877. *The Decomposition of Crystalline Uranyl Oxalate induced by Reactor Radiation.*

By D. A. Young.

The decomposition of isotopically-normal and ^{235}U-depleted anhydrous uranyl oxalate has been studied under various conditions of reactor- and γ-irradiation. The products are carbon monoxide and carbon dioxide in the ratio of about 1 : 3 with a solid residue of approximate composition $UO_{2\cdot5}$, which is more reactive than the corresponding macroscopic oxide prepared by low-temperature reduction of the trioxide. Some separation of the contributions to the decomposition by recoiling fission fragments, fast neutrons, β-particles, and reactor γ-rays has been effected. For recoiling fission fragments the G-value and the number of oxalate molecules decomposed per fission are respectively 5·1 and 8200×10^3; the corresponding figures for reactor γ-rays are 0·1 and 3×10^3. The form of the decomposition–dose curve is accurately given by a first-order expression, and this is interpreted to mean that decomposition occurs where fission-recoil tracks traverse virgin reactant.

The thermal decomposition of uranyl oxalate is enhanced by a small degree of pre-irradiation. The kinetics of this effect are discussed on a topochemical model.

In the past much attention has been paid to the fundamental nuclear physics of the fission process, whilst more recently studies of the purely physical effects of the fission on the medium in which it occurs have gained an importance.[1] Less attention, however, has been paid to the chemical consequences of the fission as expressed, for example, by the decomposition of the uranium-containing medium itself or by the acquisition by that medium of enhanced chemical reactivity which may later be employed in a catalytic or other reaction.

Wright and Sangster [2] examined the reactor decomposition of the two heterogeneous systems uranium dioxide–graphite and uranium dioxide–anthracene. In the former system the fission fragments passed from the particles of origin into graphite specimens which would have evolved permanent gases when heated to about 500°. The gas evolution at 75° in the reactor from the dioxide–graphite system was about 16 times greater than the evolution from pure uranium dioxide, and some 10^4 times greater than the evolution from zinc oxide–graphite in the same reactor flux. On the basis of these results it was suggested that the fission fragments from the uranium dioxide particles were markedly more effective in procuring degasification of the graphite than were the fast neutrons and reactor γ-rays, though it was not possible to make these results quantitative because no reasonable estimate could be made of the fraction of the recoil energy retained in the dioxide particles.

In the second series of experiments, Sangster [2] examined the uranium dioxide–anthracene system, for which gas analyses would be worth while. Making the simplifying assumptions that all the fission recoil energy is dissipated in the anthracene and that the effects of interface reactions between irradiated dioxide and anthracene adjacent to the particles could be neglected, he concluded that fission fragments are 27 times more effective in procuring the decomposition of anthracene than is general pile radiation. The principal gas products were hydrogen, lower hydrocarbons, and oxides of carbon. The overall evolution rate fell steadily during the irradiation, but it was noted particularly that the carbon dioxide and hydrocarbon content of the evolved gases fell more rapidly from the beginning of the irradiation than did the hydrogen content. The overall decrease in rate can be accounted for only in part by the consumption of anthracene within the fission

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[1] Billington, Proc. Int. Conf. on Peaceful Uses of Atomic Energy, or Geneva, 1955, **7**, 421.

[2] Wright and Sangster, *Nature*, 1952, **170**, 368; A.E.R.E. Memorandum C/M.290.

fragment range, and Sangster suggested that a polymer more resistant to decomposition, and which can inhibit further decomposition, may be formed. The present author's view associates the production of oxides of carbon with an interface reaction between anthracene and activated uranium dioxide in which lower hydrocarbons are also formed. Erosion of the interfacial anthracene occurs in the early stages of the reaction and the interface eventually breaks. It is at this stage that the carbon dioxide and hydrocarbon contents fall to a negligible value. Subsequently the reaction proceeds as described by Sangster. This superposition of two concurrent reactions accounts for the fact that the reaction rate decreases initially more rapidly than corresponds to first order but subsequently becomes of first order. The latter dependence arises, not because the fission tracks do not overlap, but because there is a high, constant overlap, the average distance between adjacent uranium dioxide particles being about 1/30 of the fission fragment range in pure anthracene. Calculations on the geometry of the system suggest that the uranium dioxide particles act as extremely effective traps for fission fragments, though it is not yet feasible to assess the value of the energy " lost " in this way.

Because of these unassessable modes of energy deposition, it was felt that much would be gained by studying the decomposition of an initially homogeneous uranium salt. Hall and Walton [3] chose uranyl iodate and hydrated uranyl oxalate,[4] obtaining values of about 6 and 9 respectively for the number of molecules decomposed per 100 ev absorbed. These results were not known to the present author when it was decided to examine the reactor decomposition of anhydrous uranyl oxalate.

