QUANTITATIVE NUCLEAR CHEMISTRY

By D. L. Baulch and J. F. Duncan
(Chemistry Department, University, Melbourne, Australia)

(1) Introduction.—The secondary chemical effects of radioactive processes have been studied frequently during the past decade, and the qualitative aspects of valency change, bond rupture, etc., during radioactive decay have been the subject of several recent reviews.[1] We will not discuss this work, but will review the quantitative aspects of radioactivity in so far as they may be of use in obtaining physicochemical data about chemical reactions. First, however, some recapitulation of the nature of the nucleus and of nuclear reactions is necessary.

(2) Nuclear Models.—There are two theories of nuclear structure in current use.[2, 3] In the liquid-drop model one imagines the nucleus to be like a drop of water, from which particles (nucleons) can evaporate when the nucleus is excited. According to this theory, the relative energies of nuclei can be represented by a parabolic equation, the parameters of which vary systematically with nuclear charge. There are some variations in the region of " magic number " nuclei, which are much more stable than expected on the liquid-drop model. This suggests a periodic structure of some kind for the nucleus, which is the basis of the alternative " shell " model. The evidence for the existence of nuclear shells at 2, 8, 20, 28, 50, 82, and 126 neutrons or protons is now very strong.[3] They are analogous to the closed electron shells exhibited by the rare gases. Like the electrons in extranuclear orbitals, the nucleons can be excited from one energy level to another by electromagnetic radiation. Emission of nuclear particles may also cause changes in nuclear excitations. The energy level of the product nucleus is characterised by quantum numbers (different from those of the parent nucleus) just as for the excited electronic states of atoms. Nuclear energy levels corresponding to these states have been determined for a large number of nuclei.

(3) Nuclear Decay.—The several modes of radioactive decay are well known. Here we summarise the important features for our purpose.

(a) *α-Decay.* This occurs when the energy level of the nucleus is very high by comparison with the minimum of the potential energy parabola (liquid-drop model) for the same value of Z. At lower energies, decay by other modes is usually more favourable. The most important aspects of

---

[1] Willard, *Ann. Rev. Nuclear Sci.*, 1953, **3**, 193 ; *Ann. Rev. Phys. Chem.*, 1955, **6**, 141 ; McKay, *Progr. Nuclear Physics*, 1950, **1**, 168.

[2] Coryell, *Ann. Rev. Nuclear Sci.*, 1953, **2**, 305 ; Halliday, " Introductory Nuclear Physics ", Wiley, N.Y., 1950, 287 ; Blatt and Weisskopf, " Theoretical Nuclear Physics ", Wiley, N.Y., 1952, Chapters 6, 7, and 14.

[3] Flowers, *Progr. Nuclear Physics*, 1952, **2**, 235 ; Mayer and Jensen, " Elementary Theory of Nuclear Shell Structure ", Wiley, N.Y., 1955.

α-decay are that (i) except for an unimportant fine structure, the decay energy of an α-emitter is monochromatic and (ii) the emitted α-particle (^4_2He) is an atomic nucleus of large mass by comparison with the electron, and a significant fraction of the mass of the original radioactive nucleus. These features lead to a large recoil energy and complete disruption of any chemical compound of which the radioactive atom is part.

(b) *Light-particle emission.* Light particles may participate in the following types of transition : (i) direct particle emission from the nucleus, (ii) internal conversion of a γ-ray, (iii) K-capture, and (iv) positron–electron annihilation. The last three result in loss of planetary electrons, emission of X-rays from orbital electron transitions, and in Auger electrons. They are monoenergetic transitions, but unfortunately the associated electronic effects are usually too numerous to allow any simple chemical interpretation. From the present viewpoint they are unimportant.

Decay by β-emission is by far the most important for our purpose. A noticeable feature is that the energies of the emitted particles are not monochromatic, but spread over a range from zero to $E_{\text{max.}}$, the maximum β-particle energy, equal to the difference between the energies of the product and the parent nuclei. For the law of conservation of energy to hold for β-decay, we must postulate the existence of another particle, called the neutrino, of almost zero rest mass and zero charge. In each nuclear transition, this particle takes away the " missing " energy. On account of its low mass, the neutrino velocity is very high, which, together with its lack of charge, accounts for the fact that its energy has never been directly measured. It is only very recently that this particle has been detected with any certainty.[4] The existence of the neutrino is also expected in positron (β^+) decay, and in K-capture. In the last case it is monoenergetic.

The quantitative aspects of β-decay are predicted by Fermi's theory,[5] in which the distribution function for the shape of the β-particle spectrum is estimated by regarding the electrons and neutrinos as the quantisation of the nuclear force field, *i.e.*, the nucleus is regarded as made up of " nucleons ", which are converted into β- or other emitted particles as a result of the decay of the nucleus from a higher to a lower quantum level (shell model). By using this theory, the shape of the β-spectrum can be accurately predicted once the value of $E_{\text{max.}}$ and the degree of forbiddenness are known. This is very important in a study of the chemical effects of nuclear recoil, since the vector sum of the momenta of the neutrino and the recoiling atom must equal the momentum of the emitted β-particle. In section (4), below, the shapes of some recoil spectra, calculated from Fermi theory, are quoted.

(c) *Emission of γ-radiation.* The various nuclear processes in which γ-ray decay can occur are cosmic processes ($>$ 10 Mev), nuclear reactions induced by projectile bombardment (4—10 Mev), $\beta\gamma$-decay (0—3 Mev), and isomeric transitions ($\leqslant$ 1 Mev). Direct interaction between the γ-radiation

---

[4] Reines and Cowan, *Phys. Rev.*, 1953, **92**, 830.

[5] Fermi, *Z. Physik*, 1934, **88**, 161 ; Konopinski, *Rev. Mod. Phys.*, 1943, **15**, 209 Skyrme, *Progr. Nuclear Physics*, 1950, **1**, 115.

and orbital electrons usually predominates over other chemical effects ; and, in particular, bond rupture by γ-recoil (see below) is small in most cases of natural radioactivity. In the present context, interest in γ-decay is mainly confined to its subsidiary role on $\beta\gamma$ decay, in which the β-particle is the more significant.

