

(22), (27) and (28)) are required for highest precision.

### Discussion

Comparison of the position of the most deflected light,  $Y = Ct$ , based on the classical geometrical equation (5) with the intensity diagrams calculated on the wave optical basis is made in Fig. 7. This comparison indicates that equation (5) is not exactly true. The error is greatest for the most downward deflected light, and this has the effect, in the schlieren optical systems<sup>6,15,16,17</sup> of compressing the height of the peak. This is seen by reference to Fig. 7, since the region of maximum intensity in the lowest fringe would represent the location of the peak in a schlieren diagram, as obtained with a contrast plate. Moreover, the gradual falling off of intensity for this fringe indicates that the location of the peak will be uncertain, and will be particularly sensitive to the time of exposure. This error should lead to high values for the diffusion coefficient when calculated by the height and area method<sup>3,18</sup> and the inflection point method.<sup>5</sup> However, the method of moments<sup>5</sup> also gives erroneous results because the classical theory breaks down for the edges of the gradient curve. In the case of the scale method,<sup>5</sup> where a small aperture at the lens masks off all but a narrow portion of the wave front arising from each scale line, it appears that the use of Wiener's equation<sup>4</sup> may have somewhat greater validity.

For a polydisperse system which yields symmetrical diffusion curves, it can be shown readily that the application of equation (23) results in the weight average of the path difference function  $f(z)$ . The diffusion coefficient obtained for the system by further application of equation (25) is a very complicated average value, however. A general-

(15) Philpot, *Nature*, **141**, 283 (1938).

(16) Longworth, *THIS JOURNAL*, **61**, 529 (1939).

(17) Andersson, *Nature*, **143**, 720 (1939).

(18) Longworth, *Ann. N. Y. Acad. Sci.*, **41**, 267 (1941).

ized treatment may make it possible to obtain better defined averages for such a system. The extension of the theory to the case where the diffusion coefficient is concentration dependent has not been developed.

**Acknowledgments.**—The authors are grateful to L. G. Longworth of the Rockefeller Institute for Medical Research for his prompt experimental tests of the classical description of the Gouy interference phenomenon and for his sustained interest in developing from it a useful method for the study of diffusion. Correspondence with Dr. Longworth has been fruitful in pointing to the need for refinements in the theory.

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### Summary

A quantitative theory for the spacing and intensity in the interference fringe system formed by focussing light from a horizontal slit through a diffusing boundary has been presented. Observation of the fringe displacement, in combination with the theoretical path difference function, the optical constants of the system and time, permits the evaluation of the diffusion constant for ideal diffusion independently from each fringe.

In the development of this theory by the methods of wave optics, small systematic errors in the schlieren optical methods are indicated, which set a limit to the precision attainable with such methods.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE INSTITUTE FOR NUCLEAR STUDIES AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

## Chemistry of Energetic Atoms Produced by Nuclear Reactions<sup>1</sup>

BY W. F. LIBBY

### I. Nature of Recoil Excitations

Nuclear reactions in general involve energies of at least 100,000 electron volts ( $2.3 \times 10^9$  cal./mole). This energy usually is divided between two particles—the emitted light particle and the residual recoil heavy nucleus—according to the law of conservation of momentum. Table I summarizes the results for the more common types of nuclear reactions. (In this Table,  $M$  is the mass of the recoil nucleus in ordinary units,  $m$  the mass of the light particle emitted,  $\mu$  the mass of the

bombarding particle if one is involved, and  $E_\alpha$  is the energy of the  $\alpha$  particle with a similar notation for other particles. In the case of beta radioactivity,  $E_0$  is the upper energy limit of the continuous spectrum.) The derivations of these expressions are given in Appendix I.

In general these energies are so large with respect to chemical bond energies (1 to 5 electron volts) that there is little doubt that bond rupture will occur in nearly all cases. Suess<sup>1a</sup> has called attention, however, to possibilities of inefficiencies in the dissociation processes in the case that the

(1) Paper given at Nuclear Symposium, Atlantic City Meeting, American Chemical Society, April 1946.

(1a) H. Suess, *Z. physik. Chem.*, **B45**, 312 (1940).

TABLE I<sup>a</sup>  
RECOIL OR EXCITATION ENERGIES OF PRODUCT ATOMS FROM VARIOUS NUCLEAR PROCESSES

Process	Recoil energy distribution
Alpha emission	Sharp at $(4/M)E_\alpha$
Particle bombardment; particle emission	Broad constant distribution with spread of $\frac{4E_\mu}{(M+m)^2} \sqrt{Mm\mu(m+M-\mu) \left(1 + \frac{Q}{E_\mu} \left[\frac{m+M}{m+M-\mu}\right]\right)}$ around mean value of $\frac{E_\mu M \mu}{(M+m)^2} + \frac{E_\mu m(m+M-\mu)}{(m+M)^2} \left(1 + \frac{Q}{E_\mu} \left[\frac{m+M}{m+M-\mu}\right]\right)$ where $Q$ is internal energy released in reaction
Nuclear fission	Sharp at $E \frac{M_1}{M_1+M_2}$ and $E \frac{M_2}{M_1+M_2}$
Beta radioactivity	Broad rounded peak extending (in e. v.) from zero to $548 \frac{E_0}{M} + 536 \frac{E_0^2}{M}$ where $E_0$ is upper energy limit of beta spectrum in MEV. and $M$ is atomic weight of atom. It will be asymptotic at high energies to the energy axis and perpendicular to it near zero energy
Slow neutron capture, gamma emission	Sharp at $536E_\gamma^2/M$ e.v. where $E_\gamma$ is in MEV. except when two gammas in cascade are involved when broad constant distribution follows with spread of $4E_\gamma E_\gamma 536/M$
Internal conversion and orbital capture	Recoil energy sharp at $\frac{548E_e}{M} + \frac{536E_e^2}{M}$ where $E_e$ is energy of emitted electron in MEV. Following X-rays have no appreciable effect. Very serious disruption occurs, because large positive charges follow Auger transitions for medium and heavy elements
Gamma excitation; particle emission	Sharp peak at $\frac{m}{M} E_m$
Particle bombardment followed by gamma emission	Sharp peak at $\mu E_\mu / M$

<sup>a</sup> Derivations in Appendix I.

atom bonded to the recoiling atom is of low mass with respect to the recoiling atom. In fact, he shows that for mass  $m$  of the light atom and mass  $M$  of the recoiling atom only the fraction  $m/(m+M)$  of the recoil energy is available for bond rupture. (The derivation is given in Appendix II.) This means, of course, that essentially only in the case of hydrogen or deuterium bonded to the activated atom will this effect be serious. Suess has presented experimental evidence for the effect in these cases. In general, however, we shall expect rupture to occur in nearly all cases.

Figures 1 and 2 present typical recoil energy distributions for slow neutron capture and beta radioactivity, respectively.

## II. Chemical Kinetics of Fast Recoil Atoms

### A. General Principles; Validity of the Assumption of Non-Ionizing "Billiard Ball" Collisions.

—The rapidly moving recoil atoms will be assumed to produce no appreciable ionization by the processes of electron ejection and capture which constitute the principal mechanism for energy loss by alpha particles, protons and fission products. It is generally accepted that ionization by a rapidly moving particle will be probable only at velocities comparable to the effective velocities for free electrons.<sup>2,3</sup> For example, a 100,000 e.v.

<sup>128</sup>I atom will have a linear velocity of  $3.9 \cdot 10^7$  cm./sec., which is the velocity of a 0.43 e.v. electron, which is too slow to effectively ionize. From this argument we can set a reasonable upper limit to the energy range in which ionization is improbable. Such limits are given by

$$E = 10^3 M \text{ (e. v.)} \quad (1)$$

where  $M$  is the mass of the recoiling atom in ordinary units. Very few cases involve energies above this limit. When they do, we shall expect energy loss (cooling) to occur partially by ionization until energies of the order of those given by equation (1) are reached, when an entirely different mechanism will prevail.