Uranyl oxalate is normally prepared from cold solution as the trihydrate. This material can be dehydrated in two stages *in vacuo*, to the monohydrate at 100—120° and to the anhydrous compound at 190—220°.[5] No changes occur in the X-ray pattern during this dehydration, and no changes in the external form of the crystals are observed under the microscope. The anhydrous material readily takes up one molecule of water in the laboratory though the trihydrate is re-formed only slowly under these conditions. It is therefore concluded that the anhydrous salt is a pseudomorph of the trihydrate. Thus gases of small molecular diameters formed within sub-grains will normally diffuse even from undamaged crystals at moderate temperatures.

If the anhydrous pseudomorph is heated *in vacuo* to above 275° it decomposes slowly to form uranium dioxide and carbon dioxide with " less than 1% of carbon monoxide in some cases," whereas in the presence of oxygen the decomposition is explosive at 325° owing, presumably, to the exothermic formation of uranium trioxide—which thus leads to superheating of the oxalate.[5] Our work has shown that carbon monoxide is only formed if the oxalate is decomposed below 290°, whence it is supposed that this oxide is a primary product, as has been found for other oxalates, but that the non-stoicheiometric oxide so formed is reduced back to dioxide by the carbon monoxide produced. This back reaction proceeds more rapidly at higher temperatures, thus accounting for the absence of carbon monoxide above 290—300°.

In addition to studying the reactor-induced decomposition of uranyl oxalate, it was desired to investigate the effects of reactor irradiation on the subsequent thermal decomposition of this salt. The reason is that it has now been shown that it is the topography rather than the chemical nature of an insulating solid reactant which determines the kinetics of its decomposition.[6] If, as is supposed, the radiation decomposition occurs along the actual recoil tracks, there cannot be complete annealing of damage because the solid products act as a pinning or precipitated impurity, whence permanent lattice damage having the topography of the recoil tracks will be retained by the reactant. This damage

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[3] Hall and Walton, *J. Inorg. Nucl. Chem.*, 1958, **6**, 288.

[4] Mr. G. N. Walton, personal communication.

[5] Boullé *et al.*, *Compt. rend.*, 1950, **230**, 300.

[6] Bartlett, Tompkins, and Young, *J.*, 1956, 3323; Tompkins and Young, *Trans. Faraday Soc.*, 1956, **52**, 1245.

would be expected to contribute a parabolic acceleratory component to the early stages of the isothermal decomposition, with a consequent decrease in the " induction " period and concomitant increase in the maximum velocity, provided the extent of reactor decomposition is small.

EXPERIMENTAL

Materials.—Uranyl oxalate trihydrate, prepared by precipitation from aqueous solutions of potassium oxalate and uranyl nitrate, was filtered off, washed, and aged in the form of a slurry in contact with mother-liquor at 75° for 24 hr. in order to increase the average particle size. This slurry was cooled slowly, and the oxalate filtered off being kept at room temperature overnight. The crystals so obtained were transparent, well-formed platelets about 3 μ across. The size distribution appeared to be sharp. A similar preparation was made from a sample of uranyl nitrate depleted 40-fold in uranium-235.

Encapsulation.—Samples of the trihydrate varying in size from 2 to 500 mg. were loaded into quartz capsules fitted with break-off seals and heated to 210° in air to remove most of the water of crystallisation. If this initial heating was conducted *in vacuo* the samples " bumped " badly. The final dehydration was performed at 220° and a pressure of *ca.* 10^{-4} mm., and the capsules of volume 1—2 cm.^{3} were sealed off at this pressure.

Irradiation.—(*a*) Most of the samples were exposed in the pneumatic-tube device in the reactor core of BEPO and the thermal dose was monitored by the usual gold-foil technique. During most of the period of the experiments a fuel channel adjacent to the irradiation position was empty. This resulted in a local increase in the thermal neutron flux and in the cadmium ratio for gold. Typical values for these two quantities in this operating condition are $\phi = 1{\cdot}44 \times 10^{12}$ n cm.$^{-2}$ sec.$^{-1}$ and $2{\cdot}8_3$ respectively. (*b*) On a few occasions the irradiations were carried out in the reactor core with the reactor at reduced power (60 kw) and in the upper end of the thermal column with the reactor at normal power. The thermal neutron flux was then *ca.* 3×10^9 n cm.$^{-2}$ sec.$^{-1}$ and the cadmium ratio for gold was $>10^3$. (*c*) Some irradiations were performed in a 700-curie ^{60}Co source. For this purpose, 1—2 g. samples were dehydrated and sealed in Pyrex capsules and irradiated for periods of 16—64 hr.

Gas Analysis.—The gases evolved were transferred from the capsules into thimbles by a Toepler pump which delivered gas at atmospheric pressure. Analysis carried out by the Blacet–Leighton technique showed the presence of only carbon monoxide and dioxide. It was found necessary to heat samples irradiated below reactor-core temperature (80°) and in the Co source (40°) to about 100° to ensure complete desorption of gas.