TABLE 1. *Types of γ-decay*

Process	Decay energy (MeV)	Main features
Cosmic processes, high-energy decay	10	Complete rupture of all chemical bonds
Low-energy nuclear bombardments	4—10	Rupture by recoil frequent, but not obtained in low-energy γ-emission or when successive γ-quanta are emitted in oriented directions relative to nuclear dipole
$\beta\gamma$-Decay	0—3	Probability of γ-emission depends on vector change in nuclear angular momentum, and on quantum numbers (shell model)
Isomeric transitions	1	N or Z 39—49 or 69—81, in which last nucleon in nearly completed shell fills a different level from that expected. Large spin change necessary. Internal conversion often obtained

(4) **Fundamental Considerations in the Chemistry of Radioactive Processes.**—The physical aspects of radioactivity have now been given in sufficient detail for our purpose. We next consider how the radioactive process itself can affect the chemistry of the emitting atom. When a nucleus emits radiation, the following types of extranuclear process are possible :

(a) *Direct interaction between the emitted particle and the atomic electrons.* The nuclear particle might " knock-out " some orbital electrons as it passes through them. This is more likely with α-emission than in β-emission, but in both cases there is general agreement[6, 7] that other effects (b and c, below) are more important by a factor of the order of 1000. In γ-emission, interaction with the orbital electrons by Compton scattering,[8] internal conversion, etc., can be very efficient, but these interactions are of limited interest in the present context.

(b) *Disturbance of the atomic electron shells.* The sudden change in nuclear charge on emission of a nuclear particle may result in considerable disturbance of the atomic electrons. Thus, on β-emission from an atom of atomic number Z, the electrons must take up new equilibrium positions which are nearer the nucleus of the daughter atom (charge $Z + 1$) than in the parent (charge Z). The atomic electrons will still have the same quantum numbers but they will have different energies. This energy

[6] Migdal, *J. Phys.* (*U.S.S.R.*), 1941, **4,** 449 ; Feinberg, *ibid.*, p. 423.

[7] Winther, *Kgl. danske Videnskab. Selskab*, 1952, **27,** No. 2.

[8] Compton, *Bull. Nat. Research Council*, 1922, **4,** No. 2.

difference may be accounted for in one of two ways. First, if the speed of the nuclear particle is slow by comparison with the speed of the orbital electrons, the energy difference may be transferred to the emitted particle. This (isothermal) process only takes place in β-emission with energies of less than about 4 kev for an element such as argon. On the other hand, if the nuclear particle is so fast that the nuclear process is essentially adiabatic, the daughter atom must take up the excess of energy by excitation or ionisation. This is often the case, although in β-decay where the spectrum is continuous from zero to $E_{\text{max.}}$, some of the emitted β-particles will be sufficiently slow to allow isothermal adjustment of the daughter levels.

If there is no interaction between the β-particle and the electron shells, the average excitation is approximately [9] $22{\cdot}8Z^{2/5}$ ev. Thus, even for light atoms, considerable excitation is possible. On the other hand, Feinberg and Migdal [6] have calculated the probability of ionisation in the *K*, *L*, and *M* shells, using (*a*) simple coulombic wave functions, (*b*) non-relativistic treatment, and (*c*) sudden change of nuclear charge, and have found it to be small. Others [10] have confirmed their conclusions, although there is some disagreement on the precise values for the ionisation probability. Typical figures are for Ra-*E*, $1{\cdot}28 \times 10^{-4}$ (*K*), $1{\cdot}04 \times 10^{-3}$ (*L*). For a particular shell, the ionisation probability varies inversely as Z^2. Data are not available for higher shells, although one would expect that it would be greater than for the *K* shell. But although Levinger's estimates [10] are not in disagreement either with experiment or with the calculations of Serber and Snyder,[9] yet the large excitation energies predicted by the latter are difficult to reconcile with experiment. Loss by ionisation of many electrons would be expected from Serber and Snyder's estimates, whereas, in fact, multiple ionisation in only a small fraction of the decay is usually obtained; *K*-shell ionisation in the β-emitters ^{35}S, ^{32}P, Ra-*E*, and ^{147}Pm is very small.[11] Similar measurements on the *K*-capture isotopes ^{55}Fe and ^{37}A agree with the predictions on ionisation probability,[12] and charge measurement from pure β-decay shows no abnormal ionisation (see Table 2). However, Snell's recent data [13] on $^3H_2$ and ^{85}Kr suggest that perhaps 10—20% of the decays might result in multiple ionisation in some cases. More ionisation is to be expected in the outer shells owing to the screening effect of the field of the nucleus, but no quantitative theoretical predictions are available yet.

These effects may be very important in molecular bond rupture. Even if a constituent atom does not have sufficient recoil energy to break a bond, electronic excitation with subsequent bond rupture may occur. This important process has been discussed by Wolfsberg,[15] who has estimated

[9] Serber and Snyder, *Phys. Rev.*, 1952, **87**, 152.

[10] Levinger, *ibid.*, 1953, **90**, 11; Schwartz, *J. Chem. Phys.*, 1953, **21**, 45.

[11] Boehm and Wu, *Phys. Rev.*, 1954, **93**, 518.

[12] Porter and Hotz, *ibid.*, 1953, **89**, 903; Miskel and Perlman, *ibid.*, 1954, **94**, 1683.

[13] Snell, Pleasonton, and Leming, *J. Inorg. Nuclear Chem.*, 1957, **5**, 112; Snell and Pleasonton, *Phys. Rev.*, 1957, **107**, 740.

[14] Wexler, *Phys. Rev.*, 1954, **93**, 183; Miskel and Perlman, *ibid.*, 1953, **91**, 899: Kofoed-Hansen and Nielson, *Kgl. danske Videnskab. Selskab*, 1955, **29**, No. 15.

[15] Wolfsberg, *J. Chem. Phys.*, 1956, **24**, 24.

TABLE 2. *Resultant atomic charge (from ref.* 14)

(Gaseous pressure 5×10^{-3}—5×10^{-5} mm. Hg)

Parent activity	Parent molecule	Transition†	Average positive charge	Charge expected from nuclear process only
^{3}H	H_2	β	0·9 ± 0·1	1
^{14}C	CO_2	β	1·0 ± 0·2	1
^{37}A	A	K	2·6 – 3·4	0
^{41}A	A	β	1·0 ± 0·1	1
^{80}Br*	C_2H_5Br	γe^-	10 ± 2	0
^{83}Kr*	Kr	γe^-	7·7 ± 0·4	0
Mixture of gases obtained in nuclear fission (^{83}Kr*, ^{85}Kr, ^{87}Kr, ^{88}Kr, ^{135}Xe)		$\beta\gamma e^-$	1·3	1

† e^- = Internal conversion electron.

the probability of C–N bond rupture due to electronic excitation in $CH_3{\cdot}NH_3^+$ formed from ^{14}C-labelled ethane (see below).

(c) *Electron loss by trailing.* When the nucleus recoils during β-decay, it travels with a velocity which may be comparable with, but is always rather less than, planetary electron velocities. Electron loss may then occur because the nucleus " leaves behind " some of its associated electrons. Fission recoil energies (~250 Mev) are large enough[16] to result in an atomic charge of +20—25 units, but it is unlikely that α-particle recoil will cause a loss by this mechanism of more than 0·5 unit of charge, and β-recoil will be still less efficient.[10]

(d) *Internal " Bremsstrahlung ".* Interaction of the nuclear β-particle with the nuclear radiation field may cause emission of continuous X-rays. The probability of emission decreases with increasing β-particle energy and is usually of the order of 10^{-4}. The intensity has been measured experimentally, *e.g.*, for ^{35}S, Ra-E, and ^{147}Pm with good agreement with theory.[11] This effect is ignored in subsequent discussion.