The cooling mechanism will consist of collisions between the recoil atom and the other atoms and molecules in the system. In the earlier stages when the energy of the recoiling atom is much larger than the chemical bonds in the molecules struck, the collisions will be similar in character to those which would occur with a loose assembly of atoms with no bonds. That is, transfer of momentum in a completely elastic fashion, except for the energy required to rupture the bond or bonds to the struck atom in the molecule, will occur. With this point in mind, we see that the energy loss per collision will depend greatly on the ratio of the mass  $M'$  of the target or struck atom in the molecule to the mass  $M$  of the impinging

(2) H. A. Bethe, *Rev. Mod. Phys.*, **9**, 262-265 (1937).

(3) Julian Knipp and Edward Teller, *Phys. Rev.*, **59**, 659 (1941).

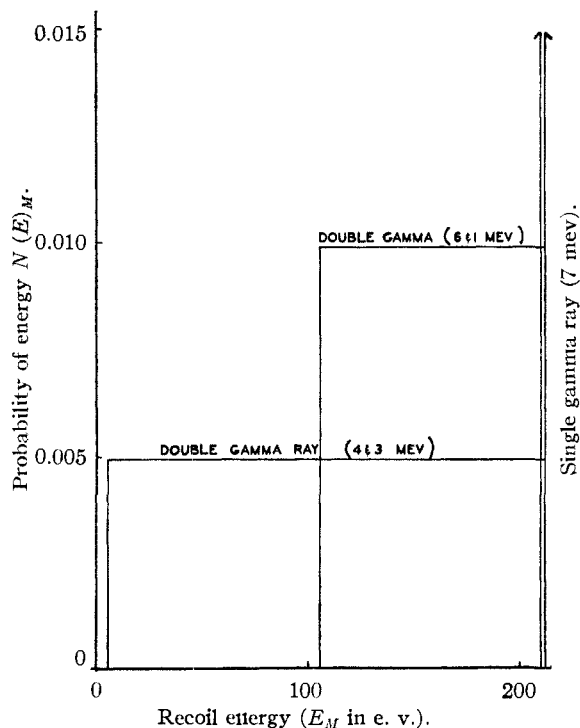


Fig. 1.—Distribution of recoil energies from neutron capture gamma rays for I<sup>128</sup>.

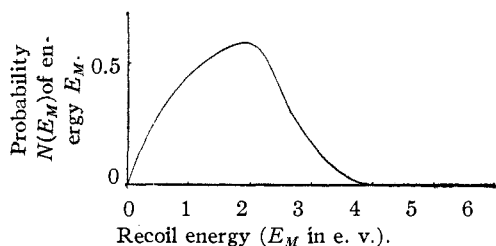


Fig. 2.—Beta radioactivity recoil energy distribution (upper limit 0.5 MEV. mass = 100). General eqns.: max. energy (e. v.) =  $548 E_0/M + 536 E_0^2/M$ , av. energy (e. v.) =  $274 E_0/M + 268 E_0^2/M$  where  $E_0$  is upper energy limit of beta spectrum in MEV. and M is atomic weight of recoiling atom.

atom. The scattering will be assumed to be isotropic in the center of mass system with the probability of all angles of scattering in this system given by  $(1/2) \sin \theta d\theta$ , *i. e.*, the solid angle for angles between  $\theta$  and  $\theta + d\theta$  divided by  $4\pi$  the total solid angle. In the general case, the average energy retained after  $n$  collisions,  $E_n$ , will be related to the initial energy  $E_0$  by

$$E_n = E e^{-Kn} \tag{2}$$

where  $K$  is given by

$$K = \frac{1 - (1 - \gamma) [1 - \ln(1 - \gamma)]}{\gamma} \tag{3}$$

in which  $\gamma$  is

$$\gamma = 4M'M/(M + M')^2 \tag{4}$$

The derivation of this result is given in Appendix

III. Figure 3 gives values of  $1/K$  which represent the relative number of collisions for a given fractional energy loss. This curve displays particularly clearly the sharp dependence of cooling efficiency on mass ratio for elastic collisions. For a given initial energy,  $E$ , the energy distribution will be uniform and constant between  $E$  and  $(1 - \gamma)E$ . For equal masses, the range extends to zero energy with constant probability, but for a case such as I<sup>128</sup> on Cl<sup>37</sup> where  $\gamma$  is 0.69, the maximum possible loss is 69% and the average loss is 37%.

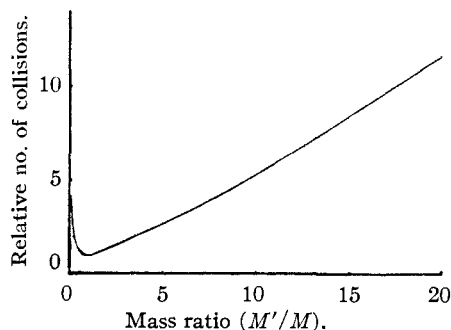


Fig. 3.—Relative number of collisions for given cooling vs. mass ratio.

When the energy of the recoil atom has decreased to the point where it approaches the energies of the bonds in the molecule, collisions with the molecule as a whole or component radicals in it will become prevalent. These collisions need not be elastic, and in fact are quite likely to be inelastic in the sense that the struck molecule or radical is likely to acquire internal vibrational energy which may be so extreme as to lead to dissociation. Figure 4 represents the expected energy distributions of a rapidly moving atom of mass 35 such as chlorine atom with slow hydrogen atoms and chlorine atoms.

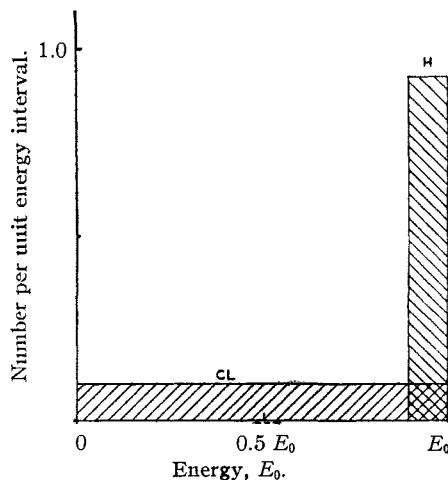


Fig. 4.—Energy distributions of fast chlorine atom (mass 35) after colliding elastically with an hydrogen atom or another chlorine atom.

## B. Processes Involving No Change in Atomic Number; Chemistry of the Szilard-Chalmers Reactions

1. **Experiment.**—Typical nuclear processes of this type are  $(n, \gamma)$ ,  $(\gamma, n)$  and  $(d, p)$ . The possibility of using the bond rupturing effects to concentrate radioactive elements was discovered by Szilard and Chalmers<sup>4</sup> in the case of the  $(n, \gamma)$  process. Several workers have investigated the process further since,<sup>5a-h</sup> and the following remarks are based mainly on these researches.

We shall consider the observed phenomena in the case of the organic halides under slow neutron exposure in some detail. The experimental procedure is to expose the pure halide, e.g., bromobenzene, to the neutron source for a period about twice the half-life of the radioelement produced. After the exposure the sample is extracted with water to which a small amount of bromine ion has been added. The latter is necessary only with the purest and least hydrolyzable organic halides in which halogen atoms can exist for appreciable periods as such without exchanging with impurity bromine ion or hydrogen bromide, both of which are soluble in water, whereas the atomic halogens are not.<sup>6</sup>

After two or three extractions, further treatment removes no additional activity. We shall define the fraction of the radioactivity resisting aqueous extraction under these conditions as the retention,  $R$ . Table II gives the observed values for certain typical organic halides exposed in the liquid state at about room temperature to thermal neutrons.