Thermal Decomposition.—The samples were dehydrated and sealed in quartz capsules whether they were to be irradiated or not. After the appropriate treatment these capsules were broken in an evacuated reaction chamber connected to a mercury manometer. A tube furnace at 302° was then raised to surround the vessel. Decomposition was followed by gas evolution measurements, zero time being taken quite arbitrarily as the time at which the temperature of the reaction vessel reached 260°. For the present purposes it was not essential to know the temperature of the reaction vessel precisely, merely that it remained constant from run to run. Once thermal equilibrium had been established the temperature remained within the limits 302° ± 0·5°.

RESULTS

Reaction Irradiation of Anhydrous Uranyl Oxalate prepared from Natural Uranium.—Samples were exposed to the reactor centre flux at 6 Mw power for periods varying from 15 sec. to 630 min., and the amount and composition of the gas evolved determined. Only carbon monoxide and dioxide were found, the ratio of monoxide to dioxide being within the range 0·32 ± 0·04 with occasional larger deviations for which no satisfactory explanation has yet been found. Thermal decomposition of the oxalate residue after partial reactor decomposition yielded only carbon dioxide and uranium dioxide above 300° whether the gaseous products of reactor decomposition had been removed or not. In both cases the total amount of carbon found in the gas phase was within ±2% of the amount calculated from the weight of oxalate according to the overall reaction $UO_2C_2O_4 \longrightarrow UO_2 + 2CO_2$. The stoicheiometry of the reactor decomposition thus appears to be:

$$2UO_2C_2O_4 \longrightarrow xCO + (4 - x)CO_2 + 2UO_{(2 + 0{\cdot}5x)}$$

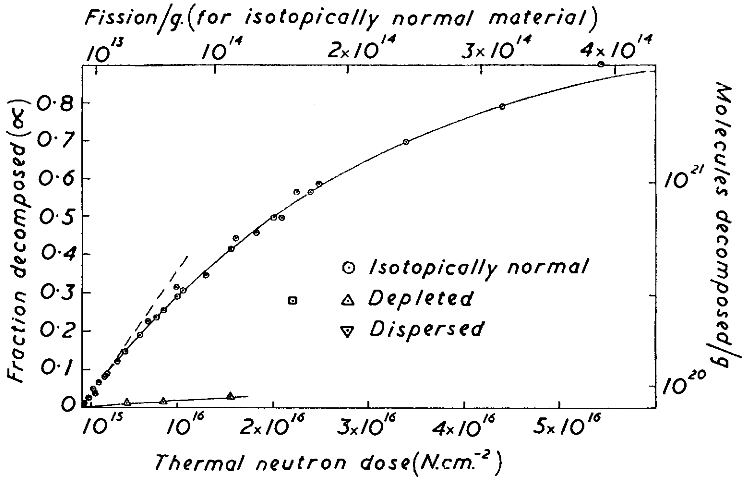
where x is about unity at 80° but decreases to zero with increasing temperature, probably owing to the reaction

$$x\mathrm{CO} + 2\mathrm{UO}_{(2+0\cdot 5x)} \longrightarrow 2\mathrm{UO}_2 + x\mathrm{CO}_2$$

The results are presented in Fig. 1 as fractional decomposition (α), calculated on the basis of the carbon balance, against total neutron dose (N).

Irradiation at Reduced Reactor Power.—In order to extend the results to low neutron doses and to check whether the flux affects the amount of decomposition per neutron absorbed, three runs were conducted at 60 kw reactor power. The results are plotted in Fig. 2, which is a 100-fold expanded diagram of the region round the origin of Fig. 1. Additional runs which properly belong to Fig. 1 have been included for comparison in Fig. 2. No substantial effect of variation in pile power was observed. The plot of fractional decomposition (α) against dose (N) passes through the origin, the line drawn being the initial slope of the plot displayed in Fig. 1.

FIG. 1. *The reactor decomposition of anhydrous uranyl oxalate plotted as fraction decomposed against the thermal neutron dose. The right hand ordinate and the upper abscissa are alternative axes referred to 1 g. The point* ⊡ *refers to a sample of isotopically normal material which had been dispersed throughout a pad of quartz wool.*



Form of the Decomposition–Dose Plot.—The plot of fractional decomposition (α) against thermal neutron dose (N) is closely given by the expression, analysed in Fig. 3,

$$\alpha = 1 - \exp(-kN) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is a constant. It can be calculated from the initial slope of this curve, as obtained from equation (1), that the overall G-value * for reactor decomposition, assuming that the energy deposition by fission fragments predominates, is 5·2, and the number of molecules decomposed per fission is $8\cdot46 \times 10^6$. The value 5·2 is known as the unrefined G-value.

For convenience, additional axes have been included in Fig. 1. The right-hand ordinate gives the number of molecules decomposed per g. and the upper abscissa gives the number of fissions per g.