(e) *Summary of electronic processes arising in radioactive decay.* It seems likely that excitation is the only purely electronic process which is important in β-decay. Unfortunately, the evidence is conflicting and it is very difficult to predict with accuracy how much excitation will take place in a given case. On the other hand, the properties of the daughter atom only determine how the excitation energy is distributed. Thus, when either X-radiation (from planetary electron transitions) or γ-radiation (from nuclear transitions) is emitted, it is characteristic of the daughter atom. The nuclear and electron shells must therefore attain equilibrium in a time which is short by comparison with the time for X-ray emission (~10^{-8} sec.).

In the case of α-decay, extranuclear processes are certainly significant,

---

[16] Bohr, *Phys. Rev.*, 1941, **59**, 270 ; Lassen, *Kgl. danske Videnskab. Selskab*, 1945, **23**, No. 2 ; Knipp and Teller, *Phys. Rev.*, 1941, **59**, 659.

since the daughter products are usually positively charged. Even the rare gas radon forms positively charged polonium atoms, whereas it would have a double negative charge as a result of the α-decay alone. Whilst the first two electrons could be lost by a spontaneous exothermic process, some other feature must cause the loss of the other two. It might be due to electron " shaking ", but since the electronic energy levels of an atom of charge $Z - 2$ are higher than in an atom of charge Z, electronic transitions between the ground states must be endothermic. The α-particle would thus have to supply the ionisation energy. The charge on an atom which leaves a metallic foil is not germane here since it depends on the relative values of the ionisation potential of the atom and the work function of the metal. Thus, in α-recoil of Ra-D from Ra-C', and of Ra-B from Ra-A, positive charges of the order of unity are obtained [17] from platinum and nickel surfaces.

(f) *Nuclear recoil.* A more important outcome of the nuclear event than electronic excitation is the recoil energy imparted to the radioactive atom. This can be precisely evaluated. The nature of the molecular fragment resulting from decay will depend on the type and energy of the nuclear transition, in which both charge and momentum will be conserved. The

TABLE 3. *Chemical consequences of nuclear recoil*

Radiation	Oxidation state of daughter	Recoil energy (ev)	Recoil spectrum	Main features
α	-2 to $\sim+2$	10^5	Line	$Z > 83$. Complete rupture of all bonds
β^-	$+1$	0—20	Spectrum	Neutron-excess isotopes. Some bond rupture possible. High oxidation state for daughter
β^+	-1 to 0	0—20	Spectrum	Neutron-deficient isotopes. Annihilation radiation indicates re-oxidation of daughter
K-capture	0	0—20	Line	Neutron-deficient isotopes with insufficient energy for β^+-decay. Considerable bond rupture due to electron deficiency. Auger electrons
γ in the presence of β	0	0—20	Line	May interact with electron shells (mainly of other atoms) by photoelectric encounter or Compton effect
Isomeric transition	0	0—1	Line	Internal conversion and bond rupture large for γ-energy below 400 kev. Photoelectric encounter and Compton effect also possible

---

[17] McGee, *Phil. Mag.*, 1932, **13,** 1; Makower and Russ, *ibid.*, 1910, **20,** 875, 882; 1915, **29,** 253.

possible nuclear reactions are summarised in Tables 3 and 4. In discussing these tables we will confine ourselves in the first instance to those reactions in which there is no direct interaction between the nuclear radiation and the extranuclear electronic shells. Chemical reactions initiated by the radiation are not discussed in any detail.

TABLE 4. *Recoil energies*

Radiation	Recoil energy (ev)
α	$m_\alpha E_\alpha/M$
β^+, β^-	$E_\beta{}^2/2Mc^2 + \boldsymbol{m}_0E_\beta/M = 536E_\beta{}^2/M + 541E_\beta/M$
γ	$E_\gamma{}^2/2Mc^2 = 536E_\gamma{}^2/M$

m_α = Mass of α-particle. M = Mass of recoiling atom.
$\boldsymbol{m}_0$ = Mass of electron. $\boldsymbol{c}$ = Velocity of light.
Energies E_α, E_β, and E_γ are in Mev.

(i) *High-energy recoil.* The two most important processes which produce high-energy recoil fragments (α, γ emission) also give monoenergetic recoils (or line spectra). All the recoil energy may not, however, be available for bond rupture. It is well known that for a diatomic molecule, $E_D = E_Rm/(M + m)$, where E_D is the energy available for bond rupture, E_R is the calculated recoil energy, and M and m are respectively the masses of the recoiling nucleus and the remaining nucleus (or an equivalent reduced mass for a polyatomic molecule). Nevertheless, E_D is usually sufficient to cause bond rupture, even if the direction of recoil is not along the line of centres of the atoms. If the direction of recoil makes an angle θ with the line of centres, a fraction, cos θ, of the energy will appear as vibrational energy and the remainder as rotational energy. On integration, it emerges that 2/3 of the total available energy initially appears as rotational energy, and 1/3 as vibrational energy. But the energy is usually so large by comparison with the spacings between the vibrational or rotational levels that rupture is inevitable. The energy necessary for rotational rupture may be somewhat greater than required for vibrational rupture of a molecule in its normal modes, since excessive energy in rotational states causes a maximum to appear in the Morse curve. But in most cases a substantial degree of bond rupture will occur *via* vibrational states even if the energy were initially present in rotational states.

Once bond rupture has occurred, there will result one or more molecular ragments in a chemically reactive state. What happens next will depend on the type of system. In liquid systems, the initial recoil atom causes secondary ionisation to form other chemically reactive species.[1] But the ecoil atom itself is still mobile and can be used to give further data. This depends on the fact that of the order of 100 molecular collisions are required or a 0·1 Mev recoil atom of mass about 200 to be slowed down to thermal velocities. Stopping by direct nuclear collisions is insignificant, and hard kinetic energy) collisions contribute only at the end of the path. Most of the slowing down process occurs by " soft " collisions in which the recoiling atom partially penetrates the electron cloud of the atom which it hits. Bohr has shown that the stopping power per unit mass is proportional to the nuclear charge of the retarding medium and proportional to the density. Thus, the range of the recoil atom will depend on the density of the stopping material, and on its nuclear composition. Remarkably little work has been done on this application, in spite of the low thicknesses which may be measured (< 1 μg./cm.^{2}). Almost all examples (see p. 146) are α-induced reactions, although $n\gamma$ (Szilard-Chalmers) processes could be used also.

