites (*6*) and arsenites (*44*) produce predominantly the parent form with a little of the oxidized (17% and 10%, respectively) state, while rhenium alone shows a great tendency toward the production of oxidized recoils. However, recent experiments of Maddock and de Maine (*51*) on As_2O_3 and Sb_2O_3 showed that within experimental error none of the higher oxidation states was produced on recoil.

Libby (*44*) has proposed an explanation of these data. He suggests that the distribution of the bonding electrons between the recoiling atom and its attached oxygens will be the same as that normally existing in the covalent bond. Depending on the relative electronegativities of the capturing atom and oxygen, either oxygen atoms or oxide ions will be lost in the recoil. In the former case the oxidation number of the recoil-

TABLE I

RETENTIONS IN IRRADIATED CRYSTALLINE OXYANION COMPOUNDS

Compound	Recoil atom	Retention (%)	Reference
$LiMnO_4$	Mn^{56}	8.8	*47*
$NaMnO_4$		9.1	*47*
$KMnO_4$		22.5	*47*
$AgMnO_4$		8.0	*47*
$Ca(MnO_4)_2$		6.0	*47*
$Ba(MnO_4)_2$		12.8	*47*
Li_2CrO_4	Cr^{51}	66	*35*
$Li_2Cr_2O_7$		54.5	*35*
Na_2CrO_4		73.6	*35*
$Na_2Cr_2O_7$		79.9	*35*
K_2CrO_4		60.8	*35*
$K_2Cr_2O_7$		89.9	*35*
$K_2Cr_3O_{10}$		69	*36*
$(NH_4)_2CrO_4$		17.5	*35*
$(NH_4)_2Cr_2O_7$		31.9	*35*
$MgCrO_4$		55.3	*35*
$ZnCrO_4$		34.6	*35*
$LiIO_3$	I^{128}	66	*20*
$NaIO_3$		67	*20*
KIO_3		67	*20*
KIO_4		86IO_3^- 4IO_4^-	*5*
$KHIO_3$		53	*20*
HIO_3		60	*20*
NH_4IO_3		22	*20*
$NaBrO_3$	Br^{82}	10	*41*
$KBrO_3$		9	*21*
$RbBrO_3$		12	*41*
$CsBrO_3$		10	*41*
$NaClO_3$	Cl^{38}	1.5	*46*
$NaClO_3$	Cl^{34}	9	*46*
$KReO_4$	$Re^{186-188}$	100	*39*
$Na_4P_2O_7$	P^{32}	58	*6*
Na_2HPO_4		45	*6*
Na_3PO_4		50	*6*
H_3AsO_4	As^{76}	75-90	*76*
Na_2HAsO_4		60	*76*
Na_3AsO_3		90	*76*

ing atom will be lower than its value in the parent molecule, and a successful Szilard-Chalmers separation should be possible. When oxide ions are lost, a successful Szilard-Chalmers separation will be possible provided the recoil species are reduced by water more rapidly than they undergo hydration reactions.

These ideas have been extended by Green, Harbottle, and Maddock (*13*) to cases where oxide ions are lost. They supposed that the important reaction of the recoil species at the end of its track was the loss of one or more oxide ions, or conversely, incomplete readdition of oxide ions to the recoil atom. Then each partially-reconstituted species (for example, MnO_4^-, MnO_3^+, MnO_2^{+++}, etc.) will suffer either hydration (which will reconstitute the parent) or reduction on dissolution in water. The argument runs that the greater the oxidation potential of the parent anion, the sooner will a species be reached (through successive loss of oxide ions) which will inevitably oxidize water on dissolution, and consequently the lower the retention. This rough relationship is indicated by Fig. 1 in which typical retentions are plotted against oxidation potentials. One would predict from this that vanadates($E_0 \sim -1.0$ volt), selenates ($E_0 \sim -1.2$ volts) and sulfates ($E_0 \sim -0.2$ volt) would all have fairly high ($> 50\%$) retentions.

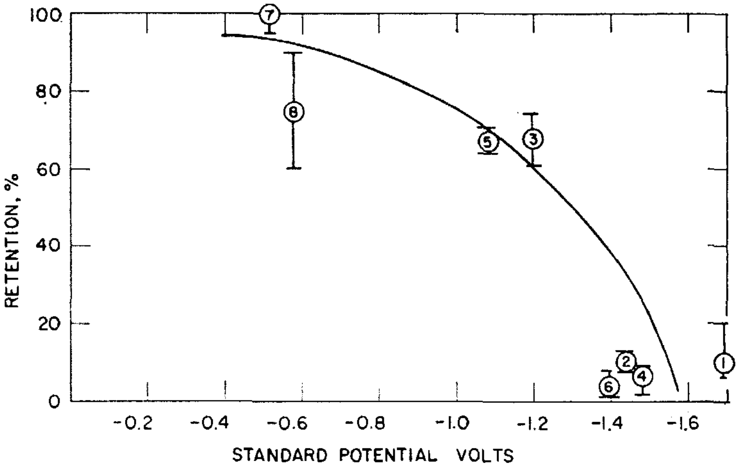

FIG. 1. Relation between retention in oxyanion salts and oxidation potential. Point 1, permanganates; 2, bromates; 3, chromates; 4, chlorate; 5, iodate; 6. periodate; 7, perrhenate; 8, arsenate

The foregoing considerations show that it is possible to explain many of the observations on the oxyanions in terms of recombination reactions between the recoil atom and oxygen atoms or ions produced in collisions.

Although the activation energy for the recombination of fragments is fairly low, the fragments may not be nearest neighbors and the activation energy for diffusion may be a few electron volts (*80*).

It is also possible that the recoil atom could gain one or more oxygens in an activated exchange with a neighboring oxyanion, during the lifetime of the hot zone. In the authors' paper cited above (*37*), equations were given which permit an order-of-magnitude calculation of the probability of this process. If one assumes an activation energy of 3 ev for oxygen transfer, in a hot zone of about 50 ev, the results indicate that oxygen transfer could occur several times before the hot zone cools down.

The theory that the oxygenated recoil species are formed in reactions between recoil atoms and surrounding oxyanions or dislodged oxygens is supported by the results of mixed crystal experiments. Mixed crystals (solid solutions) of potassium chromate in potassium sulfate (*35*) and fluoberyllate (*50*), and potassium permanganate in potassium perchlorate (*67*) have been investigated. The results are given in Table II. These data indicate that whereas recoil chromium in a sulfate crystal can find an oxyanion or debris oxide ions with which to react, producing a high retention, the same thing cannot happen in the fluoberyllate crystal. It is conceivable that the retention observed here (25%) indicates the probability that the recoil chromium does not move far enough away from its original site to avoid a short-term annealing in the hot zone. The thermal annealing of these mixed crystals, described by Maddock and de Maine (*50*), bears out this supposition, and these results will be discussed in Section III. One would predict that the activation of chromium in fluoberyllate crystals by fast neutrons would lead to still lower retentions, of the order of a few per cent, and much lower annealing rates. The increased permanganate retention in the mixed crystals

TABLE II

RETENTIONS IN MIXED CRYSTAL SYSTEMS

Recoil source	Diluent	Source molecule (Mole %)	Retention (%)	Reference
K_2CrO_4	K_2SO_4	2.77	69	*35*
K_2CrO_4	K_2SO_4	0.49	70	*35*
K_2CrO_4	K_2BeF_4	1.56	25	*35*
K_2CrO_4	K_2BeF_4	~1.	26	*50*
K_2CrO_4	None	100.	61	*35*
$KMnO_4$	$KClO_4$	40.	49	*67*
$KMnO_4$	$KClO_4$	1.	62	*67*
$KMnO_4$	None	100.	22	*67*

perhaps is due to oxidation of the recoil species in displacement spike reactions. According to the Libby hypothesis fragmentation of Cl-O bonds will liberate oxygen atoms while the Mn-O bonds will liberate oxide ions. In the mixed crystals the recoil species will find themselves in an environment of relatively higher oxidizing power. Similar considerations could account for the higher retention in chromate-sulfate mixed crystals. The results with chromate-sulfate and permanganate-perchlorate mixed crystals are in sharp disagreement with a billiard-ball model, which would predict the highest retention in the pure chromate or permanganate crystal.

The oxidation of the recoil species in the mixed crystals may be regarded as a specific chemical effect. Similarly, the anomalously low retentions observed in the two salts, ammonium iodate (22%) (*20*) and ammonium chromate (17.5%) (*35*) are in striking contrast with those of the corresponding alkali metals, and suggest that in the hot zone ammonium ion may act as a reducing agent, which the alkali metals cannot do because of their high ionization potential. There is also some evidence that water of crystallization may act as a reducing agent in the permanganate salts (*47*).

Oxidation reactions in the hot zone are probably responsible for the large yield of Cr(VI) obtained in the positron decay of Mn^{51} to Cr^{51} in crystals of cesium permanganate (*11*). Manganous ion in solution yielded only chromic ion, whereas in crystals of $MnCO_3$, 30% of the chromium recoils appeared as Cr(VI). This probably occurred as a result of reactions between chromium recoils and debris oxygen atoms or carbonate ions.

Further evidence of specific chemical effects in the hot zone appears in the work of Aten, who investigated the distribution of oxidation states of P^{32} formed by the n,p reaction in irradiated inorganic sulfur compounds (*3*). When he irradiated solid potassium sulfate or sodium sulfate decahydrate, only a few per cent of the recoils were in lower (nonphosphate) oxidation states. With sodium sulfite (hydrated) the percentage rose to about 50%, while for sodium sulfide 65% to 95% were in lower oxidation states. He found similar correlations when the P^{32} was produced by the Cl^{35} (n,α) process. Here, the irradiation of $KClO_3$ or $KClO_4$ produced 99% phosphate, while NaCl gave only 35%.

Within the category of ionic crystals, there are two similar complex ions of cobalt(III) which have been extensively studied: cobaltic trisethylenediamine nitrate (*91*) and potassium cobalticyanide (*66*). Both these crystals show fairly low inherent retentions (approximately 5% and 19%, respectively) and both give evidence of fragments having unfilled coordination spheres present after recoil. Both show typical thermal- and radiation-induced annealing reactions. In the cobaltic trisethylenediamine studies Zuber irradiated the dextrorotatory complex, added levorotatory carrier and then resolved the mixture by standard methods. He found that in the irradiated *d* crystal, of the 5% retention 4.5% was in the *d* form and only 0.5% in the *l* form. This extremely interesting result may indicate that the displacement spike zone remains hot long enough for the reconstituted molecule to assume the "correct" stereoisomeric configuration. The fact that such a decided preference is shown for the parent *d* form also sets a limit upon the amount of damage that could have been done in those displacement spikes which lead to retention. This observation is also consistent with a billiard-ball model, where one would expect that the original configuration would be preserved. It would be of great interest to repeat Zuber's experiment with the *d* complex, activating the cobalt with fast neutrons to produce Co^{58} recoils of high energy, giving larger displacement spikes.