TABLE II<sup>5a, b</sup>

RETENTIONS OF ORGANIC HALIDES FOR  $(n, \gamma)$  ON LIQUIDS AT ROOM TEMPERATURE

Compound	Retention, %
C <sub>2</sub> H <sub>5</sub> I	40
C <sub>2</sub> H <sub>5</sub> Br	75
C <sub>6</sub> H <sub>5</sub> I	65
C <sub>6</sub> H <sub>5</sub> Br	70
C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub>	31

A further point of importance is that these large retentions are not due to failure of the nuclear process to cause rupture. Either *dilution of the target substance* with solvents, all of whose atoms are of widely different mass from that of the radioactive atom, e.g., ethanol in the case of the organic halides, or *vaporization of the target substance reduces R to nearly zero*. Since neither of these changes could affect the nuclear processes and are extremely unlikely to have an appreciable effect on

(4) L. Szilard and T. A. Chalmers, *Nature*, **134**, 462 (1934).

(5) (a) E. Fermi, E. Amaldi, et al., *Proc. Roy. Soc. (London)*, **A149**, 522 (1935); (b) O. D'Agostino, *Gazz. chim. ital.*, **65**, 1071 (1935); (c) F. Paneth and J. W. J. Fay, *J. Chem. Soc.*, 384 (1936); (d) E. Gluckauf and J. W. J. Fay, *ibid.*, 390 (1936); (e) O. Erbacher and K. Philipp, *Ber.*, **69**, 893 (1936); *Z. physik. Chem.*, **A176**, 169 (1936). (f) C. S. Lu and S. Sugden, *J. Chem. Soc.*, 1273 (1939); (g) W. F. Libby, *This Journal*, **62**, 1930 (1940); (h) *Science*, **93**, 283 (1941).

(6) Don DeVault and W. F. Libby, *This Journal*, **63**, 3216 (1941).

the highly energetic initial dissociation of the halide molecule, one concludes that the large retentions shown in Table II must be due to reformation processes. Table III shows the effect of alcohol dilution on the retention of radio-bromine by carbon tetrabromide.

TABLE III<sup>5a, b</sup>

EFFECT OF DILUTION BY ETHANOL ON RETENTION BY CARBON TETRABROMIDE

Mole per cent. CBr <sub>4</sub>	R, %
100	60 ± 5
1.15	28 ± 5
0.74	13 ± 5
.45	2 ± 2
.064	0 ± 2

Table IV gives data on the effect of vaporization on retention.

TABLE IV<sup>5a, b</sup>

EFFECT OF VAPORIZATION ON RETENTION BY ORGANIC HALIDES

Compound	R, liq. (%)	R, gas (%)	Press., mm.
C <sub>2</sub> H <sub>5</sub> Br	75	4.5 ± 0.4	39 cm. + 37 cm. air
H <sub>2</sub> CBr-CBrH <sub>2</sub>	31	6.9 ± .6	4 cm. + 72 cm. air

Another pertinent fact is that the processes of re-entry result principally in the formation of the mother molecule. For example, in the case of liquid bromobenzene<sup>5h</sup> a fractional distillation, after extraction with a reducing aqueous solution, has shown that within 0.5% all of the activity is present as monobromobenzene rather than in any of the dibromobenzenes or other molecules conceivable. For this experiment, the irradiated and washed sample was carefully distilled after addition of all three dibromobenzene isomers in non-radioactive form as carriers. At least 99.5% appear in the C<sub>6</sub>H<sub>5</sub>Br cut. Other cases seem not to be so clearcut, according to Gluckauf and Fay<sup>5d</sup> as summarized in Table V together with the bromobenzene result.

TABLE V

CHEMICAL COMPOSITION OF THE RETAINED RADIO HALOGENS IN SLOW NEUTRON IRRADIATED ORGANIC HALIDES

Compound	R, %	Radiochemical composition of retained activity
C <sub>6</sub> H <sub>5</sub> Br	70	99.5% $\theta$ Br, <0.5% in $\theta$ Br <sub>2</sub>
CH <sub>3</sub> I	56	81% CH <sub>3</sub> I, 19% CH <sub>2</sub> I <sub>2</sub>
CH <sub>2</sub> Br <sub>2</sub>	57	75% CH <sub>2</sub> Br <sub>2</sub> , 25% CHBr <sub>3</sub>
CHBr <sub>3</sub>	66	71% CHBr <sub>3</sub> , 29% CBr <sub>4</sub>
C <sub>6</sub> H <sub>5</sub> Cl	50	70% C <sub>6</sub> H <sub>5</sub> Cl, 30% C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>

Finally, it was discovered by Lu and Sugden<sup>7</sup> that the addition of aniline to bromobenzene in small percentages greatly decreased the retention. Their data were

% Aniline added	0	0.25	1	2	4	6	4 (after irradiation)
Retention, %	70	55	37	34	24	24	65

(7) C. S. Lu and S. Sugden, *J. Chem. Soc.*, 1273 (1939).

Summarizing, the outstanding characteristics of the Szilard-Chalmers reactions on the organic halide molecules are

1. Considerable fractions, of the order of 50%, of the radioactive atoms are found bound in organic molecules.

2. Dilution of the target halide with hydrocarbons or ethanol before irradiation reduces this "retention" nearly to zero so nearly all of the radioactive halogen is water soluble.

3. Irradiation of the organic halide vapors reduces the retention to a very few per cent.

4. The chemical form in which the organically bound radioactive halogen atoms tend to occur is that of the target molecule.

5. Addition of aniline to bromobenzene in small percentages greatly reduces the retention.

2. **Theory.**—All of these facts are explicable on the basis of the following mechanism based on the hard sphere or "billiard ball" type of collision between the recoil atom and the atoms constituting the neighboring molecules. The recoiling halogen atom is of much larger mass than any atom other than the halogen in the organic halide molecule, so only collisions with the halogen atom in the halide molecule can result in a nearly complete transfer of momentum and energy in a single collision.<sup>7a</sup>

Collisions with hydrogen and carbon atoms and even methyl radicals will leave the recoiling atom with a considerable fraction of its energy after any single collision as shown in Fig. 4. This residual velocity will insure the escape of the radioactive atom from the vicinity of the collision and the free radical produced so the chance of combination between the free radical and the radioactive atom is nearly zero.

However, in the case of a collision with the halogen atom in the molecule, nearly complete energy transfer is a definite possibility, and a very finite probability exists for collisions which leave the radioactive atom with energy less than a given value, say  $\epsilon$ . In fact, if the energy just before collision is  $E$ , this probability will be  $\epsilon/E$  if  $E$  is large with respect to the energy,  $\nu$ , of the bond to the halogen atom. This result follows from the uniform energy distribution which must result from an elastic collision between bodies of nearly equal mass. If the energy  $\epsilon$  is identified with the energy just sufficient to insure escape from the "cage"<sup>8</sup> of solvent molecules surrounding it and the collision-born free radical, we can identify the chance of retention in any given halogen-halogen collision with  $\epsilon/E$ . Similarly, the chance of the recoiling atom's dropping below  $\nu$ , the bond energy, is  $\nu/E$ . This removes the atom from fur-

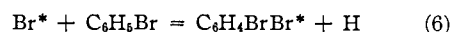
ther chance of entering the molecule in a subsequent collision. For each collision the proportion of the atoms ending their disruptive careers which are caught in the "cage" and consequently react with the free radicals and so are "retained" is  $\epsilon/\nu$ . This result being independent of the energy  $E$ , we shall identify it as an approximate expression for the retention,  $R$

$$R = \epsilon/\nu \quad (5)$$

The cage of solvent molecules holds the radioactive halogen atom  $X^*$  and the free radical  $R$  together until they can dissipate their excess energy and react with one another. The escape energy,  $\epsilon$ , will be the energy required for the  $X^*$  atom to push through the surrounding layer of  $RX$  molecules in essentially the first collision. Referring to Table II, we see that this model requires  $\epsilon$  to lie between 30 and 75% of the C-X bond energy, or between 10 and 45 kcal./mole—not too unreasonable figures in view of the requirement that transmission occur essentially on the first wall collision. It is not so clear from this simple model why ethyl dibromide should have  $\epsilon$  31% of the carbon-bromine bond while ethyl bromide should have  $\epsilon$  75% the same bond. This may be due, however, to an understandable tendency of the hot radical ethylene bromide to form ethylene and bromine atoms and so make re-formation essentially less probable so more wall collisions and a lower  $\epsilon$  value are required.