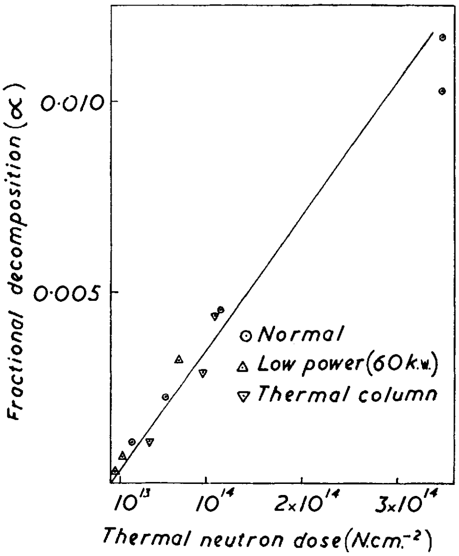
Reactor Irradiation of Depleted Uranyl Oxalate.—Three runs were carried out on the reactor decomposition of 40-fold depleted uranyl oxalate. The decomposition products were similar to those obtained with isotopically normal material with carbon monoxide : carbon dioxide ratios of about 0·25. For this reason the fractional decomposition was calculated as before and the points are included in Fig. 1. The upper abscissa scale does not apply to these points. It will be noted that the initial slopes of the two plots are in the ratio

Initial slope of " normal " plot/Initial slope of " depleted " plot = 18·2

* G-values are given as the number of oxalate molecules decomposed per 100 ev of energy absorbed.

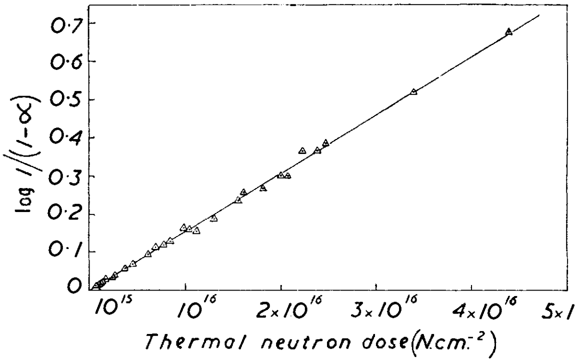
Irradiation in the 700-*Curie* ^{60}Co *Source*.—The irradiations were at a dose rate of 4×10^5 r. hr.$^{-1}$ as determined by ferrous sulphate dosimetry. Irradiations in the cobalt source were longer (16—64 hr.) than any performed in the reactor core, and the source temperature was only 40° as compared with 80° in the core. It was necessary to heat the samples to 80—100° to release the gas produced, some 30% being otherwise retained in the sample at source temperature. The carbon monoxide : carbon dioxide ratio was 0·18, which is approximately the same as the ratio for gas produced by photolytic decomposition with an ultraviolet lamp. At source temperature the rate of γ-radiolysis was low, varying between 1·5 and $2{\cdot}2 \times 10^{-3}$% hr.$^{-1}$ or 13—19% per year, giving a *G*-value of approximately 0·1. Applying this *G*-value to Anderson's calorimetric estimates of the energy absorption from reactor γ-rays,[7] we calculate the rate of γ-radiolysis in the reactor core to be about 7×10^{-3}% hr.$^{-1}$, compared with the total reactor decomposition rate of 18% hr.$^{-1}$.

FIG. 2. *This plot is an approximately* 100-*fold expanded diagram of the region near the origin of Fig.* 1.



The straight line drawn is the initial slope obtained by the analysis of the curve in Fig. 1.

FIG. 3. *The derived plot of Fig.* 1 *according to the equation log* $1/(1 - \alpha) = kN$.



Irradiation of Uranyl Oxalate in the Reactor Thermal Column.—In order to eliminate the effects of fast neutrons, three samples of uranyl oxalate were irradiated in a 5-ft. tube, partially shielded from γ-rays by a lead pot, in the upper section of the thermal column. Gold-foil monitoring was used, but owing to the length of the runs (up to 6 hr.) allowance had to be made for the decay of the gold activity during the run itself. Monitoring experiments showed that at this level in the thermal column the vertical thermal neutron flux gradient was 5% per cm. and that the flux was not steady, owing presumably to general reactor operations. For these reasons the *G*-value obtained is not regarded as being particularly reliable, but it does refer substantially to energy deposition by fission fragments. The results obtained are included in Fig. 2.

Deviations from the Plot in Fig. 1.—It was noted that when particularly small samples (<1 mg.) were used, the fractional decomposition obtained for a given irradiation sometimes fell as much as 30% below the value obtained with larger samples. This was ascribed to the escape of energetic fission fragments from the specimens. Such loss was subsequently avoided by using compacted or larger samples. A demonstration that the loss of fast fission fragments from small specimens is a real effect was provided by the decomposition of uranyl oxalate which had been deliberately dispersed in a pad of silica wool. In this case the decomposition fell to 53% of the value obtained with larger or compacted samples, confirming that a substantial fraction of the decomposition is procured by fragments which damage crystals other than the crystal of origin.

