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CHEMICAL EFFECTS OF NUCLEAR TRANSFORMATIONS IN SOLIDS (CHEMICAL CONSEQUENCES OF NUCLEAR RECOIL)

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I. INTRODUCTION

Many features of the chemical processes accompanying nuclear transformations are still obscure, and far from adequately interpreted in the literature. The ever increasing number of new facts, and the difficulty of interpreting the results, which characterise studies of this type, by pointing to the weakness and contradictions of the conventional inorganic chemistry of, apparently, even the most thoroughly investigated elements, such as manganese, chromium, phosphorus, bromine, iodine, etc., stimulate new work in different branches of chemistry. Among the

problems being re-examined are disproportionation, complex formation, the stability of intermediate valencies, the reactions of polyvalent radicals with water, and many more. There is an obvious need for more detailed studies of these phenomena, and of all the stages involved in the interaction between materials; more exact models are also needed for processes which are at present only generally (*i.e.* only approximately) understood. A detailed knowledge of the chemical effects of nuclear transformations would offer deeper insight into some relatively new branches of chemistry, such as "hot atom" chemistry, solid state chemistry, radiation chemistry, etc.

No less important is the applied side of these problems: the enrichment and separation of radioactive isotopes, the production of carrier-free radioactive isotopes, the "hot" synthesis of various labelled compounds, etc.

Existing review articles in Russian deal, on the whole, with the organic aspects of this problem[1-5]. In the present article we shall be mainly concerned with chemical processes resulting from nuclear transformations in ionic crystals. We shall examine, in particular, the after-effects of nuclear reactions, with special emphasis on neutron capture reactions.

II. THEORETICAL CONCEPTS

Atoms produced in solids by nuclear reactions or by radioactive disintegration possess energy in excess of the thermal vibration energy of the crystal lattice. As a result, their chemical properties differ from those of the same atoms under normal temperature conditions. Atoms with high energy parameters have been called "hot atoms", and reactions involving such atoms have been called "hot reactions" or Szilard–Chalmers reactions (or effects).

According to their origin, "hot atoms" may possess varying degrees of excitation, which may influence their subsequent chemical fate. It may not be out of place, therefore, to discuss at this stage problems such as the magnitude of the energies acquired by atoms as a result of nuclear transformations, the origin of these excited states, and their influence on the chemical behaviour of hot atoms.

1. Nuclear Recoil as a Source of Atomic Excitation

In 1934 Szilard and Chalmers noticed[6] that radioactive iodine can be extracted by water from ethyl iodide which has been irradiated with neutrons. They ascribed the phenomenon to an "impact" effect of the neutrons, which they envisaged as a transfer of momentum from the neutron to an iodine atom, causing the radioactive iodine atom to be ejected from its parent molecule. This hypothesis was later refined by Fermi and coworkers[7], who showed that the "recoil" of the γ-quantum, produced in accordance with the law of conservation of momentum during neutron capture, is sufficient to overcome the chemical binding forces of the atom undergoing the nuclear reaction (called the recoil atom), and to convert it into a new chemical state. The magnitude of the recoil energy acquired by the hot atom depends on the type of nuclear reaction and on the mass of the recoil atom. In (n, γ) reactions the recoil energy amounts to tens or hundreds of electron-volts; in reactions causing the emission of heavy particles (including photonuclear reactions) the recoil energy can rise to tens or hundreds of kiloelectron-volts.

During radioactive disintegration, recoil energies reach the latter values only if α-particles are emitted. In β-emission, as a rule, the recoil amounts to a few eV, and in isomeric transitions or electron capture it can be as small as 10^{-2}–10^{-1} eV.

The recoil energy acquired by an atom as a result of nuclear processes is dissipated in breaking the chemical bonds holding it in the original molecule, and in imparting some kinetic energy to the excited atom. Since the energies of chemical bonds are usually of the order of a few eV, it is obvious that the majority of nuclear reactions will result in bond breaking, with the hot atom left in a "free" state. We shall be mainly concerned with cases where the recoil energy is sufficient to break chemical bonds. Radioactive disintegration processes, with the exception of α-emission, are characterised by low recoil energies which cannot rupture chemical bonds. These processes also produce hot atoms, but in this case the excitation is of quite a different type, and calls for separate detailed discussion.

2. Energy Loss Processes Available to Recoil Atoms

In 1947 Libby[8] put forward a model according to which the recoil atom loses its kinetic energy exclusively as a result of elastic interactions with lattice atoms, the interactions being treated as collisions between billiard balls (rigid spheres). Libby's model requires the acceptance of the following propositions[4]: (a) the energy of the recoil atom is set free after a few collisions with lattice atoms, over a path amounting to a few Ångstrom units; (b) the sudden evolution of a large amount of energy (up to several keV) raises the temperature, locally, to 10^6–10^7°K, causing melting and partial intermingling of the material in a volume comprising $\sim 3 \times 10^5$ atoms; (c) the molten region exists for a time of about 10^{-8} s, and this is sufficient for thermal equilibrium to be established and for many chemical processes to occur in the molten region, since the normal lattice vibration period is $\sim 10^{-13}$ s; (d) in view of the high mobility and of the disorder of the atoms in the melt, we can expect lattice atoms originally quite remote from the recoil atom to influence its chemical fate; (e) the distribution of recoil atoms over various chemical forms must be in keeping with the initial recoil energy of the hot atom, *i.e.* with the type of nuclear reaction.

Without rejecting Libby's model outright, we may suggest that Harbottle and Sutin's model[9] of the "hot" zone is more consistent and well-founded. It is firmly based on the concepts of solid-state physics[10-13] derived from the work of Seitz and Koehler, and concerned with the motion and retardation of charged particles in a crystal lattice.

The hot atom, endowed with some kinetic energy, will penetrate a certain distance through the solid, losing its energy as a result of interactions with the surrounding medium. The nature of the interaction varies continuously during the atom's excursion, since it is in some way related to the kinetic energy.

All the collisions suffered by the atom can be divided into two categories: elastic collisions and inelastic collisions. Elastic collisions are those in which the total kinetic energy of the moving and the fixed atom is conserved; inelastic collisions are characterised by a loss of kinetic energy, resulting from electronic excitation and ionisation.

Whereas the only role of the electrons in elastic atomic collisions is to screen the nuclear charges to a greater or lesser extent, in inelastic collisions the moving atom interacts directly with an electron of the target atom, promoting the electron to an excited state, or even dislodging it from its orbital, and thus causing ionisation of the medium along the track of the recoil atom. Similarly, electrons of the recoil atom are extracted from their orbitals by the electrostatic field of the target atoms, and the moving atom can thus be freed of all or some of its outer electrons. Direct interactions of this kind between atoms and electrons are, of course, only possible when the recoil energy is large and the orbital velocity of the electrons is comparable with the velocity of the recoil atom. Seitz [10] gives the following expression for the limiting kinetic energy leading to ionisation, E_i:

$$E_i = \frac{1}{8}\left(\frac{M}{m}\right)\varepsilon_i, \qquad (1)$$

where M and m are the masses of the recoil atom and of the electron respectively; ϵ_i is a quantity of the same order as the energy gap between the valence band and the conduction band for the case of ionisation of the target atoms. If we are interested in the possibility of ionisation of the neutral recoil atoms, we equate the energy term ϵ_i to the ionisation potential of the recoil atoms in the gaseous state. Limiting ionisation energies for recoil atoms of different masses are set out in Table 1.

If the energy of the recoil atom is $E \geq E_i$, it is dissipated mainly in the ionisation and excitation of electrons from the target and the moving atom. When the recoil energy drops to $E < E_i$, ionisation ceases, but electron excitation can still take place, because exciton energies are lower than the corresponding ionisation energies, and the limiting excitation energy is several times lower than the limiting ionisation energy E_i. Lastly, if the energy of the recoil atom is less than the limiting excitation energy, the electron clouds begin to react adiabatically on the close approach of atoms, and all further energy losses by the moving atom occur *via* elastic collisions with lattice atoms. The electrons set free in the early stages may be collected by the recoil atom as long as the latter's electron affinity remains higher than the ionisation potentials of the lattice atoms.

We must distinguish two energy regions in which a moving atom can lose energy as a result of elastic collisions: the Rutherford scattering region and the region of scattering according to the laws of rigid spheres.

The main difference between the two kinds of collision lies in the different degrees of screening of the nuclear charges by the electron clouds. In the Rutherford region, corresponding to a high kinetic energy of the recoil atom, there is deep mutual penetration of the electron clouds, *i.e.* small screening of the positive nuclear charges. When a "rigid sphere" impact takes place, on the other hand, the mutual repulsion of the electron shells exceeds the kinetic energy of the moving atom. Under these conditions the electron shells do not interpenetrate, and screening is complete. It is obvious that the transition from one kind of scattering to the other takes place gradually, as the moving atom loses kinetic energy, and that there must be a fairly wide intermediate energy region within which neither mode of scattering occurs to the complete exclusion of the other.

TABLE 1. Limiting ionisation energy of neutral recoil atoms

Recoil atom	Atomic weight	ϵ_i, eV	E_i, keV
C	14	11.26	36.06
P	32	10.55	77.65
Co	60	7.86	109.17
Br	80	11.84	217.86
I	127	10.44	304.9

It follows directly from the absence of screening that collisions of this type between two atoms, in which a significant fraction of the energy of the moving atom is transferred to the lattice atom, must have a small effective cross-section. If the energy given by the collision to an atom of the medium exceeds the threshold displacement energy E_d, estimated as 25–30 eV, the elastic collision will displace the stationary atom from its crystal lattice site. If energy considerably in excess of E_d is transferred during the collision, the displaced atom produces secondary displacements, which give rise to a whole shower of displacements.