We note that the energy  $\epsilon$  will drop as the liquid  $RX$  is vaporized because the particles will encounter many less collisions in escaping from the collision site. Thus we have explained the large reduction of retention on vaporization.

The tendency to form the mother molecule is now explicable on the basis that all collisions with atoms other than  $X$  in the organic halide have no chance of producing  $X^*$  atoms of energy less than  $\epsilon$  unless the incident energy  $E$  is itself close to  $\epsilon$  (and greater than  $\nu$ ). The chance of an atom occurring in this energy range is relatively small, so the over-all chance of reactions like



is small relative to that for the collision with the bromine atom



It is true, however, that the inelastic collisions with the molecule as a whole or groups within it become relatively more probable as the cooling proceeds and these collisions may result in the ejections of H atoms or radicals under conditions where the  $X^*$  loses a considerable fraction of its incident energy  $E$ , but such collisions are not probable if  $E$  is much greater than the average bond energy. In addition, the rupturing of carbon-hydrogen and carbon-carbon bonds by this mechanism is unlikely to give any free radicals sufficient energy to escape the cage, whereas H atom may receive enough. This will tend to favor H substitution for the small fraction of the re-

(7a) It is true that the mass of the struck atom will not in general be exactly equal in most cases because the addition of one neutron has increased the mass of the recoiling atom by one unit and the occurrence of isotopes will lead to further inequalities. However, these effects will amount in general to only two or three mass units at most, and will not be of great significance in the collisional transfer of momentum.

(8) J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **80**, 125 (1934).

tention which does not occur by the main halogen-halogen collision process represented in equation (7). In this way we understand the tendency to reform the mother molecule in the system in the main with a smaller tendency to substitute H atoms.

The freshly reformed  $RX^*$  molecule is certain to possess considerable vibrational energy which it must dissipate to the "cage" walls. On this basis we can explain the Lu and Sugden aniline effect. A general class of reactions, the Menschutkin Reaction



is known, and proceeds in general at appreciable speeds on heating. In other words, *the aniline does not react appreciably with the bulk of the alkyl halide because the molecules are cold, but does react with the freshly reformed  $RX^*$  molecules before they can cool.* This means, of course, that there should be at least one aniline molecule in each cage for maximum efficiency if the reaction is bimolecular as written in equation (8)—in other words, a mole fraction of 5 to 10%, as observed.

*The general effect of dilution with a solvent none of whose atoms are of mass comparable to that of the radioactive halogen is to cool the  $X^*$  atom by cage escaping collisions until the energy is less than the bond energy  $\nu$ , when it can collide with an  $RX$  molecule without danger of retention.* In other words, if the solution is sufficiently dilute so that the average number of collisions occurring with molecules containing no halogen before a halide collision occurs is sufficient to drop the initial energy  $E_0$  to  $\nu$  or less, no retention will occur. In this sense the dilution curve is a kind of absorption curve, for the  $X^*$  atoms in the diluent, and may conceivably be used when sufficiently carefully standardized to measure the initial energies  $E_0$ . The detailed interpretation of the dilution curve at present is extremely difficult, but the high dilution tail is somewhat more tractable. In this range, where the chance of more than one collision with a heavy atom is negligible, the retention will be given by

$$R = (\epsilon/\nu)\alpha n \quad (9)$$

where  $\alpha$  is the ratio of the collision cross-section for the heavy atom to that for the light, all multiplied by the atomic concentration of heavy atoms;  $\epsilon/\nu$  is the retention per collision, and  $n$  is the total number of collisions necessary to drop the initial energy  $E_0$  to  $\nu$ , the bond energy. Taking the data in Table III for which  $\epsilon/\nu$  is 60%, and assuming the cross-sections of bromine and hydrogen atoms to be 1.5 to 1, the limiting slope of  $R_0^2$  against  $\alpha$  is 31. This, then, is the approximate number of collisions,  $n$ , required to slow the hot  $Br^*$  atom down to the carbon-bromine bond energy,  $\nu$ . In these 31 collisions, 31 carbon-hydrogen and oxygen-hydrogen bonds were broken at total cost of about 124 e.v. In addition, the loss to the ejected hydrogen atoms amounted to  $E_0(1 - e^{-K\alpha})$

where  $K$  as given by equations (3) and (4) is  $1/20$ , so the translational loss is 78.7% of  $E_0$ . Then

$$\begin{aligned} E_0 &\geq 0.787 E_0 + 124 & (10) \\ E_0 &\leq 0.787 E_0 + 124 + 2.4 \end{aligned}$$

where 2.4 is the value of the carbon-bromine bond. Finally,  $E_0$ , according to these considerations, should lie between 584 and 595 e.v.

Returning to Table I, the energy of the capture gamma ray causing the ejection is found to be 9.3 MEV., which seems to be a little large. These results do indicate, however, that a careful calibration of such dilution curves by study of cases where the energies are known may result in a useful technique for nuclear chemistry and physics.

**3. Effect of Multiple Processes at High Radiation Levels.**—It must be stated that the rather elementary theory of the preceding paragraphs tacitly assumes that the chance of two recoil atoms reacting with one another or with the radicals they produce is negligible. It is assumed also that anomalous species produced by action of gamma radiation, X radiation, fast neutrons, and disintegration electrons on the abundant molecular species are sufficiently rare so they are not likely to react with the recoiling or otherwise activated radioactive atoms produced by the nuclear reaction. In other words, the considerations of this paper are concerned primarily with the low flux limit where only reactions between the principal molecular constituents of the system and the hot radioactive atom are involved.

The radiation levels at which these complications will enter are difficult of prediction. It does seem clear, however, that radium beryllium neutron sources containing up to 500 milligrams of radium are relatively safe from this danger, while cyclotrons and pile irradiations probably are dangerous. The best experimental procedure is to vary the radiation intensity and observe whether the nature of the reactions is independent of the intensity. The remarks in this paper are intended to apply to those conditions where such an independence exists.

### C. Processes Involving a Change in Atomic Number

**1. Introduction.**—Among the processes in this class are the following: alpha and beta radioactivity,  $K$  capture, and all of the transmutation processes without charge balance, such as  $(\alpha, n)$ ,  $(\alpha, p)$ ,  $(d, n)$ ,  $(d, \alpha)$ ,  $(p, \alpha)$ ,  $(p, n)$ ,  $(p, \gamma)$ ,  $(n, \alpha)$ ,  $(n, p)$  and nuclear fission.

The high velocity bombarding and ejected particles are in the ionizing range with the result that they eject electrons and form positive ions which may dissociate in secondary processes. If the ions produced are stable in the environment afforded, the ejected electrons will be recaptured eventually to reform the original molecules. If, however, as is frequently true, the positive ion is unstable, the recapture will still occur but to form new molecules. The recombination is possible

because the electrons ejected are of low energy, certainly less than 30 e.v., the total average energy of ionization. As a result of the low energy the distance of separation in condensed media is small and recombination occurs very rapidly in most cases, though certain ionic solids exist in which the ejected electrons can find metastable sites due to the electrostatic force fields in the solid lattice, and remain dissociated for very long periods. In the case of gases recombination is slower in that the cage effect is nearly absent and the electrons proceed to considerable distances from the positive ions. This reduces the attractive electrostatic forces and makes recombination more nearly a matter of chance diffusion than would be true in the case of a liquid hydrocarbon, for example. In ionic solids the recombination will be slower in general for a similar reason, namely, the electrostatic forces from the ions in the lattice will reduce by dielectric action the forces between the ejected electron and the positive ion.

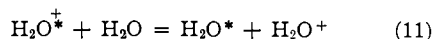
Since the singly positively charged ion of many molecules dissociates readily, emitting atoms and radicals with sufficient energy to escape the cage, molecular dissociation can result, particularly if the radiation density is sufficient to allow reactions between ejected atoms or radicals to form new and stable molecules; *e. g.*, liquid water is dissociated by intense  $\alpha$  particle irradiation into hydrogen and oxygen gas. This entire subject of the chemical effects of ionizing particles has been the subject of considerable investigation<sup>9</sup> by physicists, physical chemists, and biochemists. The biological implications are of great importance, of course.