Thermal Decomposition.—Unirradiated uranyl oxalate was decomposed at 302°, and the reaction followed by pressure measurements. The theoretical amount of carbon dioxide was evolved within experimental error. The decomposition run is illustrated in Fig. 4, curve *A*. Two other samples were pre-irradiated in the reactor core for 2 min. (*B*) and 5 min. (*C*), and the results obtained on thermal decomposition at 302° are similarly illustrated in Fig. 4. The important features of these plots are the enhancement of the maximum velocity and the change in shape during the acceleratory period. The effect of the irradiation is most clearly seen in Fig. 5, where the difference between curve *A* and curve *B* is plotted against time. This difference curve is fitted by the equation, analysed in Fig. 5,

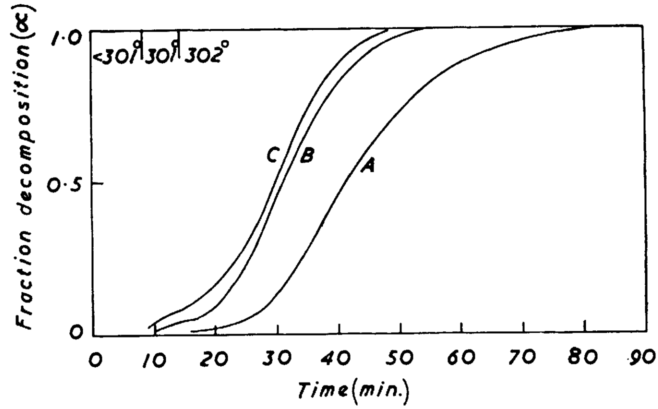


FIG. 4. *The kinetics of the thermal decomposition at* 302° *of*

A—Unirradiated uranyl oxalate.
B—Uranyl oxalate which had been pre-irradiated in the reactor core up to a dose of $1{\cdot}7 \times 10^{14}$ *thermal neutrons cm.*$^{-2}$.
C—As for B but to a dose of $4{\cdot}2 \times 10^{14}$ *thermal neutrons cm.*$^{-2}$.

The thermal lag is indicated in the top left hand corner.

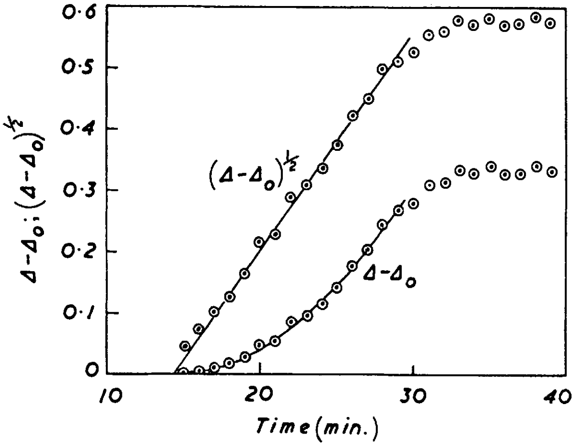


FIG. 5. *The analysis of the difference between curves B and A in Fig.* 4. Δ_0 *is the difference between the curves at* t_0 *and* Δ *is the difference at t.* t_0 *is determined by the method of successive approximation.*

$$\Delta - \Delta_0 = k(t - t_0)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where Δ is the difference at time t and Δ_0 that at time t_0, the end of the thermal lag.

DISCUSSION

Reactor Decomposition.—One of the principal aims of this study was the determination of the decomposition procured by fission-fragment recoils. For this purpose it is desirable to separate and assess the individual contributions of all components of reactor radiation to the decomposition. Even here we have to make the simplifying assumption that the activation of the reactant by one type of radiation is not affected by the presence of another type of radiation. Initially, it is convenient to divide the contributions to the decomposition into three classes. These are the energy-deposition mechanisms associated with the effects of thermal neutrons, fast neutrons, and pile γ-rays.

(a) *Thermal neutrons.* Neutrons moving with thermal velocity will not cause lattice damage except through the initiation of nuclear reactions. The most probable reaction, and also the most energetic, is the slow neutron fission of uranium-235. Other reactions to be considered include radiative capture by uranium-235, uranium-238, oxygen and carbon, the (n, α) reaction with oxygen-17 and the fission of uranium-239. For convenience we include the energy deposition by the decay of fission-product activity in the sample itself and of uranium-239 to give neptunium-239 in this group.