It can be shown that in the Rutherford scattering region the effective cross-section for displacement, σ_d, is smaller than the geometrical dimensions of the atoms, leading to a large mean free path (~ 100 Å) of the recoil atom between collisions able to displace lattice atoms.

As the atom slows down, and its store of kinetic energy decreases, the effective cross-section for displacement σ_d increases, and reaches a maximum in the region where collisions occur by the rigid sphere mechanism. The free path of the recoil atom correspondingly decreases, tending towards the interatomic distance.

To discuss this problem in greater detail, we must introduce the concept of the "temperature spike". [10,11] The temperature spike is a well defined region within the solid, in which the amount of energy scattered is sufficient to heat the atoms above the temperature corresponding to the normal thermal vibrations of the lattice (~ 0.03 eV). The dimensions, lifetime, and maximum temperature of this hot region are a function of the amount of scattered energy and of the thermal conductivity of the medium.

We can distinguish two types of temperature spike: "displacement spikes" and "thermal spikes". The difference between them is that more energy is scattered in the former, this energy being introduced mainly through a chain of displacements triggered off by the recoil atom. This leads to fusion and mixing of the material in the displacement spike, which includes (according to Brinkman [14,15]) several thousands of atoms. After a short time (a few tens or hundreds of lattice vibrations) the displacement spike cools down and "freezes", and the displaced atoms which have not been able to find correct lattice positions are quenched into a state of complete disorder.

If the energy transferred to a lattice atom is insufficient to cause a chain of displacements, and only few atoms are expelled from their sites, the region is called a "thermal spike". A thermal spike is formed also when the energy transferred to a lattice atom by a collision is less than the threshold energy for displacement, E_d. In this case the excitation is conveyed to the surrounding crystal lattice by large-amplitude vibrations of the lattice atom having suffered the collision, which cause vibrational excitation of other particles of the solid. Both phenomena (thermal spike and vibration spike) are analogous to the rapid heating

of a confined volume to a high temperature (sufficient to "melt" 5–10 atoms), followed by rapid cooling as the heat diffuses into the bulk of the crystal.

Displacement spikes and thermal spikes appear all along the track of a recoil atom, as though they were "branching off". In the Rutherford scattering region the temperature spikes are fairly well spaced out (~ 100 Å), and do not form a continuous damaged region. As the recoil atom slows down, it begins to interact with the material at shorter intervals, and after a short time the individual spikes begin to merge. The time required for the excited regions to coalesce in this way is determined by the thermal conductivity of the medium.

By the time the atomic interaction takes the form of collisions between hard spheres the recoil atom has lost most of its initial energy, which becomes scattered over a track of appreciable length (~ 1000 Å) originating where the hot atom was produced. It is in this respect that the conclusions of Seitz and Koehler's review[10] differ most significantly from Libby's model, which requires that the whole of the kinetic energy of the recoil atom, whatever its magnitude, shall be dissipated in a track no more than ~ 10 Å long. This can only be true if the recoil energy is low, when Libby's and Seitz and Koehler's models give identical results. It seems probable, therefore, that Libby's model is a special case of the Seitz–Koehler theory.

It can be shown mathematically that atomic collisions of the hard sphere type have an effective displacement cross-section very close to the geometrical cross-sections of the atoms, and that the mean free path approximates to the interatomic distance[12,13]. In this case the recoil atom must dissipate the last few hundred eV of energy in a few thermal spikes situated close together in the crystal. The distance between these spikes is so small (of the order of the interatomic distance) that after a very short time (a few vibration periods of the lattice atoms) the spikes merge into a single excited region which Harbottle and Sutin have termed the "hot spot".[9] This view of the formation of a hot zone in which the recoil atom is arrested ("sticks") was put forward by the authors in order to describe the chemical behaviour of recoil atoms in solids.

We shall now discuss some quantitative characteristics of the hot zone.

3. Parameters of the Hot Zone

We shall consider the most typical nuclear reaction, the n,γ reaction, in which the recoil atom dissipates an energy of ~ 300 eV in the hot zone. We have to determine the number of displaced atoms in a thermal spike of this energy. If $\nu(E)$ is the average number of atoms displaced by an atom of energy E, and $2E_d < E < E_i$, we find both theoretically and experimentally that

$$\nu(E) = \frac{E}{2E_d}, \qquad (2)$$

where E_i is the limiting ionisation energy.

The physical significance of Eqn. (2) is not difficult to see: on the average, one-half the energy of the moving atom goes to produce displacements, each displacement accounting for an energy E_d, whilst the other half of the energy is scattered by collisions in a region below the threshold energy, causing high-frequency phonons to appear in the lattice.

Thus, in a hot zone of energy 300 eV we find 5–6 atoms displaced from their normal sites ($E_d \simeq 25$ eV), which have enabled the recoil atom to dissipate its residual kinetic energy by collisions and come to a halt. The sudden loss of energy in a very short time (~ 10^{-13} s) causes a local rise in temperature, given as a function of time t and distance r from the centre of the zone by the expression

$$T(r, t) = \frac{Q}{2\pi^{3/2}cd} \times \frac{1}{(Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right), \qquad (3)$$

where c is the specific heat, d the density, D the thermal diffusivity (taken as ~ 0.001 cm^2 s^{-1}), and Q is the energy given out by the recoil atom in the hot zone.

Eqn. (3) assumes that the whole of the energy is evolved in a time of ~ 10^{-13} s at the centre of the hot zone, and diffuses away with spherical symmetry. The ratio $r^2/4D$ has the dimensions of time, and characterises the propagation of heat in the zone. At time t, and distance

$$r = \sqrt{4Dt} \qquad (4)$$

from the centre of the zone, the temperature has dropped by a factor of e.

The heat liberated by the hot atom is sufficient to heat ~ 1000 atoms of the crystal lattice to above the melting point. If the melting point is T_m = 1000°K, and the energy expended in melting is $Q \simeq 300$ eV, we have

$$\frac{Q}{3kT_m} \simeq 1000,$$

and the radius of the hot zone, r_m, is ~ $10r_s$, where r_s is the atomic radius, and can be found from the relation

$$\frac{4}{3}\pi r_s^3 = \frac{1}{n_0},$$

n_0 being the number of atoms in 1 cm^3.

From Eqn. (4), assuming a value of $D \simeq 0.001$ cm^2 s^{-1}, we can calculate the time for the spherical thermal spike to spread over this region, of radius $r = 10r_s$ (~ 15Å). The result is approximately 6×10^{-12} s. It readily follows from Eqns. (3) and (4) that after 2×10^{-11} s the radius of the hot zone is 30 Å, and the mean temperature has fallen to 150°. Since by this time the hot zone has effectively ceased to exist, its lifetime works out at about 10^{-11} s, and the volume heated beyond the melting point comprises about 10^3 atoms.

The statement that the material has been heated to above its melting point describes the degree of thermal excitation in the hot zone, but does not necessarily mean that the material has achieved the amorphous structure of a true liquid, because the spreading time (6×10^{-12} s) of the thermal energy in a region of radius $r_m = 10r_s$ is comparable with only a few tens of atomic vibration periods, and is therefore too short to allow the establishment of full thermal equilibrium. Since the temperature of this region rises extremely rapidly, and owing to the influence of the surrounding medium, it is probably best to think of the hot zone as a superheated solid, though melting may actually take place at the very centre.

4. Reactions in the Hot Zone

The highly activated atoms to be found during the lifetime of the hot zone can undergo chemical reactions which are precluded for those same reactants under normal energy conditions. These so-called "hot" reactions do not

depend on the temperature of the medium, and give rise to products which cannot form at thermal energies.

One type of hot reaction is the replacement of a lattice atom by the moving atom upon collision, a process which does not increase the overall number of displaced atoms. Replacement must occur[16,17] if the energy transferred to the target atom is greater than E_d, whilst the recoil atom after collision has an energy less than E_d. This is closely akin to the fluid reaction cell model proposed by Franck and Rabinowitsch[18] and developed by Libby[8,19] and by Miller *et al.*[20]

Replacement will take place also if an atom acquires an amount of energy lying between E_p and E_d (where $E_p < < E_d$), whilst the kinetic energy retained by the moving atom is less than E_d. In this case the recoil atom remains at a vacant lattice site. Kinchin and Pease[21] have estimated a ratio $E_d/E_p \simeq 10$ for alloys, and calculated that 4.7 replacements occur for each displacement. This means that something like 5 out of 6 recoil atoms are captured by the original molecule if all the atoms are identical. In a system containing atoms lighter than the recoil atoms, the proportion of displacements is much higher than 1/6.

We need not confine our attention to reactions resulting from purely mechanical effects: we should also consider typical chemical processes occurring in the localised high temperatures of the hot zone. Due to the high temperature, to the radiation, and to the displacements generated by the moving atom, molecules in the hot zone are dissociated and decomposed with formation of charged or neutral radicals, residues, and recoil fragments. Thus the breaking of the original chemical bonds, the formation of new bonds, the recombination of free radicals, charge transfer effects, and the distortion of electronic structures are the phenomena most likely to occur during the lifetime of the hot zone. Reactions between a recoil fragment and the parent molecule (the so-called ion–molecule reactions), exchange reactions, and diffusional jumps by interstitial or vacancy mechanisms are also possible.