(ii) *Low-energy recoil processes.* We include here (*a*) processes with a

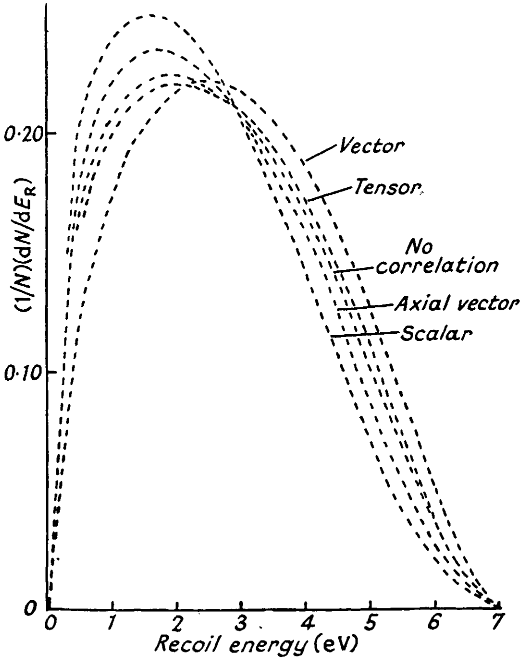

FIG. 1

Calculated recoil energy (E_R) *spectrum of* ^{14}C, *for different* β*-particle neutrino interactions.*

continuous energy spectrum, the maximum of which is comparable with that of chemical bonds, and (*b*) monochromatic recoil processes with energies less than chemical bond energies.

(A) *Binding energies.* In many β-decay processes, the maximum recoil energy is greater than the chemical binding energy. Nevertheless, because the β-spectrum extends from zero to $E_{\text{max.}}$ a fraction of the recoils will be too small to cause bond rupture. Fig. 1 shows the recoil spectrum of ^{14}C, calculated from Fermi theory for $E_{\text{max.}} = 0{\cdot}158$ Mev. For this calculation it is necessary to know the angle between the directions of emission of the neutrino (ν) and the β-particle, which has still not been settled beyond dispute. Experimental study [18] of the systems $^6\text{He} \longrightarrow {}^6\text{Li} + \beta + \nu$ and $^{19}\text{Ne} \longrightarrow {}^{19}\text{F} + \beta + \nu$ suggests that, for allowed transitions, the Fermi part of the interaction is scalar, while the Gamov–Teller part is tensor. The exact value of the interaction depends on the matrix elements of the nuclei involved in the decay. However, in most cases little error is introduced if the above assumptions are used as a working basis for the calculation of recoil spectra.

As with α-recoil, some of the recoil energy is lost as kinetic energy. But the energy available for removing the atom from its environment (E_D) is now of the same order as the chemical binding energy (E_B). In general, we may write the residual recoil energy as $E_\text{RR} = E_\text{D} - E_\text{B}$. If $E_\text{RR} > 0$, the atom will be removed from its environment. If $E_\text{RR} < 0$ it will not, unless the transition causes extranuclear processes (see above). Provided that correction for the latter can be made, measurement of the frequency of obtaining free atoms, or of the energy distribution of recoils, would allow the chemical binding energy to be estimated (see Table 5 and Fig. 2). Alternatively, if we calculate the degree of bond rupture for a bond of known energy, any excess observed experimentally must be due to electronic excitation or to other extranuclear processes.

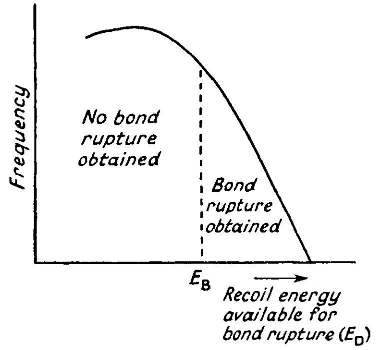

FIG. 2

Diagrammatic illustration of the proportion of recoils causing bond rupture.

If we set an arbitrary limit of, say, 57·5 kcal./mole (2·5 Mev) for the energy necessary to break stable chemical bonds by β-decay, and write

$$E_\text{R} = \frac{M + m}{m} E_\text{D} = \frac{541 E_\beta}{M} + \frac{536 E_\beta^2}{M}$$

we may calculate E_β, the maximum β-energy necessary to cause molecular disruption. Then, by use of the liquid-drop model, the value of $Z_0 - Z_M$ necessary to provide the β-energy required for bond rupture by recoil may be estimated, where Z_0 is the (non-integral) value of Z_M at the minimum

---

[18] Allen and Jentschke, *Phys. Rev.*, 1953, **89**, 902 ; Rustad and Ruby, *ibid.*, p. 880 ; Alford and Hamilton, *ibid.*, 1954, **95**, 1351 ; Maxon, Allen, and Jentschke, *ibid.*, 1955, **97**, 109 ; Robson, *ibid.*, 1955, **100**, 1933 ; Alford and Hamilton, *ibid.*, 1957, **105**, 673.

TABLE 5.

Parent molecule	Daughter molecule	E_β (max.) (Mev)	E_D (max.) (ev)	Expected behaviour
^{14}CO	$^{14}NO^+$	0·158	3·75	E_B = 6·49 ev (N–O) ; 11 ev (N–O$^+$). Bond unbroken
$H^{14}CHO$	$H^{14}NHO^+$	0·158	3·50	E_B = 3·1 (NO). Some disruption of the molecule
$H_2C{:}^{14}CH_2$	$H_2C^{14}NH_2{}^+$	0·158	3·50	E_B = 3·1 (C–H) ; 4·5 (C–N) ; 3·7 (N–H). No C–N bond rupture
$HC\vdots^{14}CH$	$HC^{14}NH^+$	0·158	3·75	E_B = 4·5 (C–N). No C–N bond rupture
$^{34}ClO_2$	$^{34}SO_2{}^-$	0·713 (β^+)	8·58	E_B = 1·9 (Cl–O) ; 5·18 (S–O). Production of SO and O. Some dissociation from electron-deficient bonds
$^{77}AsCl_3$	$^{77}SeCl_3{}^+$	0·8	5·86	No data available. Probably loss of at least one chlorine
$^{144}CeCl_3(s)$	$^{144}PrCl_3(s)$	0·35	1·77	Lattice energy 25 ev. No loss from solid

All values of E_B, E_D, and lattice energies are quoted in ev/molecule and are taken from Gaydon, " Dissociation Energies and Spectra of Diatomic Molecules ", Chapman & Hall, 1947, and from Szwarc, *Chem. Rev.*, 1950, **47**, 75.