The slow neutron fission of uranium-235 yields 162×10^6 ev per fission in the form of kinetic energy of the fission fragments. This is the largest single source of energy which will be encountered, and all other energies will be quoted as electron volts deposited per slow neutron fission of uranium-235. On this scale we find that for the larger samples the energy deposition by the β-particles from the fission products is approximately 3×10^6 ev, but is quite negligible for the smaller samples. The fission of uranium-239 deposits an insignificant amount of energy, but the remaining sources listed above deposit $8{\cdot}7 \times 10^5$ ev, of which perhaps 85% is expended as ionisation and 15% in producing displacements.

These sources of energy are eliminated for all practical purposes if the samples are covered with a 1-mm. thick cadmium sheath.

(b) *Epi-cadmium neutrons.* These more energetic neutrons cause energy deposition principally by two processes. First, they are strongly scattered by the light atoms in the oxalate ion and thereby cause displacements; Anderson's calorimetric estimate [7] of the energy absorbed by fast neutron scattering from carbon and oxygen gives a value of $1{\cdot}4 \times 10^5$ ev per slow neutron fission of uranium-235 in this case. Secondly, the epi-cadmium neutrons will cause some fast fission of uranium-238 with a certain amount of epi-cadmium fission of uranium-235. At the present stage no *ab initio* calculation of these contributions can be made, but it is expected that the total energy contribution from the recoiling fission fragments produced in these processes will not exceed 5% of the contribution from the slow neutron fission of uranium-235. No attempt is made to separate the epi-cadmium fission of the two isotopes.

(c) *Pile γ-rays.* Calculation from Anderson's calorimetric results suggests that the energy absorbed from γ-rays would be 3×10^6 ev per slow neutron fission of uranium-235, *i.e.*, approximately 1·5% of that deposited by fission fragments.

It must be remembered that in assessing the relative contribution of these three principal types of radiation we are not merely concerned with the amounts of energy absorbed, but also with the chemical decomposition which this energy absorption procures. The situation can be summed in the equation

$$N = \sum_i E_i G_i \quad \ldots\ldots\ldots\ldots \quad (3)$$

where N is the number of molecules decomposed, E_i is the amount of energy absorbed in mode i and G_i is the corresponding G-value. The subscripts i are as follows: fission fragment recoil (F); radiolysis due to β-decay of fission products (β); reactor γ-radiolysis (γ); fast neutron scattering (s); fast fission, epi-cadmium fission and associated β-radiolysis (f), and reactions induced by slow neutron capture (r), where contributions F, β, f, and r arise from neutron capture within the sample. For normal uranyl oxalate, equation (3) is written

$$N_n = E_F G_F + E_\beta G_\beta + (E_\gamma G_\gamma + E_s G_s + E_f G_f + E_r G_r) \quad \ldots \quad (4)$$

and for depleted uranyl oxalate

$$N_D = (E_F G_F + E_\beta G_\beta)/D + (E_\gamma G_\gamma + E_s G_s + E_f' G_f + E_r' G_r) \quad \ldots \quad (5)$$

where D is the depletion, in this case 40. Terms E_f' and E_r' are smaller than E_f and E_r, though not by as much as a factor of 40. Since they are so much smaller than E_F, the

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[7] Anderson, A.E.R.E. Report C/R. 2253.

change in value on depletion is neglected and the terms in parentheses in equations (4) and (5) are set equal. On this basis, using the experimental value $N_n/N_D = 18{\cdot}2$ obtained from the slopes of the α–N plots in Fig. 1, we find that the parenthetical term is 3·26% of $(E_F G_F + E_\beta G_\beta)$, whence equation (4) may be written

$$N_n = 1{\cdot}033(E_F G_F + E_\beta G_\beta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

N_n is measured, E_F and E_β are calculable, whence G_F is found to be 5·1, if G_β is given the reasonable value of 0·1 obtained from γ-radiolysis. On this basis we find that 8187×10^3 molecules are decomposed by fission recoils and 3×10^3 molecules by fission-product β-radiolysis for each fission, leaving 270×10^3 molecules to be accounted for by the parenthetical terms in equations (4) and (5). Using Anderson's results to calculate E_γ and assuming G_γ to be 0·1, we obtain $E_\gamma G_\gamma = 3 \times 10^3$. This leaves 267×10^3 molecules to be shared amongst modes s, f, and r. The value of G_r is chosen to be 2. This is a weighted value allowing G-values of 10 and 0·1 for that part of E_r arising from displacements and ionisation, respectively. We thus obtain $E_r G_r = 17 \times 10^3$ for $G_r = 2$. The value $G = 10$ is adopted on the basis of Hall and Walton's work on the decomposition of potassium nitrate,[3] in which the recoiling fission fragments were artificially slowed down, coupled with the assumption that heavy recoil atoms from (n, γ) radiative capture will behave in the same way as slowly moving fission fragments. The value $G = 0{\cdot}1$ is obtained from γ-radiolysis. This leaves 250×10^3 molecules decomposed per slow neutron fission of uranium-235 to be divided between terms f and s. Now the ratio $(F + \beta + r + f + s + \gamma) : (f + s + \gamma)$ should be comparable to the ratio of the rate of decomposition of bare uranyl oxalate to the rate for material shielded from thermal neutrons by cadmium foil. The calculated ratio is 32 : 1, and the experimental ratio is 36 : 1. The correspondence is sufficiently close to give some confidence in our assignment of the $E_i G_i$ values to terms F, β, γ, r, and $(f + s)$, but the comparison is confused by the introduction of radiolysis induced by the γ-rays from the ${}^{113}\text{Cd}(n, \gamma){}^{114}\text{Cd}$ reaction. The calculated and experimental cadmium ratios for decomposition can be made to agree if it is assumed that the cadmium shield enhances E_γ by a factor of 10. This is believed to be a reasonable value, but has not yet been checked experimentally.