We must now consider the extent to which these reactions can proceed in the short time of $\sim 10^{-11}$ s, *i.e.* during the lifetime of the hot zone. The frequency ν of a chemical process whose free energy of activation is F is given by the expression

$$\nu = \nu_0 e^{-F/kT}, \tag{5}$$

where ν_0 is the frequency factor, equal $\sim 10^{13}$ s^{-1}.

Integration of this expression gives n_j, the number of times the process occurs at the centre of the hot zone:

$$n_j = \int_{t_0}^{\infty} \nu_0 e^{-F/kT(t)}\, dt, \tag{6}$$

where $T(t)$ is obtained from Eqn. (3). For crystals which obey Dulong and Petit's law for lattice vibrations, Seitz and Koehler give the solution

$$n_j = 0.095 \frac{\nu_0 r_s^2}{D} \left(\frac{Q}{F}\right)^{2/3}. \tag{7}$$

For the reaction between a given fragment and another strictly defined fragment, taking Q = 300 eV and F = 1 eV, we find $n_j \simeq 4$. On the other hand, if our fragment is allowed to react with any other fragment, we find $n_j = 4\eta$, where η is the number of independent paths by which the reaction can occur.

Studies of the thermal and radiation-induced annealing of recoil atoms in solids have shown that all these processes do not by any means go to completion during the lifetime of the hot zone. Some of the processes are quenched at some intermediate stage, and additional energy has to be supplied to the system (*e.g.* by annealing) to allow the chemical reaction to proceed. The following effects may cause reduced yields:

a. The fragments are not nearest neighbours, and diffusion in the hot zone is necessary in order to bring them together.

b. As pointed out by Seitz and Koehler, Eqn. (5) applies only to simple atomic crystals. Systems used in studies of the Szilard–Chalmers reactions, which have as a rule a more complicated structure, involve steric factors not considered in Eqn. (5). In such systems Eqn. (5) must be replaced by an equation of the type

$$\nu = \left(\frac{kT}{h}\right) e^{\frac{\Delta S^{\neq}}{k}} e^{\frac{\Delta H^{\neq}}{kT}}, \tag{8}$$

in which the entropy of the activation term, $e^{\frac{\Delta S^{\neq}}{k}}$, allows for steric and other probability factors, the universal frequency $\frac{kT}{h}$ replaces ν_0, and the quantity $\Delta H^{\neq}$ is identified with the activation energy.

It is clear that the quantity $n_{\neq}$ indirectly determines the probability of the process occurring during the lifetime of the hot zone. This probability is higher the lower the activation energy of the process. Thus, for low activation energies of no more than a few eV there is an appreciable probability of reaction between the recoil fragment and its nearest neighbour. When the substance irradiated is pure, the nearest neighbour is nearly always a molecule of the parent compound, which suggests that ion–molecule reactions (*e.g.* exchange reactions) may play an important role during the existence of the hot zone. Such reactions may well be responsible for the wide variety of products obtained from nuclear transformations. This view was put forward by Harbottle and Sutin[9], in contrast to Willard's claim[22] that the multiplicity of products resulting from Szilard–Chalmers reactions can be ascribed to random bond breaking along the track of the recoil atom. Harbottle and Sutin's objection to this theory stems from the low concentration ($\sim 10^{-2}$) of free radicals along the path of the moving atom.

III. METHODS OF STUDYING THE CHEMICAL STATE OF RECOIL ATOMS IN CRYSTALS

The atoms resulting from various nuclear reactions are present, as a rule, in vanishingly low concentrations in the target crystal, and their determination by other than radiochemical methods is extremely difficult.

The isotopic carrier method–one of the commonest procedures — enables the conventional operations of semimicro quantitative analysis, such as precipitation, extraction, etc, to be applied to the study of radioactive atoms. The shortcoming of this method is the lack of suitable carriers for unstable forms of the recoil atoms, exhibiting intermediate valencies. The existence and chemical state of such intermediate forms must be guessed from various indirect considerations. Information of this kind may be obtained from studies of the changes suffered by the recoil atoms during thermal or radiation-induced annealing of the irradiated crystals.

Thermal annealing as a method of investigation has the advantage that the crystal returns to its initial unexcited state, the energy required for the conversion being a measure of the depth of the metastable energy levels of the recoil atoms (or, in general, of the lattice defects), and also of the activation energies of the relevant processes. Furthermore, any form of annealing may be followed by monitoring various physicochemical properties of the irradiated specimens, whence conclusions may be drawn regarding the nature and the underlying causes of the observed phenomena.

More accurate results can be obtained by chromatography or electrophoresis in the absence of carriers. These methods often given unambiguous indications of the existence of recoil atoms in unstable chemical forms, but the interpretation of the chromatograms and histograms still presents serious difficulties. Furthermore, these methods presuppose high specific activities of the target materials, which are not always available to the experimenter.

Clearly, dissolution of the target as a preliminary to any form of radiochemical analysis can bring about a significant perturbation of the distribution of a radioactive isotope among various chemical states, as compared with the original distribution in the crystal. It would be very desirable, therefore, to have some physicochemical method of analysis which did not require conversion of the crystal into a liquid phase.

In the study of radiation damage in solids valuable information on structural defects and on the presence of unstable radicals in the lattice can be deduced from optical, electrical, and magnetic measurements. But since the radioactive atoms are present at very low concentrations, lower than the concentrations of radiation-induced defects by several orders of magnitude, it has not yet been found possible to study radioactive atoms by these procedures. Some information can be derived from experiments on the diffusion of radioactive atoms in the irradiated solid specimens at high temperatures, with and without externally applied electric fields[23-26]. Unfortunately, these experiments offer little concrete evidence as to the initial chemical state of the radioactive atoms, because the high temperatures involved can affect the relative amounts of radioactive atoms in different valency states.

The study of chemical processes induced by various kinds of radioactive disintegration rather than by nuclear reactions offers a wider choice of techniques. For example, the state of daughter atoms in the gas phase can be conveniently studied by collecting the recoil ions by means of an electric field or mass-spectrometrically. In solids, the Mössbauer effect has been used to study various unstable complexes formed during β-disintegration by a daughter atom in the crystal lattice. One section of the present review is specially devoted to the Mössbauer effect.

The retention† of activity after recoil in each of the various chemical forms provides the basic quantitative characterisation of the chemical effect of recoil. Existing methods of investigation depend on monitoring the final products by means of radioactive atoms, and do not give any information on the nature of the *primary* recoil fragments. Hence, present-day studies of these processes are confined to measurements of retention and of its dependence on various factors, which are variously combined to give the final result. We shall now discuss the most important factors, and the main principles which have been deduced from experimental results on retention in various chemical systems.

IV. BASIC EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

1. Dependence of Retention on the Chemical Nature of the Recoil Atom and of Its Environment

We have already remarked that a recoil atom can become ionised at a given point in its path if its kinetic energy is in excess of the limiting ionisation energy E_i, which is measured in tens or hundreds of keV, and depends on the ionisation potential and mass of the recoil atom. Ionisation of this kind can occur in any crystal, whatever its structure. The more complicated ionic crystals, comprising complex ions, can show ionisation of another kind. In these materials ionisation sets in even at low recoil energies: in (n, γ) reactions, for example, when the bond between the complex-forming ion (recoil atom) and its ligand groups is broken. According to Libby[19], this process involves the following mechanism.

In (n, γ) reactions, the velocity of the recoil atom is so much lower than the orbital velocities of the electrons that the latter may have time to take up a configuration of minimum free energy between the central atom and its surroundings. The final distribution of the electrons during fission of the bonds between the complex-forming ion and its ligands will depend on their relative electron affinities. If the complex-forming ion is highly electropositive, and the ligands are highly electronegative, there is a high probability of finding the electrons on the substituents, whilst the central ion is expelled from its surroundings bearing a multiple positive charge. Under these conditions, the charge on the recoil atom will be higher the greater the number of ligands lost due to recoil.

In his study of the chemical state of radio-manganese in potassium permanganate[19], Libby suggested (in conformity with his hypothesis) that a whole series of radio-manganese fragments, bearing different charges, is formed: MnO_3^+, MnO_2^{3+}, MnO^{5+}, Mn^{7+}. An analogous series can be postulated for chromium in neutron-irradiated potassium chromate: CrO_3, CrO_2^{2+}, CrO^{4+}, Cr^{6+}, and for rhenium in potassium perrhenate: ReO_3^+, ReO_2^{3+}, ReO^{5+}, Re^{7+}.

Since in Libby's model the central ion does not change its valency during recoil, it could be thought that the retention must always be 100%. This is not so, however, because the fragments formed during recoil may react in different ways with water during the subsequent dissolution, depending on their respective oxidation potentials[27]. Thus, the series CrO_3, CrO_2^{2+}, CrO^{4+}, Cr^{6+} forms a sequence in which the oxidation potential and the tendency towards reduction increases from left to right.

It is known that CrO_3 and CrO_2^{2+} (the chromyl ion) are hydrolysed by water to chromate at all pH values, but are not reduced by water to lower valency states. The other radicals oxidise water, and are reduced to Cr^{III}. The

† The term "retention" is widely used in the literature. Qualitatively, it denotes the occurrence of radioactive atoms in a given chemical form; quantitatively, it denotes the percentage of radioactive atoms in that form. As used in the present review, it refers invariably to retention in the parent compound.

reactions of the chromium residues during dissolution are of the form

$$\left.\begin{aligned} CrO_3 + H_2O &\rightarrow CrO_4^{2-} + 2H^+ \\ CrO_2^{2+} + 2HO^- &\rightarrow CrO_4^{2-} + 2H^+ \end{aligned}\right\} \quad (9)$$

or

$$CrO^{4+} + H_2O \rightarrow Cr^{3+} + O_2 + 2H^+. \quad (10)$$

Thus, retention will be a function of the relative numbers of the various recoil fragments. Table 2 shows the retention of chromium, manganese, and halogens in different compounds irradiated by neutrons at room temperature (neutron capture reaction with γ-emission).