In the immediate discussion, however, we are not concerned primarily with this subject, now generally known as Radiation Chemistry, but rather with the eventual fate of the energetic and generally radioactive atoms produced by the nuclear reactions resulting in a change of nuclear charge. These particles, though highly energetic, are essentially non-ionizing in most cases because their masses are so large that their velocities are low. We shall treat them as particles which ricochet about, transferring energy to other atoms, ions, and molecules in the system and finally attain some stable or metastable state in the system; and it shall be our task to *predict and explain these final states*. This point of view rests on a principle which needs further explanation, namely, that *the probability of dissociation of any particular molecule by ionization generally is very low*. In other words, suppose the process of X-ray absorption, for example, were in some strange way to be capable of rendering the oxygen atom in water molecules radioactive every time that electron ejection occurred. Then the above statement

(9) S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," 2nd ed., The Chemical Catalog Company, New York, N. Y., 1928; G. Glockler and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley and Sons, New York, N. Y., 1939.

means that the evolved oxygen gas would not contain nearly all of the radioactive oxygen and in fact, might contain little more than its fair share on the basis of uniform distribution among all of the water molecules in the system—just as if the processes of ionization and radioactivation were independent.

The reason for this is that electronic exchange between states of equal or nearly equal energy is very rapid. If we represent radioactivity in the oxygen by an asterisk, we can write



as a very rapid reaction. The neighboring molecules, in other words, afford a mechanism for *the diffusion of the positive charge away from the radioactive atom* which was the original site of ionization. Of course, eventually some one  $\text{H}_2\text{O}^+$  ion will dissociate into  $\text{H}^+$  and  $\text{OH}$ , and the over-all process will in no way be upset except in the one respect that the radioactivity will not follow the ionization dissociation mechanism. For these reasons, we shall treat the chemistry of the hot new element atoms rather independently of the ionization which is associated with their birth and cooling processes.

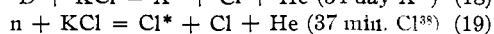
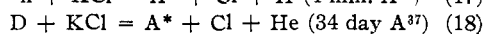
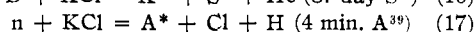
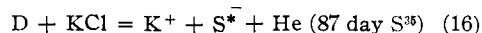
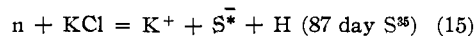
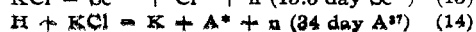
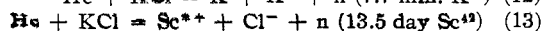
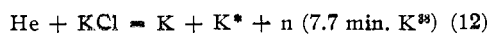
**2. Ionic Crystal Targets and Method of Concentration of Radioactivity.**—We shall discuss now the case of ionic crystal targets and shall suppose that a particular atom has been given a considerable jolt, and simultaneously had its atomic number changed by  $\pm 1$  or  $\pm 2$  units, and its mass changed by 0,  $\pm 1$ ,  $\pm 2$ ,  $\pm 3$  units corresponding to the usual nuclear reactions.

If the change in mass is relatively small as compared to the total mass of the target atom, the collisional energy transfer coefficients  $K$  will approach unity for collisions with atoms identical with the target atom. If the target atom is an abundant constituent of the crystal, *e. g.*, the only positive or negative ion present, this means that very few collisions will suffice to cool the particle to an energy sufficiently low that it will be incapable of disrupting the lattice locally. This will be of the order of magnitude of the heat of sublimation,  $L$ , of the crystal into constituent ions and atoms taken per average constituent ion or atom. As a rough estimate for hard crystals subliming above  $500^\circ$ , this will be of the order of 5 e. v. Further cooling below this energy will occur much less rapidly, but will be attended by relatively less diffusion because the walls of the "cage" will be more impervious. In other words, after about ( $n = \ln E_0/L$ ) collisions, the particle will be trapped in a cavity formerly occupied by a target atom the same as that which produced the energetic radioactive ion or atom, and it will proceed to heat the crystal locally until its energy,  $L$ , has been dissipated vibrationally over the crystal. The energy  $L$  will in most cases be sufficient to melt the crystal locally out to at least the first layer of nearest neighbors, so we shall think of the

situation immediately after trapping of the radioactive atom as though it were contained in a small liquid droplet of about a dozen ions or atoms at most, resting in a cavity in the crystal about the size of one coordination sphere. This hot zone then transmits heat vibrationally to its crystalline wall until it freezes and the immediate fate of the radioactive atom is determined. The distance between this site and that of the nuclear reaction will be about  $\lambda\sqrt{n}$ , where  $\lambda$  is the lattice spacing between target atoms and  $n$  is the number of collisions to cool to the energy  $L$ . If for example  $L$  be taken as 5 e.v. and  $\lambda$  as  $2\text{\AA}$ , and  $E_0$  as 10,000 e.v. the number of collisions is 8 and the mean distance  $2\sqrt{8}\text{\AA}$ . These results reveal how *remarkably short-ranged the hot recoil particles must be*. The calculations apply as given only to crystals where all ions are nearly of the same mass, e. g., potassium chloride. It is expected in other cases that the presence of lighter particles will increase this range and heavier particles will leave it essentially the same as in the case of equal masses.

Returning now to the hot droplet, we shall discuss the chemical reactions which are likely to occur in this stage to establish the chemical form in which the radioactivity will be left frozen in the lattice. Due to the extremely high local temperature, we shall expect that the stablest combination involving the radioactive atom and the ions in the coordination sphere will be formed. The problem resolves itself, therefore, into the determination of the combination of minimum free energy. This must be done, of course, by use of standard theoretical physical chemical methods—use of ionization potentials, electron affinities, ionic radii and repulsive potentials.

For example, consider a potassium chloride crystal as a target. Any charged particles entering or leaving the crystal will eventually be compensated by the acquisition (or loss) of the appropriate number of electrons from the environment to balance the charge and return the crystal to its original uncharged state. We shall assume, therefore, that for our problem, where the crystal is to be heated and allowed to stand for extended periods after exposure, this neutralization has occurred, and we shall incorporate this assumption by writing all equations with *atoms* rather than for projectiles and emitted particles unless the final state is expected to be ionic. It is realized, of course, that the unneutralized state can persist for some time and have a real existence. It is just that the present problem is the prediction of the chemical identity of the radioactive atoms after the crystal has been heated and allowed to settle into its most stable condition. Therefore the following reactions can occur to form known activities.



In equation (12) the question is the solubility of potassium metal in potassium chloride. This is low, so heating will evolve potassium metal vapor. The difficulty is that exchange will occur before the vaporization so no concentration can be obtained. In equation (13)  $\text{Sc}^{*+}$  will be the stable ion because no sufficiently stable sites for additional electrons exist.<sup>9a</sup> Since  $\text{Sc}^+$  is appreciably larger than  $\text{K}^+$ , probably 0.3  $\text{\AA}$ ., the repulsive forces will operate to force it to the surface. Estimating this energy as 10% of the binding energy for  $\text{K}^+$  it will be 8 kcal./mole at most. Set against this is the entropy change. In the interior of the crystal, the entropy will be  $R \ln N_v$  where  $N_v$  is the number of positive ion sites in the body of the crystal, and on the surface  $R \ln N_s$  where  $N_s$  is the number of positive ion sites on the surface. Therefore the entropy of migration will be

$$R \ln (N_s/N_v)$$

which for a cubic crystal of side  $l$  (cm.) will be  $R \ln 6(A/l)$  where  $A$  is the distance between the closest  $\text{K}^+$  ions in potassium chloride, or 3.1  $\text{\AA}$ . This entropy change of  $-26.3$  cal./mole/deg. for a 1-mm. crystal amounts to 7.9 kcal./mole at  $25^\circ$ , so it *seems that crystals much smaller than this will be required to make  $\text{Sc}^*$  diffuse to the surface* at baking temperatures where the time of migration would be reasonable. A  $1 \mu$  crystal will have an entropy of migration of only  $-12.5$  cal./mole/deg., giving a free energy of migration of  $-4.2$  kcal./mole at  $25^\circ$ , so small crystals favor the separation. In addition, the time of diffusion,  $\tau$ , obeys

$$l^2 = 2D\tau \quad (12)$$

where  $D$  is the diffusion coefficient, so the rate of separation for a  $1 \mu$  crystal will be  $10^6$ -fold greater than for the 1-mm. crystal. This principle, *that separations by baking will be favored in equilibrium as well as in rate by the use of small crystals*, probably will prove useful in the preparation of radioactive sources of high specific activity.