The value G_s refers to direct energy transfer to the oxalate ions by slowly moving displaced atoms and should therefore be high. We adopt Hall's value of 10, giving $E_s G_s = 14 \times 10^3$, leaving 236×10^3 molecules to be accounted for by the epi-cadmium fission of uranium-235, the fast fission of uranium-238, and β-radiolysis by the fission products so produced. The value of E for this last process is small enough for G_f to be put equal to 5·1. This value of G_f requires that E_f shall be $4{\cdot}6 \times 10^6$ ev per slow neutron fission of uranium-235, which suggests that the ratio of *all* epi-cadmium fissions to slow neutron fission of uranium-235 must be about 0·027. This is a reasonable value. The results of these calculations are collected in the Table below. The energy and decomposition terms are given per slow neutron fission of uranium-235.

Energy source	Energy (ev)	G	No. of oxalate ions decomposed
Fission recoils	162×10^6	5·1	8187×10^3
Fission produce radiolysis	3×10^6	0·1	3×10^3
Fast neutron scattering	$1{\cdot}4 \times 10^5$	10	14×10^3
Nuclear reactions induced by slow neutrons	$8{\cdot}7 \times 10^5$	2	17×10^3
Epi-cadmium fission	$4{\cdot}6 \times 10^6$	5·1	236×10^3
Pile γ-radiolysis	3×10^6	0·1	3×10^3
Total	$1{\cdot}74 \times 10^8$	$\bar{G} = 4{\cdot}87$	$8{\cdot}46 \times 10^6$
Cadmium-shield γ radiolysis	30×10^6	0·1	30×10^3

The form of the decomposition curve for reactor decomposition is accurately given by equation (1). The term N can be replaced by ϕt, where ϕ is the average thermal neutron flux and t is the time of irradiation, making the equation of first order with respect to time for a constant rate of energy input. This form is completely consistent with a decomposition rate $(d\alpha/dt)_\phi$ or $(d\alpha/dN)$ proportional to the amount of undecomposed material remaining, which in turn is consistent with decomposition located where fission fragments traverse virgin reactant. It is not consistent with chemical utilisation of energy absorbed by the reaction product in, say, an interface reaction, at least below 85% decomposition. At these high degrees of decomposition, at which stage the reaction product can acquire some of the properties of bulk uranium oxide, there is fragmentary evidence that $(d\alpha/dN)$ rises above the value expected from the first-order equation. This question is, however, better studied by using enriched material or irradiations at higher fluxes (DIDO) to avoid possible interference by fission of plutonium-239.

The Stoicheiometry of the Reaction.—In order to discuss the stoicheiometry of the reaction it is first necessary to consider the processes occurring along the recoil tracks. At the beginning of its recoil the fission fragment carries a charge of about +20. It will therefore be dimensionally small. Near the beginning of the track, although some direct collisions will occur, the majority of the damage done will be by ionisation and recoil of heavily ionised uranium and uranyl ions away from the track. These ions will be larger than the recoiling fission fragment and during their progress towards an interstitial position will transfer energy directly into the vibrational modes of the oxalate ion, thus causing decomposition at or near the site of the original track. The secondary and tertiary displaced ions will probably rest in interstitial positions in the highest available valency state (U^{6+} or UO_2^{2+}), first, because they started as highly charged positive ions, secondly, because the strain interaction with the lattice is lower for smaller ions, and thirdly, because the Madelung potential of the lattice does not normally favour electron trapping at interstitials.

As the fission fragment slows down, its own degree of ionisation is reduced, the ionisation which it can produce becomes less, and the probability of displacement becomes greater. That is to say, the recoil away from the track of highly ionised ions by mutual coulombic repulsion is replaced by the recoil of knocked-on ions. It is suggested that these recoiling atoms do not behave in a fundamentally different way from those produced near the beginning of the tracks, though it appears that there may well be many more of them per unit length of track as the fission fragment slows down. In this connection, Hall and Walton [3] have shown that the *G*-value for the decomposition of nitrates tends to rise towards the ends of the fission-fragment tracts.