The relatively high retention (60–70%) in chromates can be explained by the above considerations. The CrO_4^{2-} anions must pass, during recoil, through three forms before giving a form capable of oxidising water. On the other hand, oxy-anions of higher oxidation potential need to be taken through fewer states of oxidation to give a form which oxidises water. Hence, high oxidation potentials of the ion correspond to low retention of the recoil atom in its upper oxidation state. This is shown graphically in Fig. 1, which is based on Harbottle and Sutin's experimental results[36].

Further confirmation of this model could be obtained from systematic studies of retention in the oxy-salts of a given element in different oxidation states (*e.g.* potassium permanganate and manganate, etc.). Work of this type is now in progress[37].

TABLE 2. Retention values for various compounds.

Compound	Recoil atom	Retention, %	Literature reference	Compound	Recoil atom	Retention, %	Literature reference
Li_2CrO_4	Cr^5	66	28	$Ca(MnO_4)_2 \cdot 5H_2O$		6.0	
$Li_2Cr_2O_7$		54.5		$NaClO_3$	^{38}Cl	1.5	7, 19
Na_2CrO_4		74		$NaClO_3$		3.5	30
$Na_2Cr_2O_7$		80		$NaClO_3$	^{38}Cl	12.5	31, 32
K_2CrO_4		61		$NaClO_4$	^{38}Cl	0	
$K_2Cr_2O_7$		90		$KClO_3$		3.5	
$(NH_4)_2CrO_4$		17.5		$KClO_4$		0	
$(NH_4)_2Cr_2O_7$		32		$KClO_4$	^{38}Cl	2.2	32
$Na_2CrO_4 \cdot 4H_2O$		88		$LiBrO_3$	^{82}Br	8.0	33
$Na_2Cr_2O_7 \cdot 2H_2O$		73		$NaBrO_3$		11	
$MgCrO_4$		55		$KBrO_3$		11	
$ZnCrO_4$		35		$RbBrO_3$		13	
CrO_3		78		$CsBrO_3$		12	
$AgMnO_4$	^{56}Mn	8.0	29	$AgBrO_3$		15	
$LiMnO_4$		8.8		$Ba(BrO_3)_2$	^{80m}Br	9	33
$NaMnO_4$		9.1		$LiIO_3$	^{128}I	66	34
$KMnO_4$		22.5		$NaIO_3$		67	
$Ca(MnO_4)_2$		6.0		KIO_3		67	
$Ba(MnO_4)_2$		12.8		NH_4IO_3		22	
$NaMnO_4 \cdot 3H_2O$		6.9		$KHIO_3$		53	
$LiMnO_4 \cdot 3H_2O$		4.0		KIO_4		4.0	35

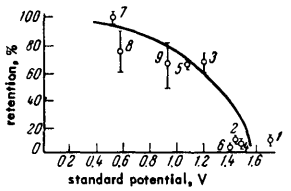


Fig. 1. Relationship between retention in neutron-irradiated crystalline salts and their oxidation potentials:
1) permanganate; 2) bromate; 3) chromate; 4) chlorate; 5) iodate; 6) periodate; 7) perrhenate; 8) arsenate; 9) iridate.

It should be noted that the behaviour of oxy-anions in Szilard–Chalmers processes is different from their behaviour towards radiolysis or thermal decomposition. Thus, radiolysis by electrons and thermal decomposition of permanganate give rise[38] to lower valency compounds: Mn^{VI}, Mn^{V}, Mn^{IV}. No such effect is observed in Szilard–Chalmers reactions.

What is the nature of the reactions which occur under conditions of high local temperature? The track of the recoil atom in an (n, γ) reaction usually amounts to a few lattice constants, and a small displacement from the fragments of the original molecule enables such an atom to recombine with oxygen ions, thus:

$$CrO^{4+} + O^{2-} \rightarrow CrO_2^{2+}. \quad (11)$$

We can also postulate activated exchange of oxygen ions between the recoil fragment and a neighbouring CrO_4^{2-} ion (the so-called ion–molecule reaction[9]):

or

$$\left.\begin{aligned} Cr^{*6+} + CrO_4^{2-} &\rightarrow Cr^*O^{4+} + CrO_3 \\ Cr^*O^{4+} + CrO_4^{2-} &\rightarrow Cr^*O_2^{2+} + CrO_3 \end{aligned}\right\}, \quad (12)$$

leading, of course, to increased retention. If we assume that the Cr^{*6+} ion produced by radioactive recoil can take up oxygen atoms from the surrounding crystal lattice, the last two reactions can be envisaged as occurring consecutively during the excursion of the chromium atom through the thermal spike. The activation energy for the transfer of oxygen is of the order of 3 eV. Thus we can calculate that oxygen transfer may occur several times during the lifetime of the hot zone[36]. Experiments on solid solutions of potassium chromate and fluoroberyllate[39,40] also provide some indirect evidence of the reality of these reactions (see below).

Evidently, a different situation will exist when the central complex-forming ion has an electronegativity comparable to that of oxygen, as in the case of the halogens. Here the oxygen may come away from the halogen leaving its electrons on the latter, and thus lower its valency. The effect will be strongest with chlorine, and less marked with iodine. The result will be to form the radicals XO_4^-, XO_3^-, XO_2^-, XO^-, and X^-, (where X is a halogen atom), which react with water to give the corresponding acids.

The following distribution of radio-iodine among the various chemical forms has been observed[34] after neutron irradiation of iodate and periodate solutions:

$$IO_3^- + n \rightarrow \begin{vmatrix} IO_3^- & 6\% \\ IO_2^- & 34\% \\ IO^- & 54\% \\ I^- & 6\% \end{vmatrix} \qquad IO_4^- + n \rightarrow \begin{vmatrix} IO_4^- & 6\% \\ IO_3^- & 28\% \\ IO_2^- & 60\% \\ IO^- & 6\%. \end{vmatrix} \qquad (13)$$

In both cases the loss of two oxygen atoms appears to be favoured. However, we must also consider at least two other factors, which can influence the relative abundance of the various fragments: (1) the mass of the halogen atom affects the recoil energy and therefore also the number of atoms lost and the extent to which the recoil fragment is reduced; (2) the enthalpy of formation of the XO_3^- ion governs the tendency towards reduction or decomposition of the parent molecule. Note that ΔH° values for IO_3^-, BrO_3^-, and ClO_3^- are -55, -9.6, and -23.5 kcal mole^{-1} respectively[41].

Under the combined influence of these three factors retention in (n, γ) reactions decreases, as expected, from iodine to chlorine. It amounts to 67% for $NaIO_3$,[34] 11% for $NaBrO_3$,[33] and 12.5% for $NaClO_3$.[31,32] From this point of view, Vlatkovic and Aten's results[42] on the chemical state of chlorine in KIO_3 crystals are not difficult to understand. The chlorine, produced from potassium by an (n, α) reaction, was found exclusively in the chloride fraction.

This picture, based on Libby's model[19], is probably a coarse approximation, and ignores other possible processes. For example, the results of electron paramagnetic resonance measurements[43] on V-centres in $KClO_3$ crystals irradiated with X-rays point to the presence of ClO radicals covalently bound to ClO_3^- ions. The authors also postulate the presence of the O_2^- molecule-ion. The presence of the oxide Cl_2O_6, and of a small amount of ClO_2 and ClO_4^-, was deduced from studies of the optical absorption spectra[44] of of potassium chlorate irradiated with X-rays. In the KIO_3 crystal lattice, on the other hand, neutral radicals of the type IO and IO_2 are most likely to be formed. Studies have been made also of the influence on the retention of the pH of irradiated iodate solutions and of the nature of the medium used to dissolve irradiated crystals. The retention has been investigated also as a function of the presence of various oxidising agents in the solution being irradiated (oxidants do not affect the retention when added after irradiation of the solution). From all this work it appears that compounds showing various valencies, or unstable radicals tending to disproportionate or to exchange, can be formed during recoil[34]. This tendency can have a profound influence on retention in crystalline halogen oxy-salts.

In spite of the large number of processes which may accompany nuclear recoil, simplifications such as Libby's model of the ionisation of recoil fragments[19], are very convenient at certain stages of the investigation, since they go a long way towards surmounting the difficulties of interpreting phenomena as complicated as the Szilard–Chalmers reaction.

2. Influence of the Cation upon Retention Processes

This effect is appreciable only in the case of the ammonium ion (see Table 2). Harbottle ascribes[36] the decrease in retention to the reducing action of hydrogen in the hot reactions between recoil fragments and the ammonium ion.

The salts of Group II elements also show a lower retention than the corresponding salts of the alkali metals. The reducing action in this case is probably a consequence of the high ionisation potentials of divalent metals. Their stronger electrostatic field promotes the disintegration and rearrangement of excited molecules. Metal oxide molecules, containing oxygen, may be formed under these conditions: this would hinder reactions of type (11), and lower the retention. The alkali metals must have a similar effect, but it is difficult to distinguish between them because of the smaller difference in ionisation potentials.

The stability of permanganates towards thermal decomposition (which can be visualised as retention in the form of the parent substance) also increases in the sequence[45] Ag^+, Li^+, Na^+, K^+, Rb^+, Cs^+, and Mg^{2+}, Ba^{2+} for the case of divalent metals (*cf.* the results of Table 2).