(9a) The ionization potential of  $\text{Sc}^{+1}$  probably is at least 10 e.v., so a stable site for the electron is required if the second ionization is to occur. The gain in electrostatic energy by doubling the scandium ion charge will be about the electrostatic energy of  $\text{K}^+$  in potassium chloride, which will amount to 4 or, at most, 5 e.v. The solvation energy of an electron in a potassium chloride crystal even at sites of lattice imperfections cannot amount to the remaining 5 e.v. The reason for this is that the low mass of an electron requires it to have a zero point energy of motion which will amount to a considerable fraction of the electrostatic energy of a single negative charge introduced into a potassium chloride lattice. These considerations are well borne out by the facts about "F-centers,"<sup>10</sup> which consist of electrons introduced into crystals in a metastable condition by photochemical or radiation chemistry methods. They impart color to the crystal—a phenomenon which allows estimates of their energies of binding to be made.

(10) Rollefson and Burton, "Photochemistry," Prentice-Hall Co., New York, N. Y., 1939, Chap. VI.



TABLE VI

Activity produced	Target	Reaction expected	Product chemistry	Expected removability to surface on baking
T ( $^3\text{H}$ )	Be	$\text{Be} + \text{D} = \text{T} + 2\text{He}$	BeT	Large
	Li	$\text{Li} + \text{n} = \text{T} + \text{He}$	LiT	Large
$\text{Be}^7$	Li	$\text{Li} + \text{D} = \text{Be} + \text{n}$	Be solution in Li	Very small
	LiF	$\text{LiF} + \text{D} = \text{Be}^+ + \text{F}^- + \text{n}$	Surface $\text{BeF}_2$	Medium
(11) $\text{C}^{11}$	$\text{B}_2\text{O}_3$	$\text{BO}_{3/2} + \text{D} = 1/2\text{CO} + 1/2\text{CO}_2 + \text{n}$	CO and $\text{CO}_2$	Large

In the cases of equations (14), (17) and (18), where  $\text{A}^*$  is produced, the full energy of creation of a hole is available for separation, about 80 kcal./mole, so there is little doubt that heating will segregate it.

Equation (15) and (16) make the separation of  $\text{S}^*$  seem about as difficult as that for  $\text{Sc}^*$  requiring fine crystals, the reason being that sulfur ion is probably about 0.3 Å. larger in radius than the chlorine ion.

Following the vacuum baking at a temperature sufficiently high to allow the migration to occur in a reasonable time (as determined by experiment, though certain approximate theoretical estimates can be made), appropriate surface chemical treatment should be used to remove the surface activities produced, unless the products are permanent gases. For example, in the case of  $\text{S}^*$  from potassium chloride one might well treat the vacuum baked irradiated powder with a little hydrogen chloride vapor at about  $100^\circ$  to release  $\text{H}_2\text{S}^*$ .

Further examples of possible applications of the crystal baking procedure are given in Table VI.

### Appendix I

#### Derivations of Formulas in Table I

##### A. Alpha Emission

$$ME_M = mE_\alpha$$

from conservation of momentum. Therefore

$$E_M = \frac{m}{M} E_\alpha = \frac{4}{M} E_\alpha$$

**B. Particle Bombardment; Particle Emission.**—The vector  $\text{OB}$  in Fig. 5 represents the velocity  $V$  of the incident particle of mass  $\mu$ . The vectors  $\text{G}\alpha$  and  $\text{G}\beta$  represent the velocities of separation of the recoil nucleus of mass  $M$  and the disintegration particle of mass  $m$ , respectively. If we assume isotropic disintegration all directions of the line  $\alpha\beta$  are equally probable. The vector  $\text{O}\alpha$  is the velocity,  $\mu$ , of the recoil nucleus and  $\text{O}\beta$  that of the disintegration particle with respect to the laboratory coordinates.

In order to proceed further we must consider whether the reaction has a reaction heat,  $Q$ , taken as heat released. Then

$$E_\mu + Q = E_M + E_m \quad (1)$$

because of energy conservation. When  $Q$  is zero, the line  $\alpha\beta$  will have a length  $\omega$  which can be calculated from equation (1) choosing the position

(11) Reuben, Hassid, Kamen, THIS JOURNAL, 61, 661 (1939). These authors found carbon monoxide and dioxide produced by D bombardment of boron trioxide.

$\theta = \pi/2$  for simplicity, since  $\omega$  is independent of  $\theta$  from our assumption of isotropic reaction. Then

$$\begin{aligned} 1/2\mu V^2 &= 1/2M \left( \frac{\mu^2}{(m+M)^2} V^2 + \frac{m^2}{(m+M)^2} \omega^2 \right) + \\ &1/2m \left( \frac{\mu^2}{(m+M)^2} V^2 + \frac{M^2}{(m+M)^2} \omega^2 \right) \quad (2) \end{aligned}$$

or

$$\omega^2 = \frac{\mu(m+M-\mu)}{mM} V^2 \quad (2')$$

Now when  $Q$  is different from zero,  $\alpha\beta$  will be longer or shorter than  $\omega$  depending on whether  $Q$  is negative or positive, respectively. We shall introduce  $\gamma$  as the ratio of the length  $\alpha\beta$  to  $\omega$  so  $\gamma$  will be unity for  $Q = 0$  and  $\gamma$  will be  $< 1$  for  $Q < 0$  and  $\gamma > 1$  for  $Q > 0$ .

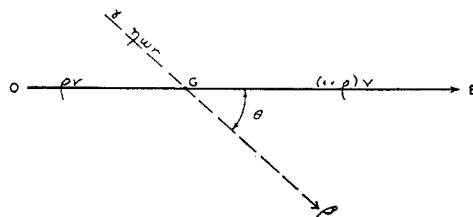


Fig. 5.— $\rho = \mu/(m+M)$ ;  $\eta = m/(m+M)$ .

Setting up the more general form of equation (1), we have

$$\begin{aligned} Q + E_\mu &= \frac{M}{2} \left( \frac{\mu^2}{(m+M)^2} V^2 + \frac{m^2}{(m+M)^2} \omega^2 \gamma^2 \right) + \\ &\frac{m}{2} \left( \frac{\mu^2}{(m+M)^2} V^2 + \frac{M^2}{(m+M)^2} \omega^2 \gamma^2 \right) \quad (3) \end{aligned}$$

Solving for  $\gamma^2$  we have

$$\gamma^2 = 1 + \frac{Q}{E_\mu} \left( \frac{m+M}{m+M-\mu} \right) \quad (4)$$

For any angle

$$u^2 = \rho^2 v^2 + \eta^2 \omega^2 \gamma^2 - 2\rho\eta v\omega\gamma \cos \theta \quad (5)$$

or

$$\begin{aligned} E_M &= 1/2 M u^2 \\ &= \bar{E} - A \cos \theta \quad (5') \end{aligned}$$

where  $\bar{E}_M$  is the average recoil and is given by

$$\begin{aligned} \bar{E}_M &= E_\mu \left( \frac{M\mu}{(M+m)^2} + \right. \\ &\left. \frac{m(m+M-\mu)}{(m+M)^2} \left[ 1 + \frac{Q}{E_\mu} \left( \frac{m+M}{m+M-\mu} \right) \right] \right) \quad (6) \end{aligned}$$

and  $A$  is the angularly dependent term given by

$$\begin{aligned} A &= \frac{2E_\mu}{(m+M)^2} \left( Mm\mu [m+M-\mu] \left( 1 + \right. \right. \\ &\left. \left. \frac{Q}{E_\mu} \left[ \frac{m+M}{m+M-\mu} \right] \right) \right)^{1/2} \quad (7) \end{aligned}$$