Mention should be made of another type of recoil experiment with ionic crystals, namely the production of S^{35} and P^{32} in the neutron irradiation of alkali chlorides (*42, 13, 23*). Here the recoil atoms are generated through heavy-particle emission from the compound nucleus, and recoil energies are quite high (approximately 15 and 50 kev, respectively). The proportions of the different oxidation states of sulfur obtained are apparently not very reproducible and whereas one investigator has found the results to depend on pretreatment of the crystals [degassing (*42*)] another does not confirm this (*23*). The main difference between the two sets of experiments lay in the temperature at the irradiation site and the quality and intensity of the concomitant fast neutron and gamma radiation. The proportion of the different oxidation states of P^{32} formed in recoil in KCl also appeared to depend on degassing before bombardment. Here the effect of concomitant and subsequent ionizing radiation was examined and found to be very marked. In the light of recent observations on thermal and radiation annealing and the temperature dependence of the latter, it would be desirable to repeat these experiments.

Summarizing the observations on the ionic crystals it may be said that there is abundant evidence that reactions in the hot zone play an important part. Thus, any theory, such as the elastic-collision model which neglects specific chemical effects, e.g., reduction by NH_4^+ and H_2O, or oxidation by ClO_4^-, under the influence of the high local "temperature," cannot give a complete explanation of the data. In none of the studies of the hot-atom chemistry of a series of oxyanion salts, e.g., the permanganates, have correlations been established between the retention and crystal properties such as the density or atomic weight of the cation. These factors should have a marked effect on the efficiency of energy transfer in a billiard-ball process, and on the cage energy.

C. MOLECULAR CRYSTALS

Recent calculations of the authors (*37*) have shown that about 16 displacements will be produced in the slowing down process in molecular crystals, and that the volume raised above the melting temperature includes about 4000 atoms. A similar volume for the hot zone can be obtained from a consideration of the latent heat of fusion. For a recoil energy of 300 ev, and a bond energy of 4 ev, about 240 ev will be left for melting the crystal. Taking a latent heat of fusion of 0.1 ev, this corresponds to a final molten zone of about 2400 molecules.

The simplest molecular crystal which has been studied is sulfur. Nilsson investigated the distribution of P^{32}, P^{33} and S^{35} in neutron-irradiated sulfur (*61*). The first two isotopes are formed by *n,p* reactions and have energies of recoil of 45 and 15 kv, respectively. The third is formed by neutron capture and would have a much lower recoil energy, of the order of a hundred electron volts or possibly even smaller. Nilsson's results give the most direct evidence yet obtained for a molten-zone displacement spike surrounding high-energy recoils in molecular crystals, for he found that a large amount of the P^{32} and P^{33}, but hardly any S^{35} followed the insoluble $S\mu$ fraction of the sulfur samples on dissolving in carbon disulfide. Since the $S\mu$ modification of sulfur is formed by melting the orthorhombic crystals, these results are strong evidence for a molten displacement spike engendered by a high-energy recoil.

The molecular crystals which have been most extensively studied are those in which the recoil atom is initially organically bound, for example, the alkyl halides (*28, 30, 43, 48, 72*), and organometallic compounds such as ferrocene (*77*) and triphenylarsine (*52*). The complexity of the hot reactions in which several different types of radicals are present is well illustrated by the alkyl halides. Products corresponding to the isomerization, polymerization, substitution, and degradation of the parent alkyl radical are formed in good yield. For example, the recent work of Evans and Willard (*26*), in which gas chromatographic techniques were used to separate the various radioactive products, has shown that no less than 16 different species containing radioactive bromine are present following neutron irradiation of *n*-propyl bromide. Although this particular work was concerned with a liquid phase, other experiments have shown that recoil reactions in solid alkyl halides are equally complex (*48*).

A recent investigation of the radiolysis of alkyl iodides in the crystalline and glassy states has revealed differences in the yields of products which were ascribed to the differing orientation of the molecules in the two states (*40*). Such effects are included in the hot-zone model through an entropy of activation term in the calculation of reaction probability. Similar differences have been found in the Szilard-Chalmers reaction in glassy and crystalline propyl bromide (*68*).

A comparison of the results of investigations on alkyl halides and organo-metallic compounds suggests that the yield of radioactive parent compound obtained in Szilard-Chalmers investigations may be related to the extent of covalent bonding of the capturing atom. This is shown in Table III which refers to irradiations in the solid phase. The dependence of yield upon number of covalent bonds shown in this table may be rationalized by reference to the energy and entropy of activation terms in the hot-zone reaction probability expressions mentioned above. The

TABLE III

RELATION OF RETENTION TO NUMBER OF GROUPS COVALENTLY BONDED TO THE CAPTURING ATOM

Number of groups covalently bonded to the capturing atom in the parent molecule	Yield of radioactive parent molecule (%)	Reference
One		
Carbon tetrabromide	93	*30*
Carbon tetrachloride	51	*30*
Methyl iodide	44	*43*
Ethyl iodide	27	*48*
n-Propyl iodide	21.7	*48*
Isopropyl iodide	39.2	*48*
n-Butyl iodide	21	*48*
Sec-butyl iodide	13.9	*48*
n-Propyl bromide	26.9	*48*
Isopropyl bromide	11.7	*48*
Tritium in glucose and galactose	~12	*69*
Tritium in benzoic acid	~25	*88*
Two		
Ferrocene	12	*77*
Three		
Triphenylarsine	2.1	*52*
Triphenylstibine	4.4	*33*
Four		
Carbon-14 in organic compounds	~1-3.5	*85, 86, 87*
Cobalt phthalocyanine	~3	*16*

greater the number of bonds, the larger the activation energy and the less favorable the steric factor.

In all the alkyl halides investigated the organic yield in the solid phase is greater than 30% with the exception of secondary butyl iodide for which it is 25%. The excited molecule of this compound is known to be unstable with respect to decomposition into the olefin and hydrogen iodide, and this could account for the lower organic yield.

In view of the large number of reactions which can occur in organic systems, the chemical nature of the environment is much more important than in the case of the oxyanions. Indeed Willard has concluded that in the alkyl halides, the chemical characteristics of the medium are more important than physical factors such as the energy, charge, strength of cage walls, and masses of the atoms involved (*82*).

A recent investigation (*48*) of the chemical effects of the $n,2n$ activation of iodine in alkyl iodides indicates that molecular structure plays an important part in determining the yield of minor products. Results with *n*-propyl and isopropyl iodides show that the yield of methyl iodide is larger in the irradiation of the former compound. A random-fragmentation model would predict a larger yield of methyl radicals from the isopropyl iodide. In several other systems yields are not consistent with a random-fragmentation model. A possible explanation for these observations on the basis of the hot-zone model is that before the hot zone cools the recoil atom can undergo reactions which require moderate activation energies.

The ratio of the organic yield in the solid phase to that in the liquid has been measured for a large number of organic halides. The ratios are generally greater than unity and bear no apparent relation to the structure of the halide or the density change on freezing (*82*). This may be ascribed to the different steric factors, stronger reaction cage, and the longer lifetime of the hot zone in molecular crystals. It may be possible to account for those few cases in which the organic yield is larger in the liquid phase on the basis of a relatively larger contribution from thermal reactions.

In liquid systems the thermalized atoms have an opportunity to diffuse freely through the medium and enter into the more familiar chemical reactions (*58*). A useful technique has been developed to determine which products are formed in hot reactions (*34, 84*). Before the irradiation of the organic halide, low concentrations of substances known to react readily with thermalized halogen atoms are added. The part of the organic yield which is insensitive to added halogen is attributed to hot reactions. In this way it has been found that both the organic and inorganic yields are formed by hot as well as thermal reactions. Such a distinction between hot and thermal reactions applies equally to all the models discussed.

The liquid alkyl chlorides exhibit several interesting properties. In contrast to the alkyl bromides and iodides, the alkyl chlorides show no scavenger effect (*15*). This is ascribed by Willard to the ease with which chlorine atoms react with carbon-hydrogen bonds to form stable hydrogen chloride. The fate of the radioactive chlorine atom is thus determined before it comes to thermal equilibrium with the medium. Willard further points out that the organic yield of the chlorides is independent of chain length and thus of the ratio of carbon-chlorine bonds to other bonds (*82*). On the other hand, such structurally similar molecules as C_2H_5Cl, C_2H_5Br and C_2H_5I have organic yields of 21%, 32%, and 41%, respectively. The "random-fragmentation" and "billiard-ball" models predict that all three compounds should have similar organic yields. This supports Williard's conclusion that the chemical characteristics of the medium are more important than physical factors in these systems and finds a ready explanation in the hot-zone model. As mentioned in Section I a similar conclusion had been reached by Miller and Dodson (*56*) on the basis of experiments with recoil chlorine atoms in hydrocarbon media.

III. Post-Recoil Annealing Effects

A. INTRODUCTION

The annealing of recoil atoms was first reported by Williams (*83*), who noticed that the specific activity of radioactive antimony produced by the pile irradiation of antimony pentafluoride and ammonium fluoantimonate decreased with increasing time of irradiation. This effect was ascribed to two phenomena: the gradual return of initially separable antimony atoms to the parent form during irradiation, and the simultaneous macroscopic decomposition of the compounds. It was also observed that the retention as the parent compound in these two substances was increased by exposing them to ionizing radiation following neutron irradiation.

Green and Maddock (*32*) subsequently found that the retention of chromium-51 in potassium chromate could be increased by heating the neutron-irradiated crystals. Thermal and radiation annealing have since been observed in a number of systems (*4, 5, 9, 20, 21, 31, 35, 39, 41, 50, 52, 53, 54, 60, 66, 67, 74, 77, 91*). In general, annealing returns a part of the initially separable recoil atoms to the form of the parent compound.

The annealing of Szilard-Chalmers recoil atoms finds a striking parallel in the annealing of radiation damage produced in solids by neutron, charged-particle, or photon irradiation (*25*). In both cases one is dealing with solids which have been altered by the production of defects in a matrix of otherwise normal crystal. In both cases the defects are the result of a particular atom having been given a sudden impulse, sufficient to displace it from its normal position in the lattice. The Szilard-Chalmers method consists of observing the defects through the change in the chemical state of the atom responsible for the defects, while radiation-damage studies have usually depended upon changes in the optical absorption, resistivity, Young's modulus, or semiconducting properties of the irradiated solids. One advantage of the Szilard-Chalmers method is that the number of atoms annealed in a particular experiment is immediately given by the result of the experiment, whereas in radiation-damage annealing studies a hypothesis must be made to connect the change in the physical property to the change in the number of atoms in the defect state. A second useful consequence of a Szilard-Chalmers investigation is that it may give directly the fraction of atoms which have suffered displacement and then have been reincorporated into normal lattice sites. Physical methods yield no direct measure of this quantity. By using the appropriate nuclear reaction one can often cause the recoil atom to be projected with either very high ($\sim 10^5$ ev) or very low ($\sim 10^2$ ev) kinetic energies. Another important difference in the chemical and physical approaches is the relatively greater sensitivity of the former. In typical Szilard-Chalmers studies only very small doses of radiation need be given. In favorable cases, integrated thermal neutron fluxes of 10^{10} neutrons/cm^2 suffice, and it is likely that the defects or displacement spikes produced by recoil atoms under these conditions are isolated events. In typical solid-state studies of annealing of radiation damage by measurement of X-ray diffraction, electrical resistivity, or Young's modulus, significantly greater damage must be done to the system to produce measurable effects. An exception is the study of semiconductors, whose electrical properties are very sensitive to the introduction of imperfections.