It is difficult to discern any correlation between the results of retention measurements and crystal density, concentration of oxy-anions in the solid phase, or crystal lattice structure. Obviously, these factors play a minor role as compared with those which, to a first approximation, control the chemical processes attending the recoil phenomenon.

3. Influence of the Degree of Complexity and of Homogeneity of the Ligands. Steric Effect

Baumgärtner and Zahn[46] have studied the retention of radioactive chromium in (n, γ) reactions involving the chromium complexes $Cr(Bz)_2$, $(Bz)Cr(CO)_3$, $Cr(CO)_6$, $Cr(Ms)_2$, $Cr(\psi - C)$, where Bz = benzene, Ms = mesitylene, and $\psi - C$ = pseudo-cumene. They were unable to detect any correlation between retention and the mass, the number, or the heat of formation of the ligands. The retention was 12% for $Cr(Bz)_2$, 9% for $(Bz)Cr(CO)_3$, 60–70% for $Cr(CO)_6$, 4.5% for $Cr(Ms)_2$, and 4.5% for $Cr(\psi - C)$.

Nor can the results be explained on the basis of the ligand–central atom bond energy alone, since these bonds are more stable in the last two compounds, and retention in these systems should amount to more than 12%.

It seems highly probable that the author's failure to demonstrate a correlation is due to the presence of some other, more powerful influence, rather than to a complete lack of connection between retention and these particular properties. Such an effect could arise as follows: the probability of regenerating the original molecule, partly disintegrated by the radioactive recoil, decreases with increasing structural complexity of the ligand molecule, and also if the ligands are not of a single kind, since the number of possible chemical forms produced by the decomposition of a few molecules by recoil now becomes very large. The latter effect can be demonstrated for inorganic compounds (*e.g.* thiosulphates).

The additional loss of retention shown by the last two compounds may be due to their large molecular masses, which give rise to steric hindrance opposing the return of the recoil atom towards its original position. A similar explanation has been advanced[47], on the basis of the steric effect, to account for the sharp decrease in retention accompanying the addition of pyridine ligands to Zn, Co, and Cu phthalocyanines.

Among inorganic crystals, the steric effect is very clearly shown by mixed crystals of potassium chromate and fluoroberyllate[39,40]. At the 1% level of potassium chromate

concentration the retention is reduced from 60–70% (for pure chromate) to 25–30%, and is found empirically to obey the law

$$R_0 = 30 + 0.4x, \qquad (14)$$

where R_0 is the retention and x is the percentage of chromate. Clearly, in these mixed crystals the molecules of potassium fluoroberyllate play no part in the chemical processes. As stated above, the hot-zone process leading to increased retention in chromates consists either in recombination of the recoil fragment with the residues of the original oxy-anion, *i.e.* with oxygen anions, or in reactions between multiply charged chromium recoil ions and the oxygen of stable oxy-anions. Probably, these processes may become inhibited, or even precluded, in mixed crystals for purely geometrical reasons.

4. Isotope Effect of Recoil

This effect is unmistakably observed with elements whose isotopic composition enables the Szilard–Chalmers reaction to be studied simultaneously on more than one radioactive isotope. The phenomenon depends on the slight difference in chemical behaviour between different isotopes of a given element during the lifetime of the hot zone or during the subsequent annealing of radiation damage. There is as yet no convincing interpretation of this complicated phenomenon in the literature.

In alkali metal bromates[33] (with the exception of lithium) retention is the same for both ^{82}Br and ^{80m}Br. However, the two isotopes behave differently during annealing. The retention of the heavier isotope increases faster, and reaches a higher plateau, as shown in Fig. 2. For $LiBrO_3$ the situation is reversed: the initial retention is smaller for ^{82}Br, but on heating, the curves for the two isotopes merge after two hours (Fig. 3).

Maddock and coworkers[48] have reported a considerable isotope effect in neutron-irradiated sodium hexachloroiridate: the retention was 47% for ^{192}Ir and 40% for ^{194}Ir. More refined analytical techniques[49] gave a retention of 20.9% for ^{192}Ir and 17.3% for ^{194}Ir in K_2IrCl_6, and 5.7% for ^{192}Ir and 2.8% for ^{194}Ir in $(NH_4)_2IrCl_6$.

An analogous isotopic difference for rhenium was observed by Apers and Maddock[50]. In K_2ReCl_6 crystals the proportion of heptavalent rhenium was found to be 32.8% for ^{188}Re, and 36% for ^{186}Re (Re^{IV}: 63% and 59% respectively). The rates of thermal and radiation-induced transformations were practically identical for the two isotopes, and the annealing graph consists of two curves which do not coalesce. It has been shown experimentally[51] that the

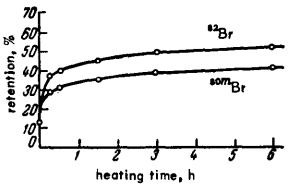


Fig.2. Difference in behaviour of bromine recoil isotopes during annealing at 200° in $RbBrO_3$.

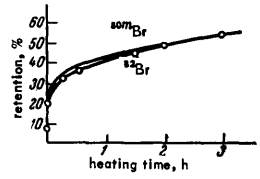


Fig.3. Difference in behaviour of bromine recoil isotopes during annealing at 200° in $LiBrO_3$.

retention of rhenium is unaffected if fast neutrons are used for the nuclear reaction. Thus the effect cannot be easily explained on purely energetic grounds. A study of the gamma-capture spectra and of the conversion coefficients of both isotopes may help to clarify this complicated phenomenon.

Conclusions as to isotopic differences in retention reached by comparing data for different nuclear reactions must be treated with greater caution; the same is true of work in which any one author has examined only one isotope of a given element. Comparative studies of retention for the different isotopes are essential in this case, since differences may arise in the irradiation of the target, in the analytical method used, and in the subjective skill of the experimenter. All these can have a profound effect on the final result.

For example, no firm conclusions can be made as to the existence and the magnitude of an isotope effect for the chlorine isotopes. When $NaClO_3$ crystals are irradiated with neutrons, the retention of radioactive chlorine for the reaction $^{37}Cl(n,\gamma)^{38}Cl$ is, according to some[7,19], 1.5%, and according to others[30], 3.5%. For the reaction $^{35}Cl(n,\gamma)^{36}Cl$, studied by a third group of investigators[31,32], the retention rises to 12.5%. In the photonuclear reaction[52] $^{35}Cl(\gamma,n)^{34}Cl$ the retention in $NaClO_3$ is approximately 9%. Although the last result does not differ too drastically from the others, it is impossible to estimate the extent to which the picture is distorted by the effect of the high gamma background on the target crystals during the photonuclear reaction, *i.e.* by radiation-induced annealing. Further studies of the effect of X-rays and γ-rays on retention are needed.

The discrepancy is much more serious when the retention of radioactive chromium in sodium and potassium chromates is investigated by comparing results pertaining to a photonuclear reaction on the one hand and to a neutron capture reaction on the other. The reaction $^{50}Cr(n,\gamma)^{51}Cr$ gives a retention[27,28] of the order of 60–80%, but in the photonuclear reaction $^{50}Cr(\gamma,n)^{49}Cr$ the retention drops[53] to 0%. It is difficult to point to the causes of this difference. Experiments on the radiation-induced annealing of neutron-irradiated K_2CrO_4 crystals have shown that the retention of radio-chromium is increased by the action of γ-rays on the crystals. Thus, we can dismiss the gamma background as a possible cause of decreased retention, although experiments in which potassium chromate was irradiated with 1.8 MeV electrons prior to neutron irradiation revealed[54] a slight decrease in retention as compared with the control crystals. It is worth noting that the difference in retention between (n,γ) and (γ,n) reactions is much smaller[53] in dichromates.

From the Seitz–Koehler theory we can state that at high recoil energies (*e.g.* in photonuclear reactions) the retention is independent of the recoil energy and of the specific nature of the primary event of the nuclear reaction: in other words, an isotope effect is not expected. This conclusion stems from the postulate that, when energy is lost in a given crystal, a particular atom must dissipate a strictly constant amount of energy in the hot zone. This is a very important concept, since it offers an experimental criterion for distinguishing between the true isotope effect and the influence upon retention of the type of nuclear reaction employed and of the magnitude of the recoil energy dissipated in the hot zone.

5. Characteristics of Some Chemical Systems. Effect of Structural Defects on Retention

There are considerable difficulties in interpreting the chemical recoil processes taking place in compounds not in their highest oxidation state at the time of irradiation. Typical of such systems are the hexahalogenorhenites K_2ReCl_6 [50,51] and K_2ReBr_6,[55] in which the rhenium is in the Re^{IV} state. When these compounds are irradiated some of the rhenium recoil atoms take up a valency of 7, and are removed from the target crystals in the form of the anion ReO_4^-. Over 30% of Re^{VII} is formed when K_2ReCl_6 is irradiated.

These results could be explained by Libby's model[19] of the ionisation of the central complex-forming atom during recoil. This involves the assumption that the radicals $ReCl_5^-$, $ReCl_4$, $ReCl_3^+$, $ReCl_2^{2+}$, etc., are formed. On Libby's model, heptavalent rhenium should be formed by the reaction between the positively charged radicals and water, with formation of radicals in which the rhenium is converted into a still higher oxidation state rather than being reduced. This seems an unlikely explanation, and it is probably more correct to postulate oxidation of the tetravalent rhenium by the neutral chlorine, formed during the irradiation of the crystals.