Since all directions of recoil in the center of mass system are taken to be equally probable by our assumption of isotropy, we can calculate the distribution of recoil energies,  $E_M$ . The fraction,  $d\rho$ , of the cases with angles between  $\theta$  and  $\theta + d\theta$  will be the solid angle lying in this zone divided by  $4\pi$ , *i. e.*,  $2\pi \sin\theta d\theta/4\pi$ , or  $1/2 \sin\theta d\theta$ . Returning to equation (5) we see, however, that

$$dE_M = A \sin\theta d\theta = 2 A d\rho \quad (8)$$

In other words the recoil energy is distributed uniformly over a range

$$\bar{E}_M = A$$

**C. Nuclear Fission.**—Same principle as A.

**D. Beta Radioactivity.**—The momentum,  $P_e$ , of the electron is given by

$$P_e^2 = 2 mE + \frac{E^2}{c^2} \quad (1)$$

where  $m$  is the mass and  $E$  the energy of the electron. Taking the rest mass of the neutrino to be zero and its energy the difference between  $E$  and the upper energy limit,  $E_0$ , of the electron spectrum, the neutrino momentum,  $P_\nu$ , will be given by

$$P_\nu = \frac{E_0 - E}{c} \quad (2)$$

If the two particles are emitted at a mutual angle  $\theta$  the resultant recoil momentum of the product atom is obtained by vectorial addition to be

$$P^2 = P_e^2 + P_\nu^2 + 2 P_e P_\nu \cos\theta \quad (3)$$

Obviously the maximum recoil will occur for  $\theta = 0$ . In this case

$$P_{\text{max}}^2 = (P_e + P_\nu)^2 \quad (4)$$

and for the case when  $E = E_0$  or

$$P_{\text{max}}^2 = 2 mE_0 + (E_0^2/c^2) \quad (5)$$

It is also obvious that the recoil distribution will extend to zero when  $\theta = \pi$  and  $P_e$  and  $P_\nu$  are equal. This condition is

$$2 mE + \frac{E^2}{c^2} = \left(\frac{E_0 - E}{c}\right)^2 \quad (6)$$

or

$$\frac{E}{E_0} = \frac{1}{2(1 + (mc^2/E_0))} \quad (7)$$

For energetic spectra where  $E_0$  is much larger than  $mc^2$  (0.5 MEV.) this is the most probable condition and even for low values of  $E_0$  (down to 0.1 MEV.). Equation (7) gives  $E$  values in a moderately abundant portion of the spectrum.

Since most beta spectra have maxima near  $E_0/2$  we shall obtain an approximate value for the average recoil by choosing this value of  $E$  and averaging over  $\theta$ , assuming the angular distribution to be isotropic (an assumption nearly correct according to the Fermi theory of beta decay). The result is

$$P^2 = P_e^2 + P_\nu^2 = mE_0 + \frac{E_0^2}{2c^2} \quad (8)$$

since the average value of  $\cos\theta$  is zero. This is just half of the maximum value.

Since beta spectra approach the upper energy limit tangentially with respect to the energy axis we shall expect that the recoil distribution curve will also approach its maximum value tangentially.

The lower limit of the recoil distribution, at zero energy, is not restricted in probability by the condition given in equation (7) on  $E$  particularly but rather by the fact that  $\theta = \pi$ . We shall expect therefore that the approach will be essentially as the probability of  $\theta = \pi$ , *i. e.*, as  $\sin\theta$  at  $\theta = \pi$  or an asymptote perpendicular to the energy axis.

With these general considerations we can sketch the general shape of the recoil distribution curve. Such a curve is given in Fig. 2 for a permitted spectrum. In energy units (electron volts) for an atom of atomic weight  $M$  the maximum and most probable recoil energies are given by

$$E_{\text{max.}} (\text{e. v.}) = 548 \frac{E_0}{M} + 536 \frac{E_0^2}{M} \quad (9)$$

where  $E_0$  is in mev.

$$E_{\text{ave.}} (\text{e. v.}) = 274 \frac{E_0}{M} + 268 \frac{E_0^2}{M} \quad (10)$$

**E. Slow Neutron Capture, Gamma Emission.**

—Since the neutron has essentially thermal velocities, its momentum can be neglected so the recoil momentum is given by the momentum of the emitted gamma radiation.

In the case that only one gamma ray is emitted the result is, in exact analogy to equation (2) of section D above, that

$$E = 536E_\gamma^2/M \quad (1)$$

where  $E_\gamma$  is given in MEV. units. This is a definite energy.

If the gamma ray energy is released as two gamma rays in succession of energies  $E_1$  and  $E_2$ , respectively, the recoil energy is no longer sharply defined but is distributed uniformly over a range of values. We shall assume that the directions of emission of the two gamma rays are unrelated. The resultant momentum,  $P$ , of the recoil atom will be given by

$$P^2 = \frac{E_1^2}{c^2} + \frac{E_2^2}{c^2} + \frac{2E_1E_2}{c^2} \cos\theta \quad (2)$$

where  $\theta$  is the angle between the directions of emission of the gamma rays. The assumption of isotropic emission means that the probability of a value of the angle between  $\theta$  and  $\theta + d\theta$  is  $1/2 \sin\theta d\theta$ .

Differentiating equation (2) with respect to  $\theta$  we have

$$dP^2 = (-2E_1E_2/c^2) \sin\theta d\theta \quad (3)$$

This means that the distribution is flat between the limits  $536[(E_1 + E_2)^2/M]$  (e.v.) and  $536(E_1 - E_2)^2/M$  (e.v.) with a spread of  $4 \times 536(E_1E_2/M)$  (e.v.) where the  $E$ 's are in MEV. and

$M$  is the atomic weight of the recoiling atom. These cases are illustrated in Fig. 1.

**F. Internal Conversion and Orbital Capture.**—In this case a gamma ray emitted by the nucleus is absorbed in the K or L shell with the emission of an electron of energy  $E_e$  given by

$$E_e = E_\gamma - E_K \text{ (or } E_L) \quad (1)$$

where  $E_\gamma$  is the gamma ray energy and  $E_K$  or  $E_L$  is the ionization potential of the K or L electrons, respectively. The energy of the recoiling atom will be

$$E = \frac{548 E_e}{M} + \frac{536 E_e^2}{M} \quad (2)$$

where  $E_e$  is given in MEV.

The X-rays following the K or L ejection give negligible recoil and can be neglected. However, the Auger effect will in most cases cause several additional low energy electrons to be ejected once a K or L vacancy has been created. This causes very serious molecular disruptions because of the large positive charges induced.<sup>6</sup>

**G. Gamma Excitation; Particle Emission.**—This is to be treated as in Section B above except that the vector OG will have a length  $E_\gamma/c(M + m)$ . Assuming isotropic emission in the center of mass system we have as before that

$$E = \bar{E}_M - A \cos \theta \quad (1)$$

where the average recoil energy is

$$\bar{E}_M = \frac{1}{2} \frac{M}{(M + m)^2} \frac{E_\gamma^2}{c^2} + \frac{m}{2(M + m)^2} \left( (E_\gamma + Q) 2(M + m) - \frac{E_\gamma^2}{c^2} \right) \quad (1')$$

and the angularly dependent term is

$$A = \frac{E_\gamma M m}{2c(M + m)^2} \sqrt{\frac{(E_\gamma + Q) 2(M + m) - E_\gamma^2/c^2}{mM}} \quad (1'')$$

However, for any values of  $E_\gamma$  below 10 MEV. the result is greatly simplified to

$$E_M = (E_\gamma + Q) \frac{m}{m + M} = E_m \frac{m}{M} \quad (2)$$

In other words for high energy gamma radiation there is a level distribution of width  $2A$ . This width is so small for  $E_\gamma$  of 10 MEV. or less as to be negligible, however, and the distribution becomes sharp at the value given by equation (2). The term  $Q$  above is the heat of reaction taken as heat released.