In a sense, Szilard-Chalmers annealing studies are complementary to those of radiation damage annealing, for while the former are concerned with fairly complex crystals, containing several types of atoms in different molecular or ionic combinations, the latter have generally been concerned with simpler substances (e.g., monatomic metals, alkali halides, diamond, graphite, silica, etc.). Thus it is necessary to study the damage in the former systems from a fundamentally chemical viewpoint, taking into account breaking and re-formation of bonds, synthesis of new chemical entities, and changes in electronic structure; while a more physical approach, invoking a mechanical, hard-sphere electrostatic model of the displacement (and annealing) processes has generally been adopted in dealing with the latter systems. Solid-state physical studies have largely ignored the influence of the chemical bond.

B. THE INTERPRETATION OF THERMAL ANNEALING

The recombination of pairs of interstitials and vacancies has usually formed the basis of models for thermal annealing. It has sometimes been assumed that the vacancy is mobile (as in the vacancy model for self-diffusion) and sometimes that the vacancy is a fixed trap or sink, having a capacity of one interstitial atom, and the interstitial is mobile. The form of the kinetic equations is usually not dependent on the choice, and this is true even if both are mobile provided there is no initial correlation of interstitials and vacancies.

However, in typical cases of Szilard-Chalmers annealing, a fundamental asymmetry appears. If we consider a recoil bromine atom in crystalline potassium bromate, the atom may come to rest in an interstitial position, but the conjugate "vacancy" is then an array of unbonded oxygen atoms or oxide ions. To assume recombination by vacancy diffusion might imply that these move through the crystal as a unit, which is difficult to accept. For our purposes a "vacancy" in a complex crystal may be regarded as a trap consisting of a fragment or any species capable of reacting chemically with the interstitial atom. In some cases this might consist of an oxygen atom or oxide ion, and these simple entities would of course be capable of diffusion. In others the trap might be an *F* center, electron deficient hole, etc.

It is convenient to make a broad distinction between models on the basis of the initial separations of the species which undergo reaction on annealing. If, as is usually the case with atoms activated by n,γ reactions, the range of the recoil atom is short [of the order of a few lattice spacings (*90*)], there will be a high degree of correlation between interstitials and vacancies, or, to put it another way, the radioactive recoil atoms and the fragments with which they combine will have small initial separations. As annealing proceeds reactions may take place between species which were initially further apart. We will also consider a phenomenological approach by which mixed kinetics may be handled and schemes in which the activation energy is permitted to vary and the kinetics are not specified.

1. *Annealing of Initially Correlated Pairs*

a. Simple Recombination of Correlated Pairs. As the simplest case we will consider that the annealing process consists of the recombination of the recoil atom with a collision fragment or with one of its originally bonded partners and that the pairs have small initial separations. Such a process in a simple monatomic crystal has been visualized by Brown *et al.* (*10*) in the following way (similar arguments probably apply to more complex systems). Close to the vacancy there is elastic deformation of the lattice which results in a lowering of the potential barrier to the jumping of the interstitial atom from one interstitial position to the next as it approaches the vacancy. The jump toward the vacancy will have the lowest potential barrier, and the barrier will be lower the closer the interstitial is to the vacancy. Since the initial separation of the interstitial and vacancy is small the rate of recombination will be determined by the jump of the interstitial from its original site in the deformed region (which may be approximately identified with the "displacement spike" zone). If this jump frequency is ν_j, then

$$\nu_j = \nu_0 e^{-E/kT} \tag{1}$$

where ν_0 is a typical frequency for the vibration of atoms in the lattice and E is the energy required by the interstitial to jump to an adjacent interstitial site. Brown *et al.* state that $\nu_0 \approx 10^{13}$ sec^{-1}. Although this is a "normal" crystal frequency, it is worth noting that ions or atoms close to vacancies do not have normal vibration frequencies. In particular, interstitial atoms as Frenkel defects have frequencies greater than those of the normal lattice (*75*).

The rate of recombination will then be given by

$$-dn/dt = \nu_j n \tag{2}$$

where n is the number of uncombined pairs correlated as described above. This equation leads to the simple first-order law that

$$n_t = n_0 e^{-\nu_j t} \tag{3}$$

in which n_t and n_0 are the number of uncombined pairs at times t and zero, respectively.

Provided the annealing process described above leads to retention (the re-formation of the parent compound, or a species which produces the parent compound on chemical analysis), Eq. (3) can be expressed in terms of retentions as follows

$$\ln (R_\infty - R_t) = \ln (R_\infty - R_0) - \nu_j t \tag{4}$$

in which R_t and R_∞ are the retentions at time t and infinite time of isothermal annealing, respectively. The quantity $(R_\infty - R_t)/(R_\infty - R_0)$ is the fraction of pairs still uncombined at time t. These quantities are shown graphically on the generalized annealing curve in Fig. 2.

In order to simplify the equations we will consider only the increase in the number of recombined atoms on annealing. Although as we have seen in Section II the initial retention (R_0) is usually not zero, and may

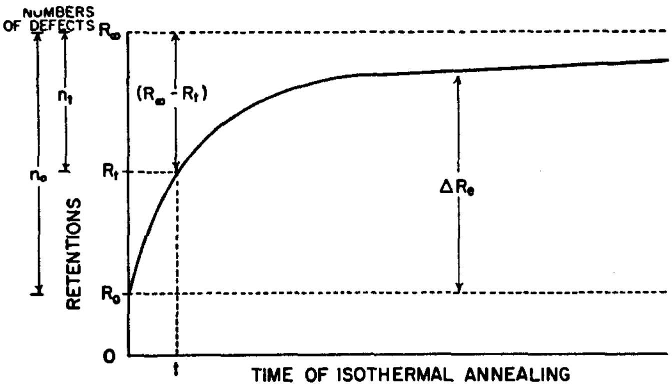

FIG. 2. Generalized annealing curve illustrating the quantities R_t, R_0, R_∞ and the numbers of uncombined defects n

be quite large, it may be taken as the base line from which annealing proceeds. This procedure is equivalent to taking $R_0 = 0$ (Fig. 2) and does not alter the form of the kinetic expressions derived.

In the event that there are several classes of fragment loci in the same, or different deformed zones, having different activation energies for annealing E_1, E_2, . . . then

$$n_t = n_{01}e^{-\nu_{f1}t} + n_{02}e^{-\nu_{f2}t} + \ldots \tag{5}$$

where $n_0 = n_{01} + n_{02} + \ldots$ and ν_{fi} is the jump frequency of the atom in the i^{th} locus from its initial position. For each ν_{fi} there will be a characteristic activation energy E_i, see Eq. (1), and the over-all approach of the quantity $(R_\infty - R_t)$ to zero will then follow a succession of exponential periods analogous to radioactive decay of a mixture of isotopes of differing half-lives.

If the annealing process is of this nature, and there is a finite number of types of recombination loci, then in principle the annealing curve can be resolved into that many exponential components. It is clear that by this procedure any arbitrary monotonic experimental curve can be fitted provided a sufficiently large number of exponential terms, Eq. (5), are taken; however, a necessary condition is that extrapolation of the linear portions of the curves thus resolved for different temperatures must give the same intercept values (at $t = 0$), since the quantities n_{01}, n_{02}, . . . are not affected by the temperature of annealing.

b. Recombination of Correlated Pairs Modified by Electrostatic Interactions. An interesting model which involves diffusion of interstitial atoms in the neighborhood of a correlated defect has been proposed by Maddock and de Maine (*49, 50*). Although they first treated their own data on potassium chromate by this model, it has been found possible to apply it with some success to other systems as well. In the case of potassium chromate, the basic annealing reaction is assumed to be

$$\mathrm{CrO^{4+} + O^{=} \rightarrow CrO_2^{2+}} \tag{6}$$

and the oxide ion is assumed to be mobile. After irradiation but before annealing, the distribution of $\mathrm{CrO^{4+} - O^{=}}$ distances (X) in the crystal is assumed to be as shown in Fig. 3. There are no distances less than X_0, because partners having this distance of separation are so close that they recombine even at room temperature, and thus add to the R_0 term in the retention (see Fig. 2). On the other hand there are none further separated than X_∞, a distance equal to the maximum range of the recoil atoms. Between these two distances the distribution is assumed to be uniform. The rate of recombination of partners is given by

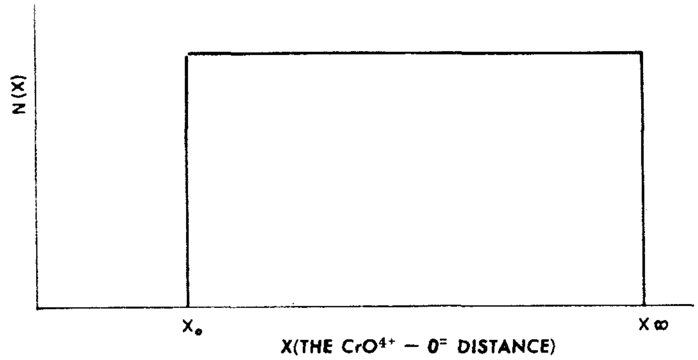

FIG. 3. Distribution of $\mathrm{CrO^{4+} - O^{=}}$ distances in irradiated potassium chromate on the Maddock-de Maine model.

$$-dn/dt = n\nu e^{-U/kT} e^{V/kTX} \tag{7}$$

where n is the number of possible pairs, U is the activation energy barrier opposing recombination, ν is the frequency of vibration of the defect oxide ion, T is the absolute temperature, X is the smallest separation of partners at time t, and V is an electrostatic potential term containing, in this case, the charge on the ions, dielectric constant, and crystal parameters. The quantity V/X is a potential gradient. Thus the kinetic expression is similar to the first case considered, Eq. (1) and (2), modified by the presence of a field term, in this case the coulombic attraction of oppositely-charged ions, which tends to assist recombination.

The annealing process is considered analogous to the growth of very thin oxide films treated by Mott (*12*, *59*). On this picture the increase in retention on annealing involves the recombination of partners having increasingly greater values of X; this may be visualized in Fig. 3 as the slow movement of the vertical line at X_0 towards X_∞, the area lying to the left of the line representing the pairs that already have recombined and the area to the right those still uncombined at time t. Thus the change in retention ΔR is a linear function of X and enters the rate expression as follows:

$$\frac{1}{(R_\infty - R)} \frac{dR}{dt} = \nu e^{-U/kT} e^{V/ckT(\Delta R + S)} \tag{8}$$

where S is a constant and c is a constant relating the retention to X.

When annealing is begun ΔR is small and the second exponential term in Eq. (8) is large and dominates the rate of reaction. This corresponds to the rapid initial growth of thin films of oxide. However, as annealing proceeds the second exponential term becomes effectively unity and the rate of increase in retention is then governed by the first exponential. This corresponds to the slowly-rising "plateau" portion of the annealing curve (*50, 53, 54*). Maddock and de Maine take the value ΔR (equal to ΔR_e) for which the second exponential term becomes effectively unity from the expression

$$\frac{V}{ckT(\Delta R_e + S)} = \alpha \tag{9}$$

where α is a small number such that e^α is arbitrarily close to unity. This state of affairs corresponds to the formation of an oxide film of limiting thickness, at which point rapid growth ceases and further growth becomes very slow (*12, 59*).