Libby's hypothesis is equally unsuccessful in explaining how the higher oxidation states, formed during neutron irradiation, are removed by thermal annealing. Whereas the annealing process in chromates can be described as recombination of the radicals $CrO^{4+} + O^{2-} \rightarrow CrO_2^{2+}$, leading to increased concentration of Cr^{VI} in solution, such a recombination mechanism can hardly be applied, say, to irradiated sodium arsenite or As_2O_3.[56,57]

The initial distribution of valencies for a number of arsenic compounds is shown in Table 3.

Annealing of the last two compounds given in the table removes the pentavalent arsenic and stabilises the whole of the arsenic in its original trivalent state. If we assume that the primary recoil products in As_2O_3 or in $NaAsO_2$ are the radicals AsO_2^-, AsO^+, and As^{3+}, it becomes difficult to understand the formation of ~ 4% of As^V. Even less likely is the hypothetical annealing reaction written, by analogy with other systems,

$$As^{3+} + O^{2-} \rightarrow AsO^+,$$

which fails to explain the increased retention in the original trivalent state on heating. In As_2O_3, for example; oxygen exchange between As^V and As^{III} in the hot zone seems more likely:

$$As_2O_3 \rightleftarrows As_2O_5. \qquad (15)$$

The high retentions of radioactive chromium in solid solutions of potassium chromate and potassium sulphate[28] irradiated by thermal neutrons, and of radio-manganese (up to 50%) in similarly irradiated potassium permanganate–perchlorate mixed crystals[58], can be explained in terms of reactions in the hot zone between recoil fragments and molecular or atomic oxygen. According to Libby's hypothesis, oxygen atoms should be set free when S–O or Cl–O bonds are broken, whilst oxygen ions are expected from the rupture of Cr–O and Mn–O bonds. The recoil products in irradiated mixed crystals of this type will find themselves in a medium of relatively high oxidising power, tending to raise the yield of recoil atoms in the highest valency state. The high concentrations of pentavalent phosphorus (70–100%) in crystals of K_2SO_4, $KClO_4$, $KClO_3$,[59] K_2SO_4, Na_2SO_4,[60-62] $CaSO_4$,[63] Na_2SO_3, and $Na_2S_2O_3$,[61-62] irradiated with fast neutrons, may arise from processes of the same type. In salts not containing oxygen as one of the lattice components, *e.g.* NH_4Cl and KCNS, the concentration of P^V fell to 30%,[61,62] in accordance with the hypothesis which postulates oxidation of the hot atoms by oxygen in the thermal spike. Water of crystallisation favours, as a rule, the oxidation of radioactive traces in crystals.

Oxidation reactions in the hot zone are probably responsible also for the high yield (~ 100%) of Cr^{VI} in the positron decay of ^{51}Mn to ^{51}Cr in $CsMnO_4$ crystals[64]. The same argument can be applied to manganese carbonate crystals. The primary positron decay event produces a molecule-ion. A process of the type

$$MnCO_3 \xrightarrow{\beta^+} CrCO_3^-$$

justifies the expectation that the radio-chromium will appear in its lower valency states. Studies of the chemical forms of the radioactive chromium detected ~ 30% of Cr^{VI} among the manganese decay products. This relatively high yield of hexavalent chromium is due, according to Harbottle, to reactions between chromium recoil atoms and dislodged oxygen atoms or carbonate ions[36].

In alkali metal halide crystals the Szilard–Chalmers effect has some specific characteristics. Recoil atoms are usually obtained in these systems by nuclear reactions involving a change in atomic number of the target element, such as (n, p), (n, α), etc., and therefore the new elements find themselves in an electrostatic field, which is unusual for them. Various authors have investigated the chemical state of sulphur[65], phosphorus,[59,66-68] and arsenic[69] in different alkali metal halide crystals.

The recoil energy of sulphur and phosphorus atoms formed in alkali metal chlorides by the nuclear reactions $^{35}Cl(n, p)^{35}S$ and $^{35}Cl(n, \alpha)^{32}P$ amounts to 15 and 50 keV respectively. When a positive particle is ejected from a ^{36}Cl nucleus, the atom becomes negatively charged if all the outer-shell electrons are retained. We might expect S^{2-} and P^{3-} anions to appear in the lattice; however, since

TABLE 3. Retention in compounds of arsenic, irradiated with neutrons.

Compound	Irradiation temperature, °C	As^V, %	As^{III}, %	As^0, %	No. of experiments
As_2O_5	room	46.8	51.9	1.32	4
As_2O_5	—78°	40.8	57.8	1.43	4
$NaHAsO_4$	—78°	55.9	43.4	0.74	2
As_2O_3	—78°	4.17	94.8	1.067	6
Na_2AsO_2	—78	4.6	94.5	0.85	2

the first electron affinity of a neutral phosphorus atom is 0.8 eV, and that of a neutral sulphur atom is 2.4 eV, one or several of the outer electrons will be lost at the recoil energies in question, and the most probable state of the recoil atoms becomes one of the lower valency forms, such as P^0 and P^+ for phosphorus and S^- and S^0 for sulphur.

Indeed, experiments have shown that the sulphur in KCl crystals is predominantly in the form of the ions S^{2-}, S^-, or of elementary sulphur, and that the fast isotope exchange causes these forms to be indistinguishable[65]. Similarly, approximately 80% of the radio-phosphorus passes into the solution in the form of phosphine and hypophosphite. The pentavalent phosphorus or arsenic in carefully degassed alkali metal halide crystals usually amounts to ~10% of the total activity of these elements.[68,69] The lack of dependence of the yield on solvent pH is evidence that the valency states are stabilised in the crystal. On heating, the lower valencies are oxidised to the pentavalent state, which may be thought to involve $KPCl_6$ complexes. It is assumed that complexes of the type K_2PCl_6 and K_3PCl_6 are also present. The oxidising agents which operate during annealing are probably V-centres, produced by the radiation.

It has been repeatedly stated that the intermediate recoil products disproportionate in contact with water. Thus, the fact that annealing KCl crystals which have been irradiated with high-energy protons increases the radioactive fractions of both P^V and P^{III} is interpreted[68] as evidence for the existence of the species PCl_4 (tetrahedral configuration) in the crystals after irradiation, this species being equally likely to suffer oxidation or reduction by water when the crystal is dissolved. Carlson and Coski[67] separated the radio-phosphorus formed in KCl crystals by the $^{35}Cl(n, a)^{32}P$ reaction into the three valency states 3-, 3+, and 5+, and found that in some of the experiments the 3- and 3+ forms were present in roughly equal amounts. They concluded that the elemental phosphorus present in the lattice disproportionates, when in contact with water, into two valency states (3- and 3+) which are extracted by the phosphine and hypophosphite–phosphite carrier[67].

If the crystals are not heated to a high temperature before irradiation, so as to remove possible traces of occluded oxygen and water and to annihilate dislocations and other structural defects, most of the sulphur and phosphorus appears in the 6+ and 5+ valency states respectively. This is difficult to explain merely by the formation of the oxide chlorides $SOCl_4$ or $POCl_3$, because oxygen or water are very sparsely distributed in the lattice of "anhydrous" alkali metal halides, and a radioactive atom is very unlikely to penetrate to the immediate vicinity of one of these impurities, particularly since oxygen diffusion is quite negligible at room temperature. Obviously, the phenomenon must involve the migration of electron vacancies (positive holes) from the oxygen to the phosphorus and sulphur.

A similar mechanism must be responsible for the oxidation of radioactive impurities under the influence of ionising radiation: the radiation accompanying neutron interaction, γ-rays from ^{60}Co, or X-rays. Radiation leads to the formation of neutral chlorine in the KCl crystal lattice. Elemental phosphorus, formed by the nuclear reaction, interacts with neutral chlorine or with various V-centres by an electron–hole mechanism; this leads to the production of radicals of the type PCl, which undergo oxidation and reduction when the crystal is dissolved. At high doses of γ-rays the concentration of free chlorine increases, and these radicals are converted into PCl_3 and PCl_5 and ionic complexes including potassium ions of the lattice. In this way the amount of pentavalent phosphorus can rise[67] to 100%. Intense irradiation with γ-rays prior to the neutron reaction will, presumably, have a similar effect.

Since each recoil atom disturbs the perfect periodicity of the lattice field, and can act as an electron donor or an electron acceptor, even the mildest electronic processes in the lattice can be expected to affect the chemical state of such an extraneous atom.

Ordinary daylight, by dissociating F-centres and setting free electrons, should give a lower yield of the more oxidised forms. The presence of foreign impurities at concentrations several order of magnitude higher than those of the radioactive atoms can affect the stability of the colour centres and thus affect the chemical fate of the recoil atom. Impurities and defects will also influence the diffusion of oxidising agents during thermal annealing: this can affect the rate and the kinetic order of the annealing reaction. Unfortunately, only one publication (by Süe and Caillat[66]) deals with these aspects. The authors attempted to correlate the ratio of the valency states of radiophosphorus in the crystals after irradiation with the presence of radiation-induced lattice defects. They investigated the state of phosphorus in crystals of LiCl, NaCl, and KCl which had not been degassed before irradiation. In all three cases the amount of P^V was ~40–50%. Also, by heating a crystal of NaCl for a few minutes at 350°, they decreased the proportion of the pentavalent form from 43% to 31%. According to the authors, electrons bound in F-centres are freed by raising the temperature (which also bleaches the crystal), and are trapped by pentavalent phosphorus ions thereby lowering their valency.

It follows from what has been said in this section that one can only speak of the ratio of oxidised and reduced forms in the context of strictly constant irradiation and other conditions (pretreatment and subsequent storage) of the crystals.