For 100 MEV. gamma radiation,  $M = 100$ ,  $m = 1$ ,  $Q = 0$ , and  $\bar{E}_M = 1,000,000$  e.v. and  $A = 160,000$  e.v., so for these energies an appreciable spread in the distribution exists.

**H. Particle Bombardment Followed by Gamma Emission.**—From the argument in Section G above and the fact that few nuclear gamma rays of energies greater than 10 MEV. have been observed, we need not seriously consider the gamma ray momentum. Then since only the bombarding particle of mass  $\mu$  and the

recoil atom of mass  $M$  are involved, we have a sharp distribution at

$$E_M = \frac{\mu E_\mu}{M} \quad (1)$$

## Appendix II

### Effect of Mass of Atoms on Efficiency of Recoil Rupture<sup>1</sup>

Consider the mass of the recoil atom to be  $M$  and the mass of the atom bonded to it to be  $m$ , then if the recoil momentum is  $P$  we have for the kinetic energy of the recoiling heavy atom in the case that essentially no large energy was lost in bond rupture

$$E_M = P^2/2M \quad (1)$$

However, in the case that the molecule resists rupture its recoil energy must be

$$E_{M+m} = P^2/2(M + m) \quad (2)$$

because the recoiling undissociated molecule must have the same momentum.

The difference,  $E_M - E_{M+m}$ , must represent the energy the molecule must absorb (and eventually radiate or lose by collision) in order to avoid dissociation, *i. e.*, the energy available for dissociation. Substitution gives this energy,  $E_a$ , to be

$$E_a = E_M(m/M + m) \quad (3)$$

## Appendix III

**Derivation of Equation (3).**—One derives equation (3) as follows. Consider the incident particle of mass  $M$  striking a particle of mass  $M'$  initially at rest. Then the vectorial diagram will be that given in Fig. 6, where OA is the velocity of  $M$  initially with respect to the laboratory system and OG is the velocity of the center of gravity. The length OG will be given by

$$\frac{OG}{OA} = \rho = \frac{M}{M + M'}$$

All possible elastic scattering events are represented in this system by a rotation of line  $\beta\alpha$  around the point G. For isotropic scattering all positions are equally probable.

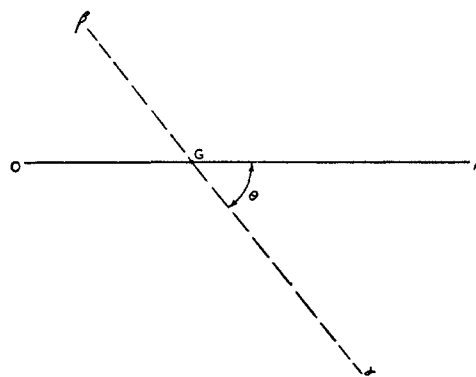


Fig. 6.

If the original velocity OA was  $v$  the final veloc-

ity of the scattered particle will be  $O\alpha$  or  $u$  and be given by

$$u^2 = \rho^2 v^2 + (1 - \rho)^2 v^2 + 2\rho(1 - \rho)v^2 \cos \theta \quad (1)$$

or

$$\frac{u^2}{v^2} = \rho^2 + (1 - \rho)^2 + 2\rho(1 - \rho) \cos \theta \quad (1')$$

or

$$\frac{E}{E_0} = \rho^2 + (1 - \rho)^2 + 2\rho(1 - \rho) \cos \theta \quad (1'')$$

where  $E$  is the final energy and  $E_0$  the initial in the laboratory system.

Considering the probabilities of various values of  $\theta$  we see that due to the integration around OA as polar axis the solid angle lying between  $\theta$  and  $\theta + d\theta$  will be  $2\pi \sin \theta d\theta$  so the fraction  $dP$  of all scattered particles lying in this band will be

$$dP = \frac{1}{4\pi} 2\pi \sin \theta d\theta = \frac{\sin \theta d\theta}{2} \quad (2)$$

Differentiating equation (1'')

$$dE = -E_0 2(1 - \rho) \sin \theta d\theta \quad (3)$$

or

$$dE = -E_0 \gamma dP \quad (3')$$

where

$$\gamma = \frac{4MM'}{(M + M')^2} \quad (4)$$

Integrating (3)'

$$E = E_0(1 - \gamma P) \quad (5)$$

where  $P$  is now the fraction of the particles scattered between 0 and  $\theta$ .

Now the average value of  $\ln \frac{E_0}{E}$  can be obtained. From (5)

$$\ln \frac{E_0}{E} = -\ln(1 - \gamma P) \quad (6)$$

So

$$\begin{aligned} \ln \frac{E_0}{E} = K &= \int_0^1 -\ln(1 - \gamma P) dP \\ &= \frac{1 - (1 - \gamma) - \ln(1 - \gamma)}{\gamma} \end{aligned} \quad (7)$$

For a complete discussion of the problem of neutron slowing, refer to "Theory of the Slowing Down of Neutrons in Heavy Substances," G. Placzek, *Phys. Rev.*, **69**, 423 (1946).

### Summary

1. The variety and nature of the recoil excitations suffered by atoms whose nuclei partake in the various possible nuclear reactions is reviewed. The chemical kinetics of the recoiling (frequently radioactive) atoms is treated by considering first the nature of the cooling deceleration process—predominantly non-ionizing collisions—and subdividing the problem into one class involving no change in atomic number, *e. g.*, the Szilard-Chalmers reactions, and another class in which changes in atomic number occur.

2. In the first class previously published data on organic halides are considered in some detail and a mechanism developed. The essential features of this mechanism are that the classical collision theory and the Franck-Rabinowitch "cage" are sufficient to explain the main facts.

3. In the second class where changes in atomic number occur the principal cases discussed are ionic solids. Few data are available. A suggestion is made for a concentration procedure consisting of baking fine irradiated crystals to drive the activity to the surface.

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## The Determination of the Gases in Meteoritic and Terrestrial Irons and Steels

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In connection with an investigation of the gases present in siderites, a general survey has been made of the methods by which gases may be liberated from meteoritic and terrestrial irons and steels. A really satisfactory method of extraction must release all the gases present as such without change of composition or addition of contaminating reaction gases. Since none of the currently available procedures fully satisfies these criteria, attention has been focussed on the choice of the method which most nearly meets the criteria, together with an estimate of the unavoidable errors. In the following text each of the possible methods is considered, the finally adopted method is de-

scribed in detail, and the results are compared with similar data secured by other methods.

### I. Discussion of Methods

**A. Heating in Vacuo.**—This classical method, developed by Graham<sup>1a</sup> for the investigation of the gas content of meteoritic irons, has since been applied to a wide variety of meteoritic and terrestrial materials. It has been established that the composition of the extracted gas is strongly dependent on the fineness of subdivision of the sample,<sup>2</sup> duration of heating,<sup>3</sup> extraction temperature,<sup>4</sup> and duration of the contact between the gas and the sample.<sup>5</sup> The variable re-

(1a) T. Graham, *Proc. Roy. Soc. (London)*, **15**, 502 (1866).

(2) A. W. Wright, *Am. J. Sci.*, **9**, 249 (1875).

(3) J. W. Mallet, *Proc. Roy. Soc.*, **20**, 365 (1872).

(4) A. W. Wright, *Am. J. Sci.*, **10**, 44 (1875).

(5) A. W. Wright, *ibid.*, **12**, 165 (1876).

(1) This work was initiated and supervised by the Committee on Meteorites of Harvard University: G. P. Baxter (Chairman), K. T. Bainbridge, H. A. Berman (deceased 1942), Francis Birch, A. B. Greninger, F. G. Watson.