We then see that values of ΔR_e characteristic of the plateaus at different temperatures T satisfy the relation

$$(\Delta R_e + S) = C'/T$$

or

$$\Delta R_e = C'/T - S \tag{10}$$

where C' is an arbitrary constant, equaling $V/ck\alpha$.

This important result, Eq. (10), states that on the Maddock-de Maine model the increase in retention on annealing to the plateau should be a linear function of $1/T$, and such a relation is in fact observed in a number of cases (*50, 53, 54*). We shall discuss this further in the section on relevant experimental data.

c. Recombination of Correlated Pairs with Electron Transfer as the Rate-Determining Step. In many Szilard-Chalmers reactions the recoil fragment acquires a high positive charge as a result of internal conversion effects. The partial or complete neutralization of this charge may be necessary before the recoil fragment can recombine with other fragments on annealing, and this electron transfer process may be the rate-determining step. In such systems the fragments which re-form the parent species may be trapped sufficiently close to one another for recombination to occur once the recoil fragment has gained the required number of electrons from its surroundings. (Alternatively the parent species might be re-formed from the reduced recoil fragment during the subsequent chemical analysis.)

Although such a mechanism could very well account for the initial retention (R_0 in Fig. 2), it is difficult to see how the apparent energies of activation for the annealing process can be reconciled with this view. There are numerous examples of annealing reactions which do not proceed at all, or very slowly, at 0°C but which go rapidly at temperatures of a few hundred degrees centigrade. Such behavior implies, if frequency factors are "normal," activation energies of the order of magnitude 1 to 2 ev. This is the order of magnitude of the activation energy for diffusion of ions in crystalline ionic lattices but seems too large for electron transfer. However, it should be noted that Pringsheim *et al.* (*14*) found that the bleaching of *F* centers in LiF required temperatures of 100°-200°C, corresponding to reasonably large activation energies for this particular type of electronic effect.

d. Recombination of Correlated Pairs after a Random-Walk Process. For the interstitials which are located outside the deformed region the probability of jumping in any direction is the same. These interstitials wander according to a random-walk process; those that wander back into the deformed region are subsequently captured by their original partners, and the rest wander off through the crystal.

Fletcher, Brown *et al.* (*10, 27*) have applied this model to the annealing of radiation damage in germanium. The deformed region is considered to be a trap or sink of radius a such that the approach of a mobile entity to within the distance a inevitably produces recombination. The medium is assumed to be infinite and isotropic. All fragment pairs are correlated and have identical initial separations b; the number of uncombined pairs n_t still present after a random walk of duration t is related to the number present at the beginning, n_0, by

$$n_t = n_0\left[1 - \frac{a}{b} + \frac{a}{b}\,\mathrm{erf}\left(\frac{(b-a)}{2(Dt)^{1/2}}\right)\right] \tag{11}$$

where D is the diffusion coefficient of the diffusing entity. The variation in D with temperature will involve the activation energy E in the usual way

$$D = D_0 e^{-E/kT} \tag{12}$$

where D_0 is a constant, roughly independent of temperature. The relation between the diffusion coefficient and the corresponding jump frequency ν_j is given by the well-known expression (*73, 75*)

$$\begin{aligned} D &= l^2\nu_j \\ &= l^2\nu_0 e^{-E/kT} \end{aligned} \tag{13}$$

where ν_0 is defined as in Section B1a above and l is a lattice constant.

In terms of retentions the Fletcher-Brown expression, Eq. (11), becomes

$$R = \frac{a}{b}\left[1 - \operatorname{erf}\left(\frac{(b-a)}{2(Dt)^{1/2}}\right)\right] \tag{14}$$

again disregarding the initial retention.

This equation has several interesting features. First, it produces a plateau after long annealing times, the corresponding retention being given by $R = a/b$. This is the "liberation" phenomenon, i.e., $(1 - a/b)$ is the fraction of pairs "liberated," or not eventually recombined with their initial partners. As Fletcher and Brown point out, "liberated" diffusing entities can still combine with traps in other parts of the lattice. This will be governed by bimolecular kinetics, if the number of diffusing entities and traps are comparable (see below). To illustrate the Fletcher-Brown expression, we have plotted in Fig. 4 the quantity $\{1 - \operatorname{erf}$ $[a/2(Dt)^{1/2}]\}$ against Dt/a^2; this is equivalent to arbitrarily taking $b/a = 2$. The abscissae of Fig. 4 are then proportional to the time of annealing and the five curves could represent one particular curve on five different time scales differing from one another by factors of 10.

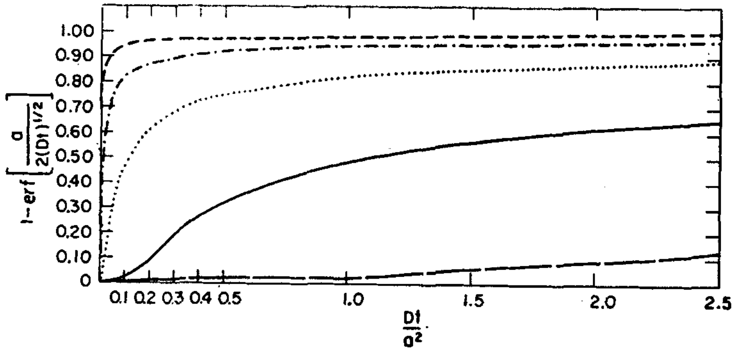

FIG. 4. The Fletcher-Brown random-walk error function expression plotted against Dt/a^2, a function of the time of isothermal annealing.

The second interesting feature of the Fletcher-Brown expression is clearly seen on the second of these curves, and that is the point of inflection near the origin.

Although we could consider the five curves as representing the annealing behavior on five different time scales for one value of D/a^2, that is to say, one temperature, we could equally well consider that all five relate to one time scale, but differ in having five values of D/a^2, that is to say, five values of D, the diffusion coefficient, differing by factors of 10. The family of curves then bear considerable similarity to the sets of isothermal annealing curves obtained in typical Szilard-Chalmers studies, except for the point of inflection near the origin, which has not been observed experimentally. It is worth noting that the Fletcher-Brown plateaus are all at the same value of R, namely a/b and independent of temperature. Even if we take the point at which the rapidly rising portion begins to level off, as we did in the case of the Maddock-de Maine model, we do not obtain the linear relation between ΔR and $1/T$ observed experimentally.

e. Recrystallization of the Hot Zone. If, as we noted above, the hot zone on cooling contains disorder of various types (i.e., broken bonds, free radicals, interstitial atoms, and vacancies) we could regard the annealing process as one of recrystallization, where the disordered region would be a second phase of the same crystal, thermodynamically unstable with respect to the first phase, which is the normal crystal. Since the two phases are in contact, the normal matrix serves as the nucleus for recrystallization. Although recrystallization of the hot zone would decrease the entropy, there would still be a large decrease in free energy owing to the highly exothermic nature of the free-radical and interstitial-vacancy recombinations, and relief of strains in the lattice. Thus the process should be spontaneous once a sufficiently high temperature is reached. A recent discussion of the kinetics of recrystallization has been given by de Boer (*8*). Unfortunately the theoretical studies deal with two perfect crystal phases in contact through a disordered layer, while in our systems the rapid cooling of the hot zone is likely to produce a glassy phase (which can give up a very large heat of crystallization) in contact with a perfect crystal. However, one may with certain assumptions derive a kinetic expression for the change in retention with time of isothermal annealing based upon a recrystallization model. These assumptions are: (1) There are initially present N disordered regions of roughly spherical shape, each containing one "annealable" Szilard-Chalmers recoil atom. (2) The locations of the recoil atoms within the disordered regions are random. (3) Recrystallization proceeds from the boundary inward at a constant linear velocity v. (This is generally assumed in mathematical treatments of recrystallization.) (4) Each recoil atom is "annealed" when the phase boundary passes over it. The dependence of the velocity of boundary movement on temperature is given by Hartshorne (*38*) as

$$v = \frac{1}{2} A_a \exp\left(-E_a/RT\right) \left\{1 - \exp\left[\frac{q}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]\right\} \tag{15}$$

where A_a is a frequency term, E_a is an activation energy, q is the heat of transformation of the disordered zone to an ordered one, and T_0 is the absolute temperature of the transition point. Since in this case the ordered zone is stable up to temperatures which are large compared to the annealing temperature T, the quantity $1/T_0$ is probably small compared to $1/T$. As mentioned above, the quantity q is probably large compared to the heats of typical crystalline phase transitions.

Subject to the assumptions listed above, one may derive (see Appendix A) the isothermal kinetic law

$$\text{fraction annealed} = \frac{R_t}{R_\infty} = \left[1 - \left(1 - \frac{vt}{r_0}\right)^3\right] \tag{16}$$

where R_t and R_∞ are the retentions at time t and at infinite time, v is the velocity given above, Eq. (15), and r_0 is the initial radius of the disordered zone.

In Fig. 5 are plotted the functions R_t/R_∞, Eq. (16), for various values

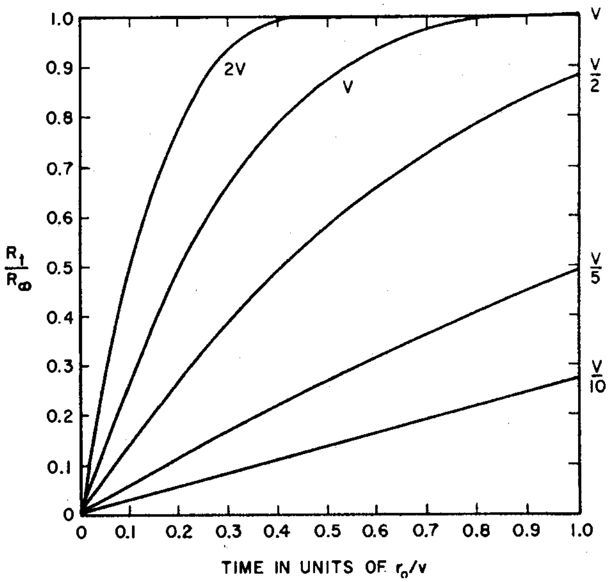

FIG. 5. The function R_t/R_∞ plotted against a function of the time. Simple recrystallization model. Curves for several velocities v are shown.

of v against the time t, in units of r_0/v. It is interesting that although these curves have, for larger values of v, shapes not unlike annealing curves at relatively high temperatures, the curves for smaller values of v do not show the characteristic plateau or pseudo-plateau usually seen in plots of experimental data. Although this treatment could be modified, viz., by adopting variable radii r_0 or velocities v for different zones or nonspherical zone shapes, it seems of little use to do this until more refined and extensive experimental data are at hand.