Evidently, systems including an oxy-anion such as chromate are more stable towards various adventitious interactions. It has been reported[27] that retention in chromates is unaffected by four hours' illumination in bright sunlight. But even in these crystals the behaviour of recoil fragments depend on structural defects or inactive dislocations[54,70]. For example, whereas for monocrystalline chromates the retention was 77.3%, it was found to be 69.9% for microcrystalline powders. Retention in chromates and in bromates is decreased also by previous irradiation with electrons of 1.8 MeV energy. The variation of initial retention in $Ca(BrO_3)_2$ with dose of electron radiation prior to neutron irradiation is shown in Fig. 4.

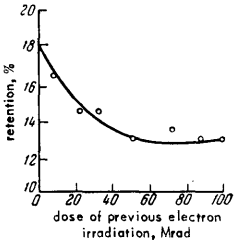


Fig.4. Influence of previous electron irradiation (energy 1.8 MeV) on retention in $Ca(BrO_3)_2$.

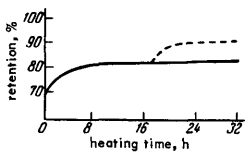


Fig.5. Effect of comminution of the crystals in the course of isothermal annealing on retention in potassium chromate. Full line — annealing of single crystal; broken line — annealing of specimen ground to a powder at a predetermined stage.

TABLE 4. Effect of temperature of neutron irradiation on retention in $KMnO_4$.

Irradiation		Storage		Dissolution			Retention, %
T, °C	time	T, °C	time	T, °C	time, min	medium	
90–190*	150 min	room	30 min	room	–	H_2O	38.8
30	15 s	+25	2 h	+2	5	H_2O	20.7
30	15 s	+25	2 h	−60	10	acetone	19.3
30	15 s	−78	2 h	−60	10	acetone	15.6
−78	15 s	−78	2 h	+21	5	acetone	18.2
−78	15 s	−78	2 h	−60	10	acetone	8.9
−195	90 min	−195	1 h	−90	15	acetone	5.1

* Value at 90–190° taken from Sano [74].

It is obvious that ionic vacancies in the crystal lattice can facilitate the diffusion of recoil fragments when the crystals are heated, and therefore also increase the rate of thermal annealing. Andersen and Maddock [71] have shown that, when small amounts of calcium are added to potassium chromate in order to introduce cation vacancies, the radioactive chromium is annealed appreciably faster, whereas the initial retention value is practically indistinguishable from that for the pure crystals.

The influence of structural defects on the rate of chemical reactions during heat-treatment can also be demonstrated in the following way. A crystal, annealed at a given temperature until it reaches its plateau, is exposed to strong ionising radiation, and annealed once again at the same temperature. Under these conditions the retention shows a rapid rise to a new plateau. Exactly the same behaviour is observed, at least qualitatively, if the exposure to radiation is replaced by comminution and grinding of the single crystals at a given stage of annealing. The full line in Fig. 5 shows the retention in K_2CrO_4 crystals as a function of annealing time at 230°; the broken line shows the retention of a portion of the same material which was powdered after 16 hours' heating [71].

6. Variation of Retention with Crystal Irradiation Temperature

Data on the thermal annealing of irradiated crystals indicate that, as a rule, retention is increased by annealing. It seems reasonable to suppose that the temperature of neutron irradiation must have a similar effect: higher irradiation temperatures should produce increased retention, and *vice-versa*. Such is in fact found to be the case in all systems investigated up to now: potassium chromate [28], bromate [72], hexachlororhenite [51], and permanganate [73]. Harbottle's results for the retention in potassium permanganate [73] irradiated at different temperatures are reproduced in Table 4 as an example of this temperature effect.

The uniqueness and the superiority of Harbottle's experiments (as compared with those of other workers) lie in his use of acetone at temperatures well below 0° to dissolve his crystals after irradiation. This enabled him to avoid to some extent recombination of the thermally unstable radioactive fragments present in the crystal, and to arrive at a retention value close to the true initial value and free from errors due to thermal annealing during irradiation at room temperature. Inspection of Table 4 suggests that the highest retention value in the absence of bond breaking in the oxy-anion is less than 5%, and that at least 3/4 of the retention observed at room temperature results from annealing, which occurs at an appreciable rate even in the temperature range from -60° to -90°. (It is quite possible that the higher retention of $KMnO_4$ as compared with other alkali metal permanganates is due to easier annealing of the manganese recoil atoms in $KMnO_4$ even at room temperature.)

It must be noted that one worker [74] has reported an increase in $KMnO_4$ retention with decreasing temperature in his low-temperature investigation of $KMnO_4$. There appears to be a minimum at about 0° in the plot of irradiation temperature against retention. These experiments involved dissolution of the crystals in water, which raises some doubts as to the reliability of the results. Clearly, an explanation of the discrepancy between these data and those of Harbottle must be sought in the processes occurring when the crystals are dissolved in water. These processes may be quite different for crystals which have been subjected to high-temperature and to low-temperature irradiation.

The irradiation temperature has a specially strong effect on the formation of different chemical forms of phosphorus during neutron irradiation of phosphates [75-78]. The phenomena reflect the specific tendency of phosphorus atoms towards polymerisation, and the complicated chemistry of the oxy-anions of phosphorus. For example, when Na_2HPO_4 is irradiated at dry-ice temperatures, ~ 80% of the radioactive phosphorus appears in the pentavalent state, although the P^V fraction has a very mixed composition. On the other hand, only a single radioactive phosphate is formed, effectively, at irradiation temperatures of 30–50°. This may be due to the extreme instability of the recoil fragments and their high sensitivity towards annealing reactions even at these temperatures. Another possible cause is too low a recoil energy of the phosphorus atom, such that this atom cannot tear itself from the very stable and compact PO_4^{3-} unit. It would be difficult to explain otherwise why the phosphorus atoms ejected from the oxy-anion produce exclusively phosphate rather than some other phosphorus compound. This argument, plausible at the moment, will become convincing if complex compounds such as pyrophosphate and trihypophosphate are irradiated, and the whole of the radioactivity is found in the form of the parent compound.

We cannot, unfortunately, draw definite conclusions about the mechanism of these processes, because our knowledge of the stability of phosphorus radicals and of their reactivity in the solid phase is quite inadequate, as is also our understanding of the γ-ray spectrum of the

reaction $^{31}P(n,\gamma)^{32}P$. Furthermore, different workers have applied different analytical procedures in these investigations.

7. Effect of Solvent pH and of Analytical Method upon Retention

In studies of recoil processes it is very important to allow for the presence of every possible radical and intermediate valency compound in the crystal after irradiation, whose reactions with water may depend on the pH of the solution. One must also bear in mind the possibility of various physicochemical processes during dissolution, which may also be sensitive to pH.

For example, the retention of permanganates increases from 10–20% when the crystals are dissolved in a neutral medium to 100% in alkali [19]. Libby explains this by postulating that heptavalent manganese radicals are reduced by water in acid and in neutral media, but are hydrolysed in alkaline media, thus:

$$4MnO_3^+ + 2H_2O = 4MnO_2 + 3O_2 + 4H^+,$$

$$MnO_3^+ + OH^- = MnO_4^- + H^+.$$

More recent work [29] has shown that this increased retention can be ascribed to adsorption of radioactive manganese on colloidal particles of inactive MnO_2 in alkaline solution, followed by heterogeneous manganese exchange (these colloidal particles are always present in permanganate to some extent). High retention in acid solutions can probably also be explained by some form of exchange, *e.g.*

$$Mn^*O_3^+ + MnO_4^- \rightarrow MnO_3^+ + Mn^*O_4^-. \qquad (16)$$

A sharp change in retention with increase in pH has been observed also in potassium chromate, if the activity is isolated in the form of chromium hydroxide [27]. There are reasons for ascribing increased retention in this case to the formation of salts of the type $Cr(OH)CrO_4$.

Table 5 shows the complicated effect [69] of solution acidity on the yield of pentavalent arsenic from irradiated crystals of the hydrate $LiBr.H_2O$.

Neither anhydrous LiBr nor the dihydrate show this dependence. Hence this behaviour of the monohydrate must be thought to result from the presence of some intermediate species in the crystal after irradiation, the reaction between water and this species being a complicated function of pH. In anhydrous LiBr or in the dihydrate this form is absent, or is present in very low concentrations. Studies of the effect of solution pH on other crystals may provide some information on the chemical forms in which the recoil atom is stabilised within the crystals.

TABLE 5. Effect of pH of solvent medium on the yield of pentavalent arsenic in $LiBr.H_2O$.

pH	As^V, %
0.5	51 ± 1
2.5— 2.8	55 ± 1
9.2— 9.6	57 ± 2
10.5—10.9	68 ± 1
10.7—11.2	72 ± 2
10.9—11.2	73 ± 2
11.1—11.6	60 ± 2
11.2—12.0	53 ± 2
12.0—13.0	54 ± 2

At the beginning of this article brief mention was made of the different methods of investigating the chemical processes accompanying recoil, and it was pointed out that the carrier method followed by precipitation of the chemical form of interest, which is most widely used, does not reflect all the complications of the problem. The retention values obtained by this method result from the combination of several unknown fractions, coprecipitated with the parent form. Hence the results usually contain a systematic positive error as compared with the true initial retention. This effect is illustrated in Table 6, which gives the retention values for hexachloroiridates obtained by electrophoresis and by caesium precipitation respectively [49,79].

Only the values obtained by precipitation can be fitted satisfactorily on a plot of retention against the standard oxidation potentials of the systems, taking the potential of the system $[Ir(III)Cl_6]^{3-}/[Ir(IV)Cl_6]^{2-}$ as 0.93 V. Thus the results obtained by electrophoresis are not compatible with the retention values obtained for other systems by precipitation.