of the energy parabola. In Fig. 3, plots of E_β versus M are given, with the corresponding values of $Z_0 - Z_M$. From this figure the following conclusions may be drawn : (*a*) Bond rupture is most likely with low M, high m, and high $Z_0 - Z_M$. (*b*) Practically no bond rupture by recoil occurs for M and $m > 100$, and $(E_{\text{max.}})_\beta < 0·5$, whereas it will be substantial for $m > 50$ and $E_\beta > 2·0$. (*c*) For M odd, the energy of β-decay to a stable isotope cannot be greater than that given by $Z_0 - Z_M = 1$. Hence, bond

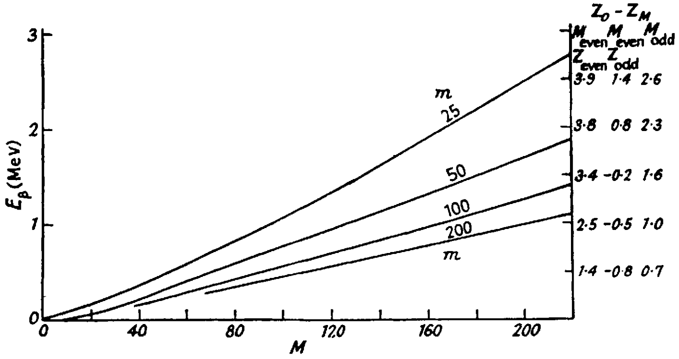

FIG. 3

β-Energy necessary to rupture a 2·5 ev (57·5 *kcal./mole) bond between a radioactive atom of mass M and an atom of mass m. Values of $Z_0 - Z_M$ are quoted for different types of nuclei, where Z_0 is the non-integral charge corresponding to the minimum of the energy–Z parabola, and Z_M is the charge on the radioactive nucleus. The values quoted for $Z_0 - Z_M$ are accurate to about* ± 10%.

rupture will always be small with M large and odd. For M even, $Z_0 - Z_M < 2$ if the atom decays to the most stable isotope of the daughter element. With Z_M also even, there is only a small amount of rupture with $M > 100$; if Z_M is odd, rupture by β^--recoil is unlikely $[(E_{\text{max.}})_\beta >> 1]$ with $M > 140$ if $m < 25$, and also if $M > 200$ for all values of m. To study nuclear chemical reactions in which (*a*) the thermodynamic properties of the daughter fragment (see below) or (*b*) rupture by electronic excitation or other extranuclear processes (see above) is of predominating importance the degree of bond rupture by recoil must be reduced to a minimum. This is best achieved by use of the radio-isotope which is closest to the minimum in the energy–Z parabola (usually closest to the most abundant isotope), preferably with M even. Conversely, if a high degree of recoil rupture is sought, an isotope decaying to a radioactive daughter—preferably from a short-lived emitter with M odd—is likely to be most suitable.

(B) *γ-Radiation.* Although molecular disruption frequently occurs by internal conversion, etc., it may also result directly from the nuclear recoil consequent upon γ-decay. In Fig. 4 the recoil energies calculated for γ-emission for decay, from the first excited states to ground states of even-even nuclei, are given. Similar results would be obtained for other nuclei,

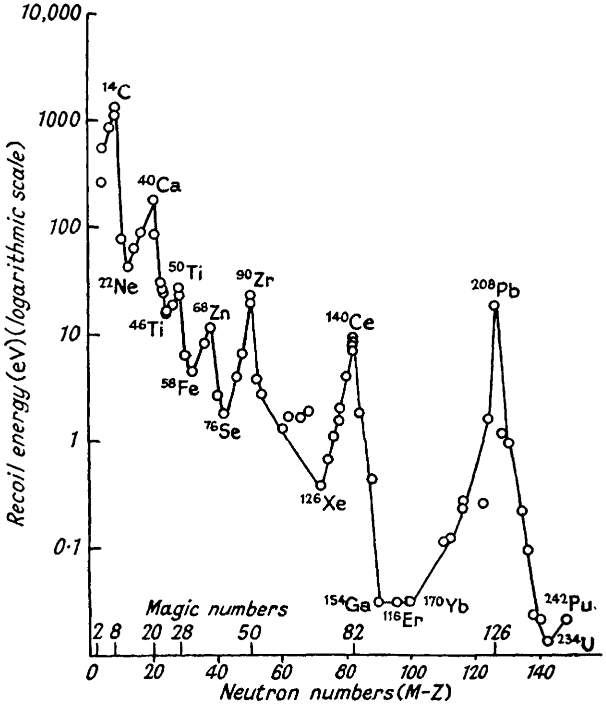

FIG. 4

γ-Recoil energies obtained from first excited states of nuclei with even charge and even mass.

with some displacement along the energy axis. Decay by γ-emission also occurs from higher excited states, but the first excitation level often accounts for the largest and most frequent decay. We may therefore generalise from Fig. 4, and conclude (*a*) that almost all nuclei with high M (> 95 for even-even types) will have recoil energies well below chemical binding energies (say 2·5 ev), (*b*) that the exceptions will be nuclei with nucleon numbers close to magic numbers, which will always give high recoil energies, and (*c*) that when M is low (< 50 for even-even types) the (monochromatic) recoil energy will be large enough (> 10 ev) to cause bond rupture in all cases—sometimes it will be large enough to remove the recoiling atom bodily from its environment, with an expected range of the order of 0·1—1% of the range of α-recoil atoms.

(g) *Thermodynamic properties of the product.* Consider now what happens to the product of a nuclear reaction in which bond rupture does not occur. It must be formed initially with the same number of electrons as its parent. One or more of the following processes may subsequently occur :

(i) The product may be stable :

$$^{14}CO_3{}^{2-}\ (aq) \longrightarrow \beta + {}^{14}NO_3{}^{-}\ (aq)$$

(ii) The product may be disproportionate :

$$H_2{}^{35}S\ (g) \longrightarrow \beta + H_2{}^{35}Cl^{+}\ (g) \longrightarrow H_2{}^{+} + {}^{35}Cl \quad \text{or} \quad H^{35}Cl + H^{+}$$

(iii) The product may react with its environment :

Molecular reaction

$$^{59}Fe^{3+}\ (aq) \longrightarrow \beta + {}^{59}Co^{4+}\ (aq) \xrightarrow{\frac{1}{2}H_2O} {}^{59}Co^{3+} + H^{+} + \tfrac{1}{4}O_2$$

Electron exchange

$$^{34}Cl^{-}\ (g) \longrightarrow \beta^{+} + {}^{34}S^{2-}\ (g) \longrightarrow 2e + {}^{34}S\ (g)$$

A wide variety of chemical entities can result, depending on the properties of the species initially formed. But by the proper choice of nuclear systems one may control both recoil effects and the thermodynamic properties of the product sufficiently to allow the consequences of each type of nuclear chemical process (recoil, electronic excitation, and chemical reaction) to be distinguished. The remainder of this Review considers the experimental aspects in terms of these three types of reaction.