2. Annealing of Initially Randomly Distributed Pairs

a. Diffusion-Controlled Bimolecular Recombination. The recombination of randomly distributed fragments follows second-order kinetics. If the number of fragments of the two recombining types is the same, then the rate expression is

$$-\frac{dn}{dt} = kn^2 \tag{17}$$

where n is the number of uncombined fragments at time t, and k is a bimolecular rate constant. The variation of k with temperature is given by

$$k = k_0e^{-E/kT} \tag{18}$$

where k_0 is a constant roughly independent of temperature and E is the activation energy.

These kinetics apply whether one or both of the recombining entities are mobile. In the case of correlated pairs produced by radiation damage Fletcher *et al.* (*10, 27*) maintain that after the first stage of recombination (governed by the unimolecular and random-walk kinetics) was complete, the "liberated" species would continue to recombine, much more slowly, by a bimolecular path. Only one activation energy, that governing the diffusion coefficient D in Eq. (11), would apply to both the random-walk and bimolecular kinetics. If bimolecular processes are important in a Szilard-Chalmers system it seems likely that the recombination rate would depend on the extent of radiation damage in the crystal before and during annealing. Experimental data bearing on this point will be discussed below.

Bimolecular kinetics lead to the following retention law:

$$R_t = R_\infty\left(1 - \frac{1}{1 + kR_\infty t}\right) \tag{19}$$

where the symbols have their usual meanings and the retention is measured from R_0.

3. Thermal Exchange Model

Another mechanism whereby activity can be returned to the parent form is through exchange reactions. For example, we can visualize the following exchange reaction occurring on heating neutron-irradiated solid organic halides (*54*).

$$X^* + RX \rightleftarrows X + RX^*$$

where X^* is the radioactive recoil atom and RX the parent species. It may be argued that the activation energy for such a process is too high to account for annealing at moderate temperatures. But just as the activation energies for diffusion are thought to be lowered in the presence of defects, so may activation energies for exchange.

If exchange between X^* and any of its c neighboring groups is equally probable it can be shown (Appendix B) that the retention should follow the law

$$(R_\infty - R_t)/(1 - R_\infty) = c \exp\left[\frac{-(c+1)}{c}\nu t\right] \tag{20}$$

where ν is the frequency of the exchange process. This predicts that the logarithm of ΔR should yield a straight line when plotted against the time t. It may also be seen that the retention can never increase to 100% but only to $c/(c+1)$.

The temperature dependence of the annealing of such a system would enter through the frequency ν, which would presumably be governed by an activation energy as in Eq. (1).

4. Phenomenological Approach. Annealing Functions Involving Mixed Kinetics

It has been shown by Fletcher and Brown (*27*) that provided the vacancy moves in a crystal by jumping to an adjacent site, the annealing should depend upon the average jump time τ and the time of isothermal annealing t only through the ratio t/τ. Since the temperature dependence of the annealing appears almost entirely through τ, it should be possible to combine data obtained from isothermal annealing experiments at different temperatures into a single curve of equivalent annealing at a single temperature. This is accomplished by multiplying the time scale of each isothermal curve by an appropriate factor, and replotting all such curves on a single graph. Then the resultant composite annealing curve may be fitted by unimolecular, bimolecular or error-function expressions (see Sections B1a, B1d, and B2 above) or any combination of any number of these. Several examples of this type of curve fitting are given in a recent paper by Clarke (*17*) including Fletcher and Brown's results on germanium. When the jump times τ have been obtained, the crystal frequency ν_0 may be calculated from

$$\frac{1}{\tau} = \nu_j = \nu_0 e^{-E/kT} \tag{21}$$

provided the energy of activation E is known. This quantity may be obtained by one of the methods described by Parkins, Dienes, and Brown (*63*), which do not require any knowledge of the mechanism of the recombination reaction. In the discussion below, we will consider the application of this method to typical Szilard-Chalmers annealing data.

5. *Processes Distributed in Activation Energy*

In all of the foregoing cases it has been assumed that the energy of activation for the process leading to recombination has one or a few discrete values. Vand (*79*) has suggested that the kinetics of annealing of metal films could be interpreted in terms of recombination of defects distributed in activation energy. We will outline the mathematical treatment of this concept of Vand, as amplified by Primak (*64*), and show how, beginning with a set of isothermal annealing curves, one can in principle obtain the spectrum of activation energies.

It is assumed that the annealing processes, though distributed in activation energy, all follow kinetics of the kind

$$dn/dt = kn^{\gamma} \tag{22}$$

where n is the number of annealable defects, γ is the order of the reaction, and k is a rate constant of the usual form

$$k = Ae^{-E/kT}. \tag{23}$$

Next, it is necessary to assume that the property p, which is actually measured, is linearly related to the number of defects n,

$$p = fn. \tag{24}$$

In the case of Szilard-Chalmers annealing this requirement presents no problem since the quantity $(R_\infty - R_t)$, where the symbols have their previous meanings (see Fig. 2), is a linear function of the number of annealable defects which remain. Equation (22) is then

$$dp/dt = fA\,[\exp{(-E/kT)}](p/f)^{\gamma}. \tag{25}$$

It is convenient to consider first the situation if E is a single, discrete activation energy, then to proceed to distributions in E. If E is discrete, we can integrate Eq. (25) to get p_t, the measured property at time t in terms of its initial value p_0. One obtains

$$p_t = p_0\,[1 - (1 - \gamma)\,Bt \exp(-E/kT)]^{1/1-\gamma} \qquad \gamma \neq 1 \tag{26}$$

$$p_t = p_0\,[\exp(-At \exp(-E/kT))] \qquad \gamma = 1 \tag{27}$$

$$p_t = p_0\theta_\gamma \tag{28}$$

defining θ_γ, the characteristic annealing function. The constant B is compounded of other constants

$$B = A(p_0/f)^{\gamma-1} \tag{29}$$

$$= An_0^{\gamma-1} \tag{30}$$

where n_0 is the initial number of annealable defects. Rearrangement of Eqs. (26) and (27) leads to the following:

$$\left(\ln \frac{p}{p_0}\right) = \frac{1}{(1-\gamma)} \ln\,[1 - (1 - \gamma)\,Bt \exp(-E/kT)] \qquad \gamma \neq 1 \tag{31}$$

$$\ln\left(\ln \frac{p_0}{p}\right) = \ln At - (E/kT) \qquad \gamma = 1 \tag{32}$$

which show that for a fixed period of isothermal annealing a plot of $\ln\,[\ln\,(p_0/p)]$ against $1/T$ should give a straight line only for $\gamma = 1$. As mentioned above, the property p can be identified with the retention

$$p_t = R_\infty - R_t. \tag{33}$$

Similarly, for a fixed degree of annealing, p/p_0

$$\ln t = \ln\left[\frac{1 - (p/p_0)^{1-\gamma}}{(1-\gamma)B}\right] + E/kT \qquad \gamma \neq 1 \tag{34}$$

$$\ln t = \ln\left[\frac{\ln\,(p_0/p)}{A}\right] + E/kT \qquad \gamma = 1 \tag{35}$$

showing that the logarithm of the time necessary to produce a given degree of annealing, p/p_0, plotted against $1/T$ should yield a straight line of slope E/k for any order of reaction γ. This is one of the Parkins *et al.* (*63*) results mentioned in Section B4 above. For Szilard-Chalmers studies a fixed degree of annealing means a fixed increase in retention, ΔR.

As mentioned above, Eq. (26) to (35) refer to a discrete activation energy. If the annealing processes are distributed in activation energy the measured value of the property P at time t will be the integral over all activation energies of all the discrete processes occurring at the annealing temperature at any instant. These will tend to lie within a narrow band of activation energies dE, centers with lower activation energy already having been annealed out, and those with higher energy as yet untouched. Thus

$$P_t = \int_0^\infty p_0(E)\theta_\gamma(E,t)\, dE \tag{36}$$

where $p_0(E)$ is the initial distribution of observable properties p with activation energy E, and $\theta_\gamma(E,t)$ the value of the characteristic annealing function at time t.

The annealing process may be visualized mathematically as the movement of the function θ_γ along the E axis of the $p_0(E)$ versus E distribution (see Fig. 6). The position of the point of inflection in the θ_γ function, E_0, at any time t is given by

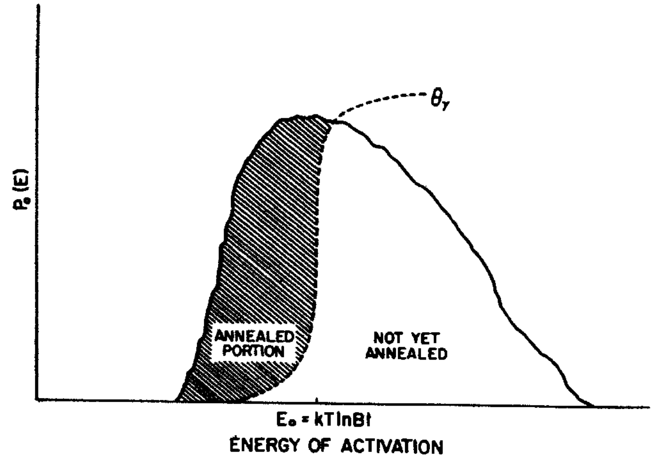

FIG. 6. Graphical representation of the annealing process in terms of the movement of the characteristic annealing function θ_γ.

$$E_0 = kT \ln (Bt) \qquad \text{any } \gamma \tag{37}$$

and as annealing proceeds at temperature T the function θ_γ sweeps across the distribution $p_0(E)$, at first rapidly, then moving ever more slowly because of the dependence on ln t. The quantity E_0 is referred to as the characteristic activation energy. At any given time t the portion of the initial spectrum to the left (i.e., at activation energies lower than E_0) of θ_γ has been annealed out and the portion to the right has not yet been annealed.

An important simplification results if the function θ is approximated by a step-function rising at E_0. This replacement is justified for small values of γ as θ_γ in these cases rises steeply. The integral, Eq. (36), then becomes

$$P_t \approx \int_{E_0}^{\infty} p_0(E)\,dE \tag{38}$$

from which one obtains, by differentiation and substitution

$$\begin{aligned} p_0(E_0) &= \frac{1}{kT}\frac{dp}{d(\ln t)} \\ &\approx p_0(E) \end{aligned} \tag{39}$$

where the designation E_0 rather than E indicates that the step-function approximation has been taken. One is now in a position to obtain a plot of $p_0(E_0)$ against E_0.

The first step is to plot the measured value of the property, P, (in the case of Szilard-Chalmers studies, $(R_\infty - R_t)$) against $\ln t$. From the slopes of these curves (one for each temperature) one obtains the quantities $(1/kT)\ dp/d(\ln t)$. These quantities are then plotted against $kT \ln(Bt) = E_0$. The factor B is arbitrarily chosen to give the best overlap between successive isothermal annealing curves: a change in B does not alter the shape of the initial spectrum of activation energies, but only the position on the E_0 axis. If one takes only the average slope of each isothermal curve and then plots the values of $(1/kT)dp/d(\ln t)$ so obtained against E_0 one obtains a segment of a horizontal straight line, lying at the appropriate value of the slope on the $p_0(E_0)$ axis and extending from $E_0 = kT \ln (Bt_1)$ to $E_0 = kT \ln (Bt_2)$ on the E_0 axis where t_1 and t_2 are the annealing times over which $p_0(E_0)$ was evaluated. This type of plot gives a rough indication of the initial spectrum of activation energies. If the annealing data are sufficiently precise, a second stage of refinement may be reached in which, instead of an average slope, one reads off the actual slopes point by point and then plots $(1/kT)$ $dp/d(\ln t)$ calculated from the actual slopes against $kT \ln (Bt)$. One obtains from this a better representation of the initial spectrum, but the method suffers from the difficulty inherent in all procedures in which slopes are obtained from experimental data, namely, that the data must be of a high order of precision. Unfortunately, such precision is difficult to obtain in annealing studies.