It is now suggested that the initial radiation decomposition induced by the passage of a fission fragment is a virtual disintegration of the oxalate anion into, say, carbon monoxide, carbon, and oxygen in both neutral and ionised states, and that the gases which we measure as decomposition products are determined in composition wholly by the recombination of these fragments in a particular disordered solid environment. The important point is that this environment presents displaced uranium and uranyl ions of essentially two types: (*a*) Uranyl ions situated at the site of the original fission fragment track which are accessible to the gaseous atomic and radical reactants formed by the breakdown of the oxalate ion. These ions are situated on the path along which the gas diffuses out of the crystal. (*b*) Uranyl ions in interstitial sites near the fission fragment track, but substantially in the oxalate matrix, which are not immediately available to the disintegration products. These atoms correspond to the tertiary and quaternary displacements of Ozeroff's theory.[8]

In order to maintain electrical neutrality, oxygen ions equal in number to the inaccessible uranyl ions are chemisorbed, probably in the tertiary region of the recoil track, and an equivalent amount of carbon monoxide is found in the gas phase. During heating to 300°, either electrons from the chemisorbed oxygen migrate to the uranyl ions of type (*b*), or these ions migrate to the recoil tracks. The latter interpretation is favoured because of the instability of interstitial cations of low valency.

On the basis of this model about 4×10^6 displaced ions of type (*b*) or their equivalent

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[8] Ozeroff, U.S. Reports A.E.C.D. 2973: K.A.P.L. 205.

in positive holes should be produced per fission, which means that on average one uranium ion is displaced per unit cell disrupted. If we further assume that the track of each fission fragment is 5 μ long, we find that the tube of decomposition has an average radius of 70 Å. Lattice disorder in its strict sense will extend beyond this, but in essence an irradiated sample of crystallite size 3 μ can be regarded as being completely traversed by highly disordered decomposed tubes of radius 70 Å. According to Ozeroff's calculations for uranium, about half the total number of displaced atoms are tertiary atoms with kinetic energies of *ca.* 20 ev. We require a maximum of one quarter of the total number of displaced ions to move into the oxalate matrix without causing substantial decomposition towards the ends of their tracks ($\sim$16 Å). This appears to be reasonable for a G-value of 10 for slowly moving ions. It is noteworthy that the calculated volume of the decomposed oxalate is of the same order as the volume into which displaced atoms move and come to rest, as calculated from Ozeroff's equations.

Thermal Decomposition.—This section is concerned with the changes in reactant topography on irradiation as reflected in the kinetics of the subsequent thermal decomposition. However, in general terms the form of the decomposition plot (A) in Fig. 4 for unirradiated material is consistent with an interfacial decomposition initiated at points of emergence of subgrain boundaries, followed by propagation of reaction over the planes of the subgrain boundaries and subsequent penetration of the interface so formed into the grains. The confirmation in detail of such a mechanism is a lengthy procedure involving a wide experimental approach, but microscopic examination of partially decomposed crystals justifies its assumption here.

The point of interest is that in irradiated material the subgrains are traversed by a fixed number of linear imperfections which are also lines of chemical inhomogeneity. It is at just such lines of strain that the activation energy for decomposition is reduced and we suggest that, the nucleation requirement having been overcome during the irradiation, interfacial reaction is established during the thermal lag. The reaction then propagates radially at a constant rate. Since the fission-fragment range is greater than the largest dimension of the individual crystals, the tracks will normally traverse the crystals forming cylinders of product of constant length. Such development proceeds according to the equation

$$V - V_0 = \bar{k}^2 L(t - t_0)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where V is the volume of product at time t, V_0 is the volume at the end of the thermal lag t_0, $\bar{k}^-$ is the averaged rate constant for radial growth, and L includes the total length of cylinders with a correction for initial overlap.

This equation holds until the growing cylinders begin to overlap significantly with each other or with the advancing interface formed at the subgrain boundaries. In practice it is found that the form of the equation without a time-dependent correction for overlap accurately reproduces the difference between the irradiated and unirradiated samples up to 40% decomposition of the irradiated sample. The analysis according to equation (7) is shown in Fig. 5.

It will be noted that a higher dose of pre-irradiation enhances the early stages of the decomposition more than the maximum rate. This is due to early overlap between the larger number of cylindrical zones. Furthermore, application of the rate constant obtained from the thermal decomposition of unirradiated material on the assumption of contracting envelope topochemistry to the expansion of the recoil tracks during the thermal decomposition of irradiated material, predicts the acceleration by pre-irradiation to within 20%. The burst of gas occurring near the beginning of runs B and C is ascribed to the thermal decomposition of disordered oxalate adjacent to the recoil tracks.

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A.E.R.E., HARWELL, nr. DIDCOT, BERKS. [*Received, January 25th,* 1960.]