(5) **Experimental Methods.**—To obtain quantitative data about a nuclear chemical event, secondary chemical effects such as ionisation of the medium by the emitted radiation must be eliminated. The radioactive source must usually be in dilute solution, or at a low gas pressure, or the daughter species must be separable from the system before secondary processes can occur. When the source is mounted on a solid substrate, one of the following methods of preparation may be used :

(i) *Precipitation or evaporation.* This usually gives sources which are several atomic layers thick, in which the recoil atom loses most of its energy. Contamination is also difficult to avoid.

(ii) *Electrolytic collection.* Electrolytic collection from a gaseous source of recoil atoms such as radon is a convenient method for any decay product of a gas.[19] Jedrzejowski [20] has shown that such sources may sometimes contain aggregates of atoms, which might either (*a*) impede the recoil atom, or (*b*) be carried off the source with the recoil atom.

(iii) *Electrolytic deposition from solution.* This method is sometimes suitable. Sources of Ra-*C* on platinum and nickel disks prepared in this manner have been found suitable for α- and β-recoil work (see below).

(iv) *Vacuum distillation.* This is by far the most reliable method.[21] The supporting material has little effect on the ease of escape of α-recoil atoms, although a smooth polished surface is to be preferred to a rough one. On the other hand, the presence of impurities, aggregates, or adsorbed gases can prevent completely the escape of β-recoil atoms. Hence solid β-recoil sources are usually prepared by this method, using material which has been previously separated by one of the three methods above. Barton [22] has successfully prepared a source by electrolytic deposition followed by heating to 400—500° to remove gas layers. Even then measurements must be made as rapidly as possible after preparation of the source. As with α-recoil, the source material is usually deposited on a metal plate, but the nature of the metal, its work function, smoothness, cleanness, and surface oxidation may considerably affect the yield and the charge of the low-energy β-recoil fragments. Recent work has shown that the β-recoil yield of a source of Th-*B* deposited on tungsten can increase by threefold or more over a temperature range of 80—150°, under some conditions.[23] It is therefore of first importance that the chemical properties of the source are fully known before recoil experiments are made.

(v) *Detection of recoil atoms.* Radioactive recoil atoms are frequently collected on a charged plate placed close to the source. From the yields obtained at various pressures and at various distances between the source and collector, the range of the recoil atoms may be determined. The nature of the collecting surface materially affects the yield of the low-energy β-recoil fragments, and to a lesser extent that of α-recoil atoms. A smooth aluminium or platinum plate is very efficient. There is some evidence that the accommodation coefficient of elements of high boiling point is very low if the pressure is low ($\sim 10^{-8}$ mm.). This is associated with the difficulty of forming condensation nuclei on the collecting surface. In the Reviewers' experience checks should always be made to confirm that collection is near 100%.

Non-radioactive recoil atoms may be detected by measuring the ionisation produced in a gas. Such methods require a gas pressure of at least several mm. of mercury, and are therefore not suitable for work with β-recoil atoms. If the chemical properties of the source are suitable, β-recoil atoms are positively charged, a feature which has been used by Leipunski [24] to

---

[19] See Baulch and Duncan, *Australian J. Chem.*, 1957, **10**, 112.

[20] Jedrzejowski, *Compt. rend.*, 1929, **188**, 1043.

[21] Donat and Philipp, *Z. Physik*, 1927, **45**, 512; Davies, *Phys. Rev.*, 1952, **86**, 976.

[22] Barton, *Phil. Mag.*, 1926, **1**, 835.

[23] Baulch, Duncan, and Kepert, forthcoming publication.

[24] Leipunski, *Proc. Camb. Phil. Soc.*, 1936, **32**, 301.

detect the positively charged ions from a ^{14}C-preparation by means of an accelerating potential applied to a grid. At present, Allen-type electron multipliers [25] are the most convenient and widely used detectors of low-energy positive (recoil) ions.

An elegant method of detecting non-radioactive daughters has been used by Wolfgang, Anderson, and Dodson [26] in the detection of the products of decay of $^{14}CH_3\cdot{}^{14}CH_3$ by a double labelling technique. If the specific activity is sufficiently high, both carbon atoms of a reasonable number of the ethane molecules will be labelled. These will decay to form the radical $^{14}CH_3\cdot NH_3^+$. The frequency of bond rupture may then be determined from the number of labelled methylamine molecules obtained. The weight of methylamine is very small ($\sim 10^{-8}$ g.) although its β-activity can easily be detected. Chemical losses may be reduced, and at the same time allowed for, by addition of inactive methylamine as carrier prior to chemical separation from the active ethane remaining after the experiment. Since the activity of the remaining ethane will be several orders of magnitude larger than the resulting methylamine, efficient and complete separation of ethane from a pure sample is essential. But after carefully checking this aspect of the problem, these workers obtain rupture of the C–N bond in approximately 53% of the cases in which $^{14}CH_3\cdot{}^{14}CH_3$ decays by β-emission of one of the carbon atoms.

(6) Some Experimental Results.—*α-Recoil.* Since α-recoil atoms always have enough energy to overcome all chemical binding forces, it is the study of the properties of the recoiling atom itself which is of interest. There are two regions: (i) that part of its track during which it is being slowed down to thermal velocities, and (ii) the subsequent movement of the free atoms by diffusion. Measurement of the number of α-recoil fragments which penetrate matter affords a convenient means of measuring the density or the thickness of the material. Since very thin layers will stop the recoiling fragment, this technique is far more sensitive than the conventional β-ray thickness methods. The range of an α-recoil atom is $\sim$10 μg./cm.^{2}, and it is quite possible to measure variations in recoil yield below 1 μg./cm.^{2}. As an example, Gregory [27] has shown that a linear yield of recoil radon atoms with thickness results when barium stearate monolayers of effectively infinite area are progressively deposited over a layer of a thorium salt. The recoil yield falls to zero with an increasing number of monolayers. This system is difficult to study, since loss of thoron from the solid must be stopped by cooling in liquid air. But other systems, such as Th-C'' (^{208}Tl) recoiling from Th-C (^{212}Bi) are also suitable. An aqueous solution of Th-C and sodium dodecyl sulphate has been used to study the concentration of soap molecules adsorbed on the liquid–gas interface, by collecting the recoiling Th-C'' on a charged plate above the surface.[27]

There are a number of applications of α-recoil to the measurement of

---

[25] Allen, *Rev. Sci. Inst.*, 1947, **18**, 739.

[26] Wolfgang, Anderson, and Dodson, *J. Chem. Phys.*, 1956, **24**, 16.