A similar state of affairs is observed with bromates. The electrophoretic results give retention values of 9–13%, showing some correlation with the nature of the cation [33]. A less accurate extraction method gave a retention of 18–22% for all cations. [70,72,80] This type of discrepancy also makes it impossible to draw definite conclusions from studies of Szilard–Chalmers processes in phosphates, as stated in the previous section.

Hence, the need for the greatest care in the choice of analytical procedure and in the interpretation of results cannot be overemphasised.

8. Possible Applications of the Mössbauer Effect in Hot Atom Chemistry

We have seen that, when an atom produced by a nuclear reaction or by a radioactive transmutation becomes part of the composition of a solid crystal, one has to resort to precipitation and separation of the products of the reaction between hot atoms and the surrounding medium. Unstable intermediates are, of course, lost in the process, and we cannot be certain that the spectrum of products obtained in this way is independent of the chosen analytical procedure. In this context it is relevant to mention the new opportunities offered to chemists by the Mössbauer method (recoilless resonance absorption of the gamma-quanta emitted by a radioactive nucleus).

The principle of the so-called Mössbauer effect lies in the ability of unexcited nuclei to absorb, by resonance, the gamma-quanta emitted by the transition of an excited

TABLE 6.

Compound	Retention, %	
	electrophoresis	precipitation
$NaIrCl_6 \cdot 6H_2O$	6.7 ± 2,0	67.9 ± 0.8
$(NH_4)_2IrCl_6$	14.1 ± 0.5	59.9 ± 0.2
K_2IrCl_6	25.5 ± 1.2	99.3 ± 0.1

nucleus to the ground state. The unexcited nucleus is thereby promoted to an excited state. A similar phenomenon is well known in conventional optics: the only difference is that the relatively large momentum of γ-quanta should impart a strong recoil to both the emitting and the absorbing nucleus, and thus make resonance absorption impossible because of the Doppler effect. Mössbauer showed, however, that at least in some cases the recoil is taken up by the crystal (or heavy molecule) as a rigid whole, so that recoil phenomena can be neglected.

The Mössbauer effect observed in iron is a good example. The source of radiation was iron (stainless steel) whose surface had been alloyed with radioactive cobalt (^{57}Co, $T_{1/2}$ = 270 days). The ^{57}Co undergoes electron capture, and is converted into ^{57}Fe in an excited isomeric state ($T_{1/2} = 10^{-7}$ s). The gamma-quanta emitted during the isomeric transition, of energy 14.4 keV, can be absorbed by resonance in ordinary iron, or, better, in iron enriched with ^{57}Fe‡.

To observe the Mössbauer effect, the absorber is set into uniform translational motion with respect to the source, and the transmission is measured as a function of the relative velocity. If absorber and source are physically and chemically identical, an absorption maximum is observed at $v = 0$. A different state of affairs obtains when the identity between absorber and emitter is destroyed. This is because the probability density of finding s electrons from the atomic shell within the volume of the nucleus is non-zero. Due to coulombic interaction, this causes a displacement of the energy levels of the nucleus, thus affecting the energy of γ-quanta emitted or resonantly absorbed (the so-called isomer shift). In different chemical compounds of a given element the density of s electrons in the nucleus is different, and therefore the values of the isomer shifts are also different.

On the other hand, the interaction between the nuclear moments and the moments of the electron shells causes hyperfine splitting of the nuclear energy levels. The nature and magnitude of this splitting are determined by the electron density distribution in the compound to which the atom belongs.

The high sensitivity of the Mössbauer effect to extremely small ($\sim 10^{-8}$ eV) changes in the energy of resonance absorption of γ-quanta sometimes makes it possible to identify the type of chemical binding of an atom, whether emitted or absorbed, from the Mössbauer spectrum.

Up to now, the compound under study has mostly been used as the absorber. However, if ^{57}Co is introduced into the molecule (or crystal) of the emitter, the energy of the gamma-quanta emitted after radioactive conversion of this isotope into ^{57m}Fe will correspond to the chemical forms produced immediately following the radioactive disintegration of the ^{57}Co by the primary interaction between the hot ^{57m}Fe atoms and the medium. Under these conditions one observes the spectra of the ^{57m}Fe atoms in exactly the states which have been produced in a time of the order of 10^{-7} s (the lifetime of the isomer state).

Experiments of this type have been made by Wertheim[81], who studied the valency states of iron produced after decay of ^{57}Co in CoO.

It should be noted that the capture of an orbital electron by a nucleus lowers the charge on the nucleus and on its electronic environment by one unit. Thus we can expect the daughter atom to have the same valency as the parent atom. But this can only happen if the atom excited after electron capture, such as ^{57m}Fe, passes into its normal state exclusively by X-ray emission. If the excitation of the atom is "relieved" by a single-stage Auger process, the iron atom appears in the Fe^{3+} state. Two-stage ionisation by this same process will lead to Fe^{4+} ions, and so on. We can assume that the electron affinity of multiply charged atoms is so large that their lifetime in the crystal works out at appreciably less than 10^{-7} s, and they cannot be detected by the Mössbauer effect.

Fig. 6 shows a Mössbauer spectrum taken at 169°K. It consists of two series of emission bands. These series, which combine two hyperfine splitting structures, differ in line intensity and line width. Such a composite picture of two series can arise either from quadrupole splitting or from the presence of two non-equivalent types of iron, distinguishable by their position in the lattice or by their valency state. The quadrupole splitting explanation can be rejected, since the intensities of the two series are very different, and this would be surprising since CoO has an almost cubic symmetry. The assumption that the ^{57m}Fe atoms occupy positions different from those of the normal cobalt atoms is untenable, since the recoil due to the neutrino associated with the electron capture process is hardly likely to displace an atom from its lattice site. The only remaining explanation is that the difference between the iron atoms concerns their state of charge, and that the two most stable valency forms of iron, Fe^{2+} and Fe^{3+}, are involved. Comparison of the isomer shifts with those observed in compounds of divalent and trivalent iron confirms this assumption.

It is clear from Fig. 6 that the emission lines are wider for Fe^{3+} than for Fe^{2+}. The line widths for divalent iron do not differ significantly from normal line widths; the greater line width for trivalent iron can arise either from differences in the immediate surroundings of the trivalent atom or from the fact that the charge of +3 is unstable, and disappears in a time not much greater than 10^{-7} s.

Differences in the immediate surroundings can arise as follows: a higher valency state, such as Fe^{4+}, disappears by capturing an electron from the surrounding divalent cobalt atoms and forming a trivalent iron atom with a Co^{3+} nearest neighbouring. In this way, local environments can be generated whose field at the trivalent iron nucleus is somewhat different. This process should be capable of reducing all the highest charged states to Fe^{3+} in a time comparable with 10^{-7} s. Whether or not trivalent iron

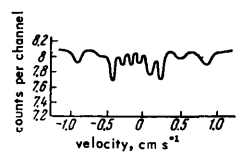


Fig. 6. Hyperfine structure of γ-transitions of 14.4 keV energy in divalent and trivalent ^{57m}Fe in cobalt oxide at 169°K (Mössbauer emission spectrum). The central part of the spectrum, consisting of narrow lines due to Fe^{2+}, can be readily distinguished.

‡ The concentration of ^{57}Fe in ordinary iron is 2.17%.

itself is stable is a question which can be partly solved by examining the relative intensities of the Fe^{2+} and Fe^{3+} emission bands. From the fluorescence yield it appears that approximately 1/3 of the disintegrations gives divalent iron, but the ratio of intensities observed is significantly higher. We may conclude, therefore, that trivalent iron is partly converted into divalent iron in a time of somewhat more than 10^{-7} s. This electron exchange process between Fe^{3+} and Co^{2+} can be quite favourable energetically.

The second paper which we shall discuss was published recently by de Coster and Amelinckx[82]. The authors introduced $^{57}CoCl_2$ into single crystals of KCl by diffusion, and studied the state of the iron formed in the potassium chloride after radioactive disintegration of the cobalt. Different results were obtained for mixed crystals of this type whose previous thermal histories were different. The Mössbauer absorption spectrum for crystals slowly cooled to room temperature from a few hundred degrees consists of a single peak, whose appearance suggests the absence of quadrupole splitting, due no doubt to the cubic symmetry of the surroundings of the cobalt atom in the $CoCl_2$ diffusion layer. The position of the peak, however, and the magnitude of the isomer shift, imply that the rays are emitted from iron in the Fe^{3+} state.

A different picture is obtained if the mixed crystals are rapidly cooled over the same temperature interval. The peak splits into two components of approximately the same height, the width of the composite peak being greater than for the slowly cooled specimen. This can be due to quadrupole splitting. The authors ascribe the effect to a large number of vacancies being "frozen" in the crystal after rapid cooling. These vacancies have a tendency to associate with impurity ions of opposite valency due to coulombic interaction. The cobalt ions attract cation vacancies, which carry an effective negative charge and are relatively mobile at room temperature in KCl. The formation of a (cobalt ion + vacancy) complex perturbs the cubic symmetry of the surroundings of the cobalt ion, and thus induces quadrupole splitting. The trivalent iron therefore appears, in this system, bound to a cation vacancy of the potassium chloride crystal lattice.

As we have seen, the Mössbauer effect offers valuable information on the chemical consequences of various nuclear transformations. It is becoming increasingly more important, owing to the growing number of suitable radioactive isotopes and of experimenters who are prepared to master the technique.

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