Several examples of analysis of actual data by this method are given in Clarke's (*17*) paper, and we shall discuss below its application to Szilard-Chalmers annealing data.

6. Activation Energy Varying with the Number of Defects

In the interpretation of isothermal-annealing data for radiation-damaged metals, Marx *et al.* (*55*) and Overhouser (*62*) suggested that the activation energy for recombination might be a function of the number of defects present. Dienes (*24*) has amplified this point in terms of a linear dependence

$$E = E_0 - \alpha n \tag{40}$$

where E is the apparent activation energy in an actual damaged sample, containing n defects, E_0 would be the corresponding activation energy of annealing isolated defects, and α is a constant. This leads to a general rate law

$$-\frac{dn}{dt} = n^{\gamma} e^{-E_0/kT} e^{\alpha n/kT}. \tag{41}$$

Such a treatment has somewhat the same effect as the Primak model, i.e., as annealing proceeds, n grows smaller and the apparent activation energy increases (*24, 62*).

Dienes points out that for kinetics obeying Eq. (41), a plot of ln t against $1/T$ for fixed degree of annealing still gives a straight line, but the slope changes with the degree of annealing. As might be expected, a relatively small perturbation in E leads to a large change in the time scale.

We thought it worthwhile to mention this approach and to call attention to the fact that the Szilard-Chalmers method represents a unique way of testing this hypothesis. Annealing of recoil atoms may be studied in crystals which have received anything from infinitesimal (a few seconds in the pile) to massive doses of radiation, corresponding to large changes in the quantity n; Eq. (40). Some experimental results bearing on this point will be discussed below.

C. THE INTERPRETATION OF RADIATION ANNEALING

It has been observed that recoil atoms undergo annealing when exposed to ionizing radiation from radioactive sources such as cobalt-60, from X-ray generators or from nuclear reactors (*9, 20, 21, 35, 66, 83*). In the reactor not only gamma rays but presumably fast neutrons also play a role. A possible explanation of this effect is that in crystals exposed to radiation, the interactions of the radiation with the crystal give rise to "thermal spikes," and that these occasionally occur sufficiently close to a recoil atom to give it the activation energy necessary to anneal. Such a view implies that radiation annealing is fundamentally similar to thermal annealing. Another possibility which permits somewhat more efficient use of the energy put into the crystal by radiation is that the lattice vibrations excited by the fast electrons produced by the radiation pass through the crystal until they encounter a defect. There they give up some of their energy, again supplying the recoil atom with sufficient energy to permit it to surmount its potential barrier to recombination. Finally, the recoil atoms may combine with fragments or electrons produced by the radiation. For the purposes of this discussion we will consider separately annealing by gamma rays and by fast neutrons.

1. Gamma Rays

Moderately energetic gamma rays lose their energy entirely by interacting with electrons. At low energies the most important interaction is the photoelectric effect, while at energies ~1 Mev, Compton scattering dominates. The maximum energy which a Compton electron of energy E can transfer to an atom of mass M is

$$E_{\max} = \frac{2E(E + 2mc^2)}{Mc^2} \tag{42}$$

where m is the electron mass and c the velocity of light. Provided that the energy necessary to displace an atom, E_d, ~ 25 ev, it can be seen that a Compton electron of energy 0.41 Mev can displace an atom of mass 50. This is about the average energy of the Compton electrons from interactions of ~1 Mev gamma rays (for example, from a cobalt-60 gamma-ray source).

However, the cross section for such displacements is small and thus the number of bonds ruptured in this manner is small compared to the number ruptured by electronic excitation and ionization of the molecules by Compton electrons. A Compton electron is pictured as losing its energy in local "hot spots," corresponding to the production of secondary electrons of energy ~100 ev. These secondary electrons dispose of their energy in a volume containing of the order of 100 molecules. At the beginning of the range of the Compton electron, the hot spots will be spaced several thousand Ångstroms apart, but by the time the energy has dropped to 1 kev, the spacing may be only 50Å.

The problem suggested by these data is whether radiation annealing is due to the local high temperatures in the hot spots or to the enhanced probability of recombination owing to the increased supply of ions, free radicals, or electrons produced by the radiation.

The first of these alternatives may be approached in the following manner. While part of the energy of the secondary electron is used in bond rupture, most of it ultimately appears as heat. We can calculate the average energy dissipated per molecule when the solid has received a sufficient dose of radiation to anneal about half the recoil atoms. In typical cases this requirement is about 5×10^7 r. Such a dose corresponds to an energy dissipation of 3×10^{21} ev/gm or about 1 ev/mol. Under these conditions every radioactive atom is included once, on the average, in a hot spot of 100 ev. Since 1 ev is the order of magnitude of the activation energy to be expected for typical annealing reactions, it is seen that this simple thermal spike mechanism probably would suffice.

The second mechanism is recombination of the recoil atom with ions or radicals produced by radiation. Because of the weaker intermolecular forces in molecular crystals, individual excited molecules are relatively more isolated and will decompose into fragments (usually free radicals) more readily than in ionic crystals. Assuming that 10 ev are necessary to produce a free radical pair in a molecular crystal, about ten such pairs would be produced per 100-ev hot spot. Since we have seen that for doses of 5×10^7 r every radioactive atom is included once, on the average, in a hot spot, it follows that every radioactive atom will have a good probability of being found in the vicinity of a free radical at least once. Although most of the free radicals would recombine with one another their concentration would probably still suffice to make this second mechanism an attractive possibility.

A third mechanism involves the movement of electrons resulting from the ionization produced in the crystal by gamma rays. Electrons released in this way may be captured relatively far away, and capture by defects could be of importance in ionic crystals. In general radiation, like thermal, annealing leads to an increase in the observed oxidation state of the radioactive atoms whereas capture of electrons would reduce the oxidation state. However, if partial neutralization of excess positive charge was a necessary requirement before the recoil species could anneal, electron movement might still play a role.

The rate of radiation annealing in potassium bromate (*21*) and chromate (*35*) has been found to depend on the temperature. Ordinary thermal annealing was negligible over the range of temperatures employed. The results suggest that there is an energy of activation, of the order of 8 kcal/mol, associated with the radiation annealing process. The fact that this process is temperature-dependent shows that the energy put into the crystal by gamma rays is effective in annealing when it has been degraded to quite a low level, or diffused widely. This conclusion supports both the second and third mechanisms proposed above, since the activation energy could apply in either case to the free radical recombination in the vicinity of the hot spot. If the radiation annealing occurred in a near-hit, high-temperature process, the rate of such annealing would not be affected by a small change in the ambient temperature.

2. Fast Neutrons

In contrast to gamma rays, fast neutrons lose their energy entirely by nuclear interactions, producing knocked-on atoms of maximum energy

$E_{\max}$ given by

$$E_{\max} = \frac{4M}{(M+1)^2} E \tag{43}$$

where M is the mass of the knocked-on atom and E the neutron energy. Thus a neutron of only 325 ev can displace an atom of mass 50 (if the displacement energy is 25 ev). These displaced, knocked-on atoms, unless very light, lose energy by collisions and not by ionization. Each energetic atom will initiate a hot zone with its attendant thermal effect, as described in Section I, and in such zones annealing could take place by any of several mechanisms. A process of particular importance in organic Szilard-Chalmers systems is the knocking-on of protons. These will lose energy by ionization as well as collision, and this should produce effects similar to gamma-ray annealing. Unfortunately there are as yet no experimental data on the annealing effects of a pure fast-neutron flux although such experiments are, in principle, easily carried out.

D. Discussion and Comparison with Experimental Data

If we are to compare the results of recoil atom annealing experiments with studies of the annealing of radiation damage it should be recognized at the outset that the chemical studies, by reason of the valence and bonding changes involved, are examining somewhat more complex systems. Still, the analogous isothermal curves of the annealing of Szilard-Chalmers recoils on the one hand and the annealing of optical centers, resistivity, or density changes on the other, all as a function of time of annealing, show such a surprising similarity in shape, viz. a rapid initial rise followed by a slowly rising "plateau," with the extent of initial rise governed by the temperature, that one is tempted to apply analogous theoretical treatment to the data, and to assume that one is observing in both cases something characteristic of crystals in general.

Several studies have revealed the complexity of typical chemical crystalline systems in regard to annealing. The work of Aten *et al.* (*5*) showed that recoil of iodine in KIO_4 led to a distribution of activity in unheated samples as follows: $I^- - I_2$ activity 10%, IO_3^- 86%, and IO_4^- about 4%. However, on annealing it was found that the $I^- - I_2$ activity passed over into IO_3^- below 100°C, with no further production of active periodate. This process was essentially complete for annealing times of 15 min at 100°C. In the range 100-240°C the iodate activity began to pass over to periodate, showing the usual shape of annealing curve with temperature-dependent plateau.

Similarly, in the case of Sharman and McCallum's (*74*) studies of recoil reactions of carbon in anhydrous sodium carbonate it was found that different products (produced by dissolving the irradiated crystals in water) began to disappear at quite different annealing temperatures. Such results as these are a clear indication that several types of fragment loci, having different annealing characteristics (very likely different activation energies), exist in the irradiated crystal. The case of potassium periodate cited above is rather good evidence for stepwise addition of oxide ions. Evidence for similar effects at a single annealing temperature was found by Maddock and Sutin (*52*) (stepwise addition of phenyl radicals to arsenic fragments) and by Rauscher and Harbottle (*66*) (addition of cyanide to cobalt fragments).

The most extensively studied crystalline Szilard-Chalmers system is potassium chromate, where the annealing of recoil chromium has been measured for a number of temperatures, over wide ranges of time (*31, 50, 53, 54*). Although stepwise addition of oxide ions probably also occurs here, there are arguments, based upon the chemistry of hexavalent chromium, for thinking that only one of these influences the observed retention, and hence that the kinetics refer to a single elementary annealing process; Eq. (6). This, combined with the great thermal stability of K_2CrO_4 and long lifetime ($t_{1/2} = 27$ days) of the radioactive chromium, make it a most valuable system for study.

In various sections above we have discussed the simple kinetic schemes, some of which have been applied to experimental data on annealing of recoil atoms. For example, it was thought at first (*91*) that the kinetics of cobaltic trisethylenediamine annealing obeyed a linear combination of two unimolecular terms. Further analysis (*53*) has shown that this interpretation was probably in error, and also that the potassium chromate and bromate data could not be fitted by a small number of simple exponential terms. We have also attempted to fit the potassium bromate and cobaltic trisethylenediamine data by the error-function expression suggested by Fletcher and Brown (*10, 27*), see Section B1d above, and although the fit is reasonably good over portions of the isothermal curves, the point of inflection near the time-zero axis in the error-function expression is not observed experimentally.