[27] Gregory, Hill, and Moorbath, *Trans. Faraday Soc.*, 1952, **48**, 643; Aniansson and Steiger, *J. Chem. Phys.*, 1953, **21**, 1299.

diffusion coefficients in solids. Thus Hevesy and Seith [28] determined the diffusion coefficient of bismuth in lead chloride, using Th-*C*. The recoil yield was determined before and after heating the lead chloride on which a source of Th-*B*/*C* had been deposited. The diffusion coefficient was calculated from the known recoil range. All previous work has used the Flugge-Zimens empirical stopping-power equation relating the recoil range to the square of the recoil energy. This equation has been recently criticised on experimental and theoretical grounds.[19] It has been shown that the first-power dependence of the range on the recoil energy is more nearly correct, in agreement with Bohr's theoretical treatment.[29]

In its passage through a gas, the recoil atom changes its charge several times, but since most α-recoil ions are atoms of electropositive metals, they have usually been found to be positively charged at the end of their path. Dee, using a cloud-chamber technique, finds that 84% of such recoil atoms are positively charged at the end of their path.[30] A recoil ion from a 6·54 Mev α-particle produces a total of some 10^3 ion pairs, of which perhaps 75% may be in the first half of the range. Since the α-particle produces 2×10^5 ion pairs, only about 0·5% of the total ionisation is obtained from the recoil atom, although this is about 75% of the ionisation obtained in the distance the recoil atom travels from the site of the initial radioactive event.

Having reached the end of its path, the atom will diffuse through the surrounding gas. The yield, N, from such a system in radioactive equilibrium at a distance x, can be shown to be [31, 32] $N = N_0 \exp(-\lambda/D)^{\frac{1}{2}}x$, from which D, the diffusion coefficient, can be calculated. In the two cases hitherto reported it has been observed that D is about 1000 times smaller than expected from kinetic theory. The reason for this is not understood.

β-Decay.—(a) *Heterogeneous systems.* Wide discrepancies between different workers, associated with experimental difficulties in preparing the source, are common. Thus the yield of Ra-*C* from sources of Ra-*B* has been variously reported [22, 33, 34] as 0·1%, 2—6% and 20—50%. Almost all workers report a rapid deterioration in β-recoil sources, sometimes of the order of 50% in 20 min. Earlier work was, of course, subject to many limitations of technique, which do not now apply. This is undoubtedly the main reason for the discrepancies, for Sherwin [35] (using ^{32}P on a lithium fluoride surface) has recently shown that recoil sources can be prepared which are quite stable. He used the constancy in the number of recoil fragments (detected by electron multiplier) as a criterion for the purity of his source, since it was only such sources which gave a satisfactory resolution of the energies of the emitted recoil atoms. These sources could be kept

[28] Hevesy and Seith, *Z. Physik*, 1929, **56**, 780.

[29] Bohr, *Kgl. danske Videnskab. Selskab*, 1948, **18**, No. 8.

[30] Dee, *Proc. Roy. Soc.*, 1927, *A*, **116**, 664.

[31] Baulch, Duncan, and Ryan, *Australian J. Chem.*, 1957, **10**, 203.

[32] Chamie, *J. Phys. Radium*, 1934, **5**, 54, 436; Chamié and Tsien San-Tsiang, *ibid* 1941, **2**, 46; Rutherford, "Radioactivity", Camb. Univ. Press, 1905, 275.

[33] Makower and Russ, *Phil. Mag.*, 1910, **19**, 100.

[34] Muszkat, *ibid.*, 1920, **39**, 690.

[35] Sherwin, *Phys. Rev.*, 1948, **73**, 1173; 1949, **75**, 1799.

TABLE 6. *Recoil in homogeneous phases*

Decay	Chemical compound	E_β(max.) (Mev)	E_R(max.) (ev)	E_γ (Mev)	Observation	Ref.
(I) $^{51}Mn \longrightarrow {}^{51}Cr$	(*a*) MnO_4^- (aq) (*b*) Mn^{2+} (aq) (*c*) Mn^{2+} in acetone–H_2O and dioxan–H_2O (*d*) $CsMnO_4$(s) (*e*) $MnCO_3$(s)	2·35 $\beta(^+)$	83·0	No γ	(*a*) 50% Cr^{3+} (*b*) 97—100% Cr^{3+} (*c*) 5—15% CrO_4^{2-} (*d*) 100% CrO_4^{2-} (*e*) 30% CrO_4^{2-}	36
(II) $^{83}Se \longrightarrow {}^{83}Br$	(*a*) SeO_3^{2-} or SeO_4^{2-} pH = 7 (*b*) ditto, pH = 11	1·5	24·5	0·17, 0·37, 1·1	(*a*) 40% BrO_3^- independent of isotope or species (*b*) 24—30% in oxidised form	37, 38
(III) $^{132}Te \longrightarrow {}^{132}I$	(*a*) TeO_3^{2-} (*b*) TeO_4^{2-}	0·36	2·0	0·22	(*a*) 75% $I^- + I_2 + HIO$, 14% IO_3^-, 11% IO_4^- (*b*) 60% $I^- + I_2 + HIO$, 28% IO_3^-, 12% IO_4^-	37, 38
(IV) $^{143}La \longrightarrow {}^{143}Ce$	La^{3+} (aq)	0·93	6·74	No γ	60% Ce^{IV}	37, 38
(V) $^{144}Ce \longrightarrow {}^{144}Pr$	Acetonylacetone (A) complex	0·35	1·77	No γ but e^-	No disruption of complex in organic solvents, but some in water	39
(VI) $^{210}Pb \longrightarrow {}^{210}Bi$	Gaseous $Pb(CH_3)_4$	0·06	0·097	Several $< 0·047$	8% Molecular disruption. Internal conversion 33%.	39 39*a*

---

[36] Burgess and Kennedy, *J. Chem. Phys.*, 1950, **18,** 97.

[37] Burgess, Davies, Edwards, Gest, Stanley, Williams, and Coryell, *J. Chim. phys.*, 1948, **45,** 165.

[38] Davies, *J. Phys. Coll. Chem.*, 1948, **52,** 595.

[39] Edwards and Coryell, see Wahl and Bonner, " Radioactivity applied to Chemistry ", Wiley, N.Y., 1951.

[39a] Edwards, Day, and Overman, *J. Chem. Phys.*, 1953, **21,** 1555.