The easiest analytical test for annealing data for which discrete activation energies are assumed is that given in Section B4 above. One constructs a composite annealing curve from all the data and then attempts to fit this curve by the appropriate expressions for the chosen order of reaction γ, or by the error-function expression, or combinations of these. Examples of such fits are given for radiation damage in germanium (Fletcher *et al.*, *27*) and in magnesium oxide (Clarke, *17, 19*). Both these cases are shown in a recent paper by Clarke (*17*). We have applied this method to some of Zuber's cobaltic trisethylenediamine data

(*91*): the composite annealing curve is shown in Fig. 7 and is there fitted fairly accurately by a single bimolecular ($\gamma = 2$) expression, Eq. (19). The interpretation of this result might be that the annealing rate, $-dn/dt$, is proportional to the density of interstitials times the density of "vacancies" multiplied by the volume of the spherical region containing the first shell of groups around the region of disorder. Such an interpretation suffers from the fact that it is difficult to visualize what physically constitutes an "interstitial" and a "vacancy" in such a complex system. It is, however, interesting that bimolecular kinetics have been found in several other cases of thermal annealing (*7, 62*).

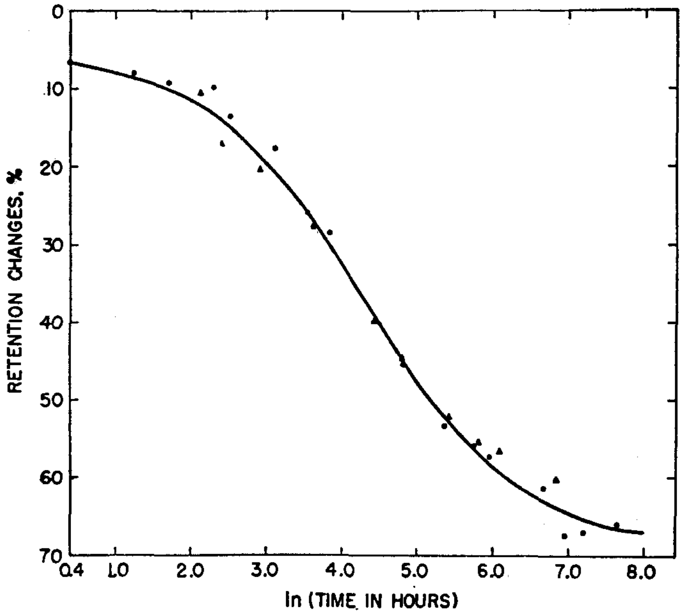

FIG. 7. Composite annealing curve of recoil atoms in cobaltic trisethylenediamine, data of Zuber (*91*). Line is a bimolecular fit.

In the case of the potassium chromate data the composite annealing curve approach does not work at all. One cannot even approximately get all the annealing data onto a single curve of retention against $\ln t$ by merely shifting the $\ln t$ scale. This difficulty was observed by Mrs. de Maine in her thesis (*53*) for short-term annealing data and we have found the same result if we consider only the long-term annealing curves (*54*). Also, a plot of $\ln t$ versus $1/T$ for a constant degree of annealing—see Eq. (34) and (35)—does not yield a straight line when applied to the chromate data. These results indicate that some other interpretation should be sought.[4]

We shall first discuss the explanation given by Maddock and de Maine (*49, 50*). Their proposal, which is described in Section B1b above, satisfactorily accounts for the linear relationship that has been observed, not only in the case of potassium chromate but for several other systems as well, between the change in retention on annealing to the plateau, ΔR_e and 1/T. Their formalism also explains the observation that, when one has annealed to the plateau characteristic of temperature T_1, an increase in temperature from T_1 to T_2 causes a new rapid "growth" to occur, tapering off at the new plateau characteristic of temperature T_2.

This model may be criticized, however, on the following grounds: (1) There is an assumed uniform distribution of fragment spacings between the minimum and maximum separations (X_0 and X_∞ in Fig. 3). This assumption is necessary to establish the linear relationship between ΔR and X (Section B1b above). (2) There is also the question of the potential V, Eq. (7). Although it is not necessary for V to be electrostatic, as was argued in the case of potassium chromate, it is required that the potential lead to a term $1/X$ in the second exponential term in Eq. (7). In the annealing of molecular solids, it seems probable that neutral atoms and radicals recombine. One can still assume that the potential V comes from the strain field of the crystal, in such a way that a $1/X$ dependence is obtained, but in view of the large repulsive forces acting on an interstitial in a lattice such a dependence would be fortuitous, particularly since such terms usually go as a rather high power of X. (3) The recent results on the slow part of the annealing process in potassium chromate by de Maine *et al.* (*54*) show that, following the initial rapid rise, the retention increases slowly and linearly to 100%. According to Eq. (8), with the second exponential term effectively unity the final slow process should be an exponential fall of the quantity $(100 - R_t)$ to zero with time. What was experimentally observed was a kinetic law

$$-dn/dt = k \qquad (44)$$

where k is a zero-order rate constant with an apparent activation energy of about 4 kcal/mol. It seems to be inherent in the Maddock-de Maine model that $-dn/dt = kn$, and it is difficult to see how zero-order kinetics could be accommodated.

The Vand-Primak treatment of annealing kinetics, in which the energy

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[4] The discrete activation energy case [Eq. (31) and (32)] predicts that if $\gamma = 1$ a plot of ln $[\ln(p_0/p)]$ against $1/T$ should yield a straight line, for fixed times of annealing. Such a linear relationship is not obtained when potassium chromate data are used.

of activation is assumed to have a continuous distribution of values, has been discussed in general terms in Section B5 above. As pointed out by Clarke (*18*) it can also be invoked to explain the potassium chromate annealing data. On this view, the rapid rise to the pseudo-plateau corresponds to the rapid initial movement of the function θ_γ over that portion of the activation-energy spectrum which contains the lowest values of E (see Fig. 6). The dependence of the position of the plateau on temperature arises from the linear dependence of E_0, the position of the point of inflection of $\theta\gamma$, on T, the absolute temperature as expressed in Eq. (37), for constant time of annealing. The portion of the spectrum annealed first is presumably identified with close interstitial-vacancy pairs, whose energies of activation are materially reduced by the attendant lattice strain. Then the slowly rising portion of the pseudo-plateau represents events of only slightly larger activation energy. If we compare the curves reproduced in Clarke's paper for the annealing of radiation damage in germanium (*27*), silica (*65*), and magnesium oxide (*17, 19*) with the potassium chromate data (*50, 53, 54*) the same general features, a rapid rise to a pseudo-plateau depending on temperature, followed by a slow upward movement are seen. The only possibly unique feature of the latter data is the zero-order approach to complete annealing. The data of Overhouser (*62*) on the annealing of radiation damage in copper from −123°C to 33°C also show a number of these plateaus.

On this view, it would seem that in general Szilard-Chalmers experimentation has been directed at the theoretically less interesting feature of the annealing curve, namely the rapidly rising part; whereas solid-state research has dealt with the kinetics of what the chemists have considered as the plateaus of their curves. It is unfortunately not always easy to obtain reliable data for long-term annealing in Szilard-Chalmers systems. The half-life of the radioisotope employed is frequently too short, and in addition the crystalline compound investigated may be thermally unstable. As mentioned above, potassium chromate is a particularly favorable case in that neither of these difficulties interfere.

We have applied the Primak treatment to the potassium chromate annealing data of de Maine *et al.* (*54*). The value of $\ln B$ was chosen as 18.5 to give the best fit. The "spectrum" obtained (Fig. 8) does not at first sight look very promising, but this is in part due to the great sensitivity of the method to experimental error and to the rather close spacing in temperature of the isothermal annealing curves, since the resolution of the method is only of the order of 3 kT. The steeply rising slopes at the low-energy side should be compared, for example, with the similar portion of Primak's spectrum for silica (*65*): it will be seen that the behavior of the slopes is similar. About 10% of the spectrum of

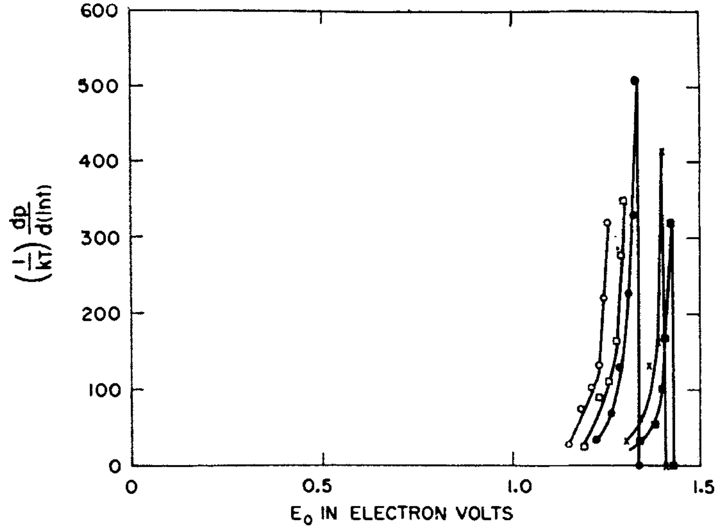

FIG. 8. The initial distribution of activation energies in the Szilard-Chalmers reaction in potassium chromate; p_0 (E_0) against E_0 in electron volts.

annealable chromium (i.e., of those centers whose annealing reactions can be followed) lies to the left of the curves shown in Fig. 8. The data seem to indicate a cutoff in the neighborhood of 1.4 ev, that is, there are no processes of higher activation energy.

At this point it might be of interest to turn the argument about, assume a simple distribution of activation energies and see to what this leads. We shall assume that in potassium chromate about 90% of the activation energies of the annealing process are uniformly distributed between 1.10 and 1.42 ev, i.e. the distribution of activation energies is flat between those two values. Then the increase in retention ΔR for a constant time of annealing will vary linearly with E_0, the position of the point of inflection of the annealing function θ_γ [Eq. (37) and Fig. 6] and the increase in retention to the plateau (for example, at a constant 20 hours heating) will vary linearly with T, the absolute temperature. A plot of ΔR against T, where the values are those taken from Maddock and de Maine, is given in Fig. 9. A flat distribution of activation energies is not entirely inconsistent with the Primak-spectrum plot of Fig. 8, and as an *ad hoc* choice may be compared to the assumption of a uniform distribution of fragment spacings X in the Maddock-de Maine treatment (Section B1b above).