Initial product	Presumed fate of initial species
(I) (*a*) CrO_4^{2-}	Considerable disruption of CrO_4^{2-} by recoil
(*b*) Cr^+	Oxidised by air
(*c*) Cr^+	Some oxidation by electron annihilation
(*d*) CrO_4^{2-}	As expected. Disruption of CrO_4^{2-} prevented in solid state
(*e*) Cr^+	Some oxidation by electron annihilation
(II) (*a*) BrO_3^- or BrO_4^-	SeO_3^- and SeO_4^- take no part in the reaction
(*b*) BrO_3^- or BrO_4^-	This confirms the rôle of the solvent. The high-energy recoil could cause rupture of a substantial proportion of Br–O bonds, and would account for reduction
(III) (*a*) IO_3^- (*b*) IO_4^-	Very similar to previous example, but recoil energy is too low to account for results. The chemical reaction appears to be initiated by initial products and/or radiation effects
(IV) Ce^{4+}	A small amount of this very strong oxidising agent could easily be reduced by oxidation of impurities or exchange with Ce^{III} impurity in La. High recoil energy could also initiate chemical reaction leading to reduction
(V) PrA_3^+	Complexes of Pr^{IV} would be reduced to Pr^{III}. Results in organic solvents show that (i) internal conversion is chemically insignificant, (ii) energy necessary to disrupt complex is greater than maximum recoil energy (1·2 ev/molecule). In aqueous solution effects are therefore due to chemical reaction between Pr^{IV} and Ce^{III} and/or solvent
(VI) $Bi(CH_3)_4^+$	No disruption due to recoil only shows that (i) $Bi(CH_3)_4^+$ is not thermodynamically unstable, (ii) Bi–C bond energy > energy available for bond rupture ($\sim$ 0·02 ev)

for several days if warmed by a small heater placed nearby, but rapid deterioration occurred at room temperature.

Owing to the lack of knowledge of the chemistry of most of the work described before about 1940, no quantitative significance can be attached to most of the results. But by using data similar to those in Fig. 2, the following generalisations can be drawn from previous work : (i) The energy necessary to remove an atom from the surface of an untreated source decreases with increasing temperature, whether the source is prepared in the atmosphere or in a high vacuum. For bismuth, it is greater than about 50 kcal./mole at room temperature (zero yield), and perhaps 20—30 kcal./mole at 110°. (ii) This behaviour is a feature of the surface properties which can be altered reversibly by surface pretreatment.[23, 35]

(b) *Homogeneous systems.* In earlier work on β-recoil it has not always been possible to distinguish clearly between the effects of radiation-induced reactions, recoil processes, and the reaction of thermodynamically unstable products. In solution, the emphasis has been on the valency changes of the radioactive atom, and unfortunately, much of the work has been marred by the presence of γ-emitters. This makes the interpretation of the results difficult. Thus, the yield of daughter product has often not been 100% in the valency state expected (see Table 6). But the results may, in large measure, be explained in terms of the profound effect of recoil. Electronic excitation processes do not apparently need to be invoked to account for most of the observations.

At least two unequivocal cases are known [cerium acetonylacetone, and $Pb(CH_3)_4$]. In these cases, novel conclusions can quite confidently be made (see Table 6). Likewise the recent work on the rupture of C–N bonds [26] in the β-decay of $^{14}CH_3{\cdot}^{14}CH_3$ in the gas phase showed that in 47% of the decays the daughter molecules survived as $^{14}CH_3{\cdot}^{14}NH_2$. This system has been theoretically investigated by Wolfsberg [14] by treating the molecule for simplicity as a diatomic molecule. Exact calculations for rotational and vibrational excitation and dissociation are very difficult since no very good wave functions have been formulated for such a system. Molecular-orbital wave functions are assumed for the easier case of electronic excitation. The probability of electronic non-dissociation is found to be 0·815. When this is combined with the fraction 0·74 of recoils in which rupture of the 2·1 eV C–N bond is not obtained, a figure of $0{\cdot}60 \pm 0{\cdot}20$ is obtained for the probability of non-dissociation, in as good agreement with experiment as can be expected. The analysis implies that perhaps one-third of the activity loss is, in this case, caused by processes other than recoil, *i.e.*, by excitation (as proposed by Wolfsberg) or by subsequent chemical reaction of the daughter $^{14}CH_3{\cdot}NH_3^+$.

γ-*Recoil.* The emission of γ-recoil atoms from gold films electroplated on nickel has been observed [40] by the reaction $^{197}Au(n\gamma)^{198}Au$. The ^{198}Au recoil atoms were collected on a nickel plate $\frac{1}{16}$ in. away from the source plate with a yield of 0·1%. Recoil was inhibited because the gold atoms

---

[40] Yosim and Davies, *J. Phys. Chem.*, 1952, **56,** 599 ; Magnusson, *Phys. Rev.*, 1951 **81,** 285.

exist on the surface of the target in clusters. Higher yields are obtained if the gold film is prepared by vacuum distillation, and the neutron bombardment and recoil collection is also carried out in a vacuum. Recoils by $n\gamma$ reactions from similarly prepared sources may be up to 90—100% efficient. In this case the γ-recoil energy is quite large enough to displace the recoiling atom from its lattice position. Unfortunately, no attempt has been made to treat this process quantitatively, except for some general predictions of the degree of bond rupture expected in neutron-irradiated alkyl halides.[41]

Internal conversion of γ-rays leads to formation of chemically active species of high charge ($^{80}Br^* \longrightarrow {}^{80}Br^{10+}$; $^{83}Kr^* \longrightarrow {}^{83}Kr^{7+}$), and Cooper [42] has carried out calculations to show how far it is possible for molecules to dissociate after formation of Auger electrons. An experiment of significance is the internal conversion of γ-rays from ^{69}Zn and $^{127}Te/^{129}Te$. Diethyltellurium has been prepared and kept at 100° in a glass bulb for several hours. Substantial activity was found on the walls afterwards, showing that internal conversion by the 0·10 Mev γ-ray was frequent. But with ^{69}Zn, the 0·47 Mev γ-ray is too energetic for significant conversion and no activity was found on the walls with diethylzinc. This experiment is usually quoted as proving internal conversion with tellurium, but two other conclusions also follow: that neither (i) electronic excitation processes, nor (ii) the γ-recoil energy can cause disruption of the diethylzinc. From the latter it follows that the zinc–carbon bond energy is greater than the energy available for dissociation. Since the recoil energy is 15 ev, the energy available for dissociation is $(15)^2/(69 + 2 \times 15)$, *i.e.*, some 2·25 ev (52 kcal./mole).

(7) **Conclusion.**—This Review has been written with the intention of stimulating work in this field. New information is urgently needed to clear up the theoretical background, much of which is obscure; but there is no doubt that the quantitative treatment of the nuclear chemical process can provide new thermochemical information in a variety of systems which are of current interest.

One of us (D. L. B.) acknowledges the support of a Graduate Research Studentship from the Australian Atomic Energy Commission. Current work by the Reviewers is also supported by a research contract from the A.A.E.C. with this department (Prof. J. S. Anderson, F.R.S.).

[41] Suess, *Z. phys. Chem.*, 1940, *B*, **45**, 297, 312.

[42] Cooper, *Phys. Rev.*, 1942, **61**, 1.