Maddock and co-workers (*53*, *54*) have also studied annealing processes in mixed crystals of potassium chromate-fluoberyllate in which

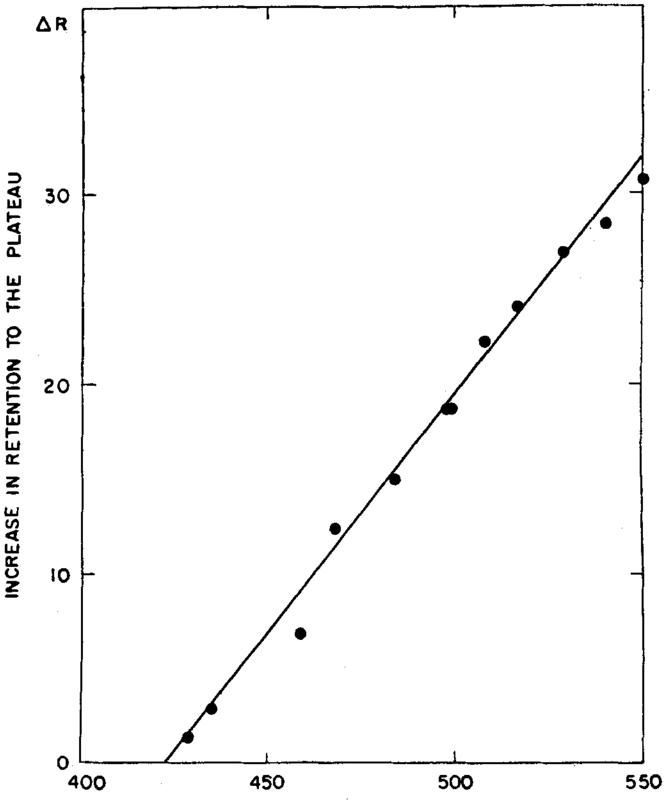

FIG. 9. The increase in retention to the plateau, ΔR, plotted against T, the absolute temperature, for potassium chromate.

the potassium chromate was very dilute (~ 1 mol per cent). The annealing curves are quite similar to those of pure potassium chromate, but rise more steeply near the origin of the time scale. This could be interpreted to mean that the spectrum of activation energies is similar in shape but that a portion of it lies shifted to lower values of E_0. The fact that the recoil chromium species anneal so readily in the dilute mixed crystals is perhaps evidence that the annealing reaction is largely a local phenomenon; i.e. that original partners recombine. It would obviously be of interest to study other similar systems, for example in which potassium bromate or iodate were diluted.

It has recently been observed (*41*) that atoms of two different isotopes of the same element do not exhibit identical annealing behavior. In particular, it was found that Br^{82} recoil atoms annealed more rapidly than

Br^{80m} atoms in neutron-irradiated alkali bromates. Presumably this difference arises from a slight shift of the spectrum of activation energies to lower values in the case of recoiling Br^{82} atoms. Whether this shift is due to differences in the recoil energy or in the average charge of the radioactive bromine, the interesting fact remains that the spectrum of activation energies is not uniquely determined by the crystal and the interstitial atom, and that isotopic atoms of the same element, at rest in the same crystal, can be associated with two different spectra. The Maddock-de Maine model can also account for an isotopic annealing difference, by assuming that the two isotopes have different average fragment spacings X [Eq. (7) and Fig. 3], for example, by virtue of different recoil energies.

When samples of crystalline compounds are subjected to pile neutron irradiation it has frequently been found that the larger the integrated flux the higher the initial retention. Such an effect is the result of radiation annealing (see above). However, it has now also been observed (*53, 54, 77*) that on thermal annealing of such crystals, the more heavily damaged anneal the more rapidly, arriving at a higher retention plateau for the same isothermal annealing time, or reaching 100% retention at a shorter time. Such effects are perhaps the result of a general downward perturbation of the spectrum of activation energies of the radioactive recoil atoms *in the* presence of the large number of additional defects introduced by pile irradiation. This effect has been mentioned in Section B6 above, and might operate with even first-order annealing reactions. If the kinetics were higher than first order then annealing would of course be accelerated even without perturbation in the activation energy. The Primak treatment of the potassium chromate annealing data indicated that for a sample bombarded one week at a flux of 10^{10} neutrons/cm^2/sec the top of the activation energy spectrum fell at about 1.42 ev. Our calculations taking the annealing data of de Maine indicate that for a sample which was irradiated one week at 5×10^{11} neutrons/cm^2/sec the top of the spectrum would be displaced downward to about 1.24 ev. It would be of great interest to carry out similar studies in which the crystals were heavily radiation-damaged, for example by fast neutron or other heavy-particle bombardment, before introduction of the Szilard-Chalmers atoms.

Although we have not distinguished between ionic and molecular crystals in the above discussion, for the reason that the latter also show typical thermal annealing effects, it is possible that their annealing reactions may be discovered to arise from quite different mechanisms. If we take the ratio T_a/T_m as a measure of the tendency of a crystal to anneal recoil atoms, where T_a is the absolute temperature at which annealing is half-complete in 10 min, and T_m is the absolute melting point, we find that whereas most inorganic, ionic crystals have values of T_a/T_m in the range of 0.4 to 0.6 (including several cases of annealing of simple radiation damage) the three organic crystals that have been studied fall in the range 0.8 to 0.95. It seems significant that this range of T_a/T_m (0.4 to 0.6) in ionic crystals brackets the ratio of the Tamman temperature to the melting point (defined as 0.5). The Tamman temperature is frequently taken as a rough indication of the temperature at which lattice diffusion becomes appreciable (*81*). It was found by Andrew (*2*) in his nuclear magnetic resonance studies of self-diffusion in molecular solids that the latter showed several stages of increasing agitation below the melting point, culminating in a form of molecular movement which could be identified as diffusion of whole molecules throughout the lattice. In cyclohexane, this occurred at 220°-240°K, which temperature is about 0.82 of the melting point. A loosening of the lattice sufficient to promote diffusion of whole molecules would certainly be expected to have a profound effect on the annealing by recombination of recoil atoms or fragments in molecular solids.

IV. Conclusion

We have hoped in this article to accomplish a twofold purpose. On the one hand we wished to make available to investigators of the Szilard-Chalmers reaction and associated recoil effects some of the results of recent work in solid state physics, in particular that part of the latter dealing with the study of radiation damage. In this way a fresh light could perhaps be cast on some of the work progressing in this now classic field of radiochemistry. On the other hand we wished to call to the attention of workers in the field of radiation damage the existence of chemical data bearing upon, and in some cases giving unique answers to, questions of interest to them.

V. Appendix

A. Rate of Increase in Retention Due to Recrystallization of Spherical Zones, Eq. (16)

Subject to the assumptions (1) to (4) listed in the text (Section 1e) let r_0 = initial radius of the disordered spherical zone, r = radius at time t, v = linear velocity of motion of phase boundary, N = number of zones (each containing one recoil atom) present initially, and n = number of recoil atoms uncombined at time t. The probability of recombination in any given disordered zone, P, per second is then

$$P = \frac{v4\pi r^2}{(4/3)\pi r_0^3}$$

and since $r = r_0 - vt$ we have

$$P = \frac{3v(r_0 - vt)^2}{r_0^3}.$$

Since $-dn/dt = (1/K)dR/dt = NP$, where K is a constant and R the retention, we have

$$\frac{dR}{dt} = KN \cdot \frac{3v}{r_0^3}(r_0 - vt)^2 = R_\infty \cdot \frac{3v}{r_0^3}(r_0 - vt)^2.$$

Integrating

$$\frac{R_t}{R_\infty} = \left[1 - \left(1 - \frac{vt}{r_0}\right)^3\right]$$

at $t = 0$, $R_0/R_\infty = 0$, and at $t = r_0/v$, i.e., complete recrystallization, $R/R_\infty = 1$.

B. Derivation of Rate Law for Exchange, Eq. (20)

The radioactive recoil atom X^* is assumed to be trapped in the midst of c inactive neighbors AX. All sites are identical. As annealing proceeds, X^* can exchange with any neighboring AX to give AX^* and X, and the process is reversible. Let ν be the frequency of exchange per group. If the number of active (X^*) atoms be $n(X^*)$, etc., then

$$n(X^*) + n(AX)^* = n \text{ (conservation of active atoms)}$$

$$n(X) + n(X^*) = n$$

$$n(AX) + n(AX)^* = c \cdot n$$

where n is the total number of sites. The frequency with which exchange processes occur through the sample is then $n\nu$.

The rate of disappearance of X^* is then

$$-\frac{dn(X^*)}{dt} = n\nu\left[\frac{n(X^*)}{n(X) + n(X^*)} - \frac{n(AX^*)}{n(AX) + n(AX)^*}\right]$$

which reduces to

$$-\frac{dn(X^*)}{dt} = \frac{\nu}{c}[(c + 1)n(X^*) - n].$$

Integrating this and putting in boundary conditions we obtain

$$n(X^*) = \frac{cn}{(c + 1)} \exp\left[\frac{-(c + 1)}{c}\nu t\right] + \frac{n}{c + 1}$$

i.e. $$n(X^*) - n(X^*)_\infty = c \cdot n(X^*)_\infty \exp\left[\frac{-(c + 1)}{c}\nu t\right]$$

where the subscript $_\infty$ refers to infinite time. In terms of retentions

$$\frac{R_\infty - R_t}{1 - R_\infty} = c \exp\left[\frac{-(c+1)}{c}\,\nu t\right].$$

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LISTS OF SYMBOLS

α	Constant relating the number of defects to the change in activation energy
γ	Order of reaction
ν,ν_j	Jump frequency of interstitial atoms
ν_0	Frequency of vibration of atoms in a lattice
τ	Average jump time ($1/\nu_j$; see ν_j above)
θ_γ	Characteristic annealing function, Vand-Primak model
A,A_a	Frequency terms
a	Sink radius, Fletcher-Brown model
B	Constant containing the frequency A
b	Initial pair separation distance, Fletcher-Brown model
c	Number of neighboring groups, exchange model; also, velocity of light
D	Diffusion coefficient
E	Activation energy, also, energy of a neutron or Compton electron
E_a	Activation energy, Hartshorne expression
E_d	Energy to displace an atom to an interstitial position
E_{max}	Maximum energy of recoil from a Compton electron, or from a neutron
E_0	Characteristic activation energy, Vand-Primak model; also, activation energy for isolated defects, Dienes' treatment
f	Constant relating measured property due to defects, and number of defects
k	Boltzmann's constant (usually as kT); also, a rate constant
l	Lattice constant
M	Atomic mass
n	Number of interstitial atoms, or uncombined pairs
n_0,n_t	Same as n, but at time zero and t, respectively
P_t	Same as p_t, but relating to variable energy of activation case
p,p_0,p_t	A property whose magnitude depends on the number of defects, and the same at time zero and t, respectively
$p_0\ (E)$	Initial distribution of properties p
$p_0\ (E_0)$	Same as $p_0(E)$, but denoting that a step-function approximation has been taken for θ_γ
q	Heat of transformation of crystalline phases

R	Retention (see footnote 3)
R_0, R_t, R_∞	Retention at time zero, t and the final, limiting value
ΔR_e	Change in retention from start of annealing to the plateau, Maddock-de Maine model
r, r_0	Radius of spherical disordered zone, and the initial value of the same radius
T	Temperature (°K)
T_a	Characteristic annealing temperature (°K) (temperature necessary to anneal one half the defects in ten minutes)
T_m	Melting point of the crystal (°K)
t	Time
U	Activation energy, Maddock-de Maine model
V	Electrostatic potential, Maddock-de Maine model
v	Velocity of movement of phase boundary, recrystallization model
X	Distance of separation of recombining pairs, Maddock-de Maine model

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