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CALCULATIONS OF YIELDS OF PRODUCTS IN HIGH-FLUX
NEUTRON IRRADIATIONS OF HEAVY ELEMENT SAMPLES

by

J. Milsted, P. R. Fields and D. N. Metta

Chemistry Division

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CALCULATIONS OF YIELDS OF PRODUCTS IN HIGH-FLUX NEUTRON IRRADIATIONS OF HEAVY ELEMENT SAMPLES

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ABSTRACT

Calculations have been made of the build-up of higher nuclides in samples of various heavy element starting materials, at neutron fluxes ranging from 4×10^{13} to 1×10^{16} n/cm²/sec, including the flux expected from the HFIR reactor at Oak Ridge (namely, 5×10^{15} n/cm²/sec). Attempts have been made to estimate yields of the heavier fermium isotopes and of Md²⁵⁹ by means of the nuclear properties predicted from systematics. The results indicate that it may be possible to detect Md²⁵⁹ in the products of californium irradiated in HFIR, and that a further two-fold increase in flux would increase the yields of the heaviest nuclides considerably.

I. INTRODUCTION

Since neutron fluxes of the order of 10^{13} n/cm²/sec first became available in the NRX reactor during the 1940's, multiple neutron capture has been a very important method for the preparation of the heaviest nuclides. Although the majority of the transuranium elements were first made in the form of their lighter isotopes by bombardments with charged particles, neutron-capture routes provide the only means of obtaining them in weighable amounts, and as heavier, longer-lived isotopes for chemical studies and as target materials for further positive-ion bombardments.

During the late 1940's, the most useful research reactor was the NRX at Chalk River, Ontario, Canada. This reactor had at that time a neutron flux of about 4×10^{13} n/cm²/sec, and long irradiations of Pu²³⁹ and Am²⁴¹ were carried out for both the Canadian and US projects.

With this neutron flux it was possible to prepare nuclides as heavy as Cm²⁴⁴ in quantities detectable by methods available at that time, but further progress was limited by the comparatively small capture cross section of Cm²⁴⁴ and the high fissionability of Cm²⁴⁵. It required a flux

higher by an order of magnitude to reach Cm^{249} , the lightest curium isotope showing detectable β^- decay. Such a flux became available during 1952 in the Materials Testing Reactor (MTR) at Arco, Idaho.

This reactor provided a flux of about 3×10^{14} n/cm²/sec with local regions as high as 5×10^{14} n/cm²/sec. During the first 10 yr of operation, long irradiations of Pu^{239} produced gram amounts of Cm^{244} , microgram amounts of Bk^{249} and Cf^{252} , and submicrogram amounts of heavier nuclides up to Fm^{255} . Shorter re-irradiations of curium, californium, and einsteinium samples increased the yields of the heavier nuclides, and led to the identification of Fm^{256} .

The present obstacle to further progress is the short (3-hr) half-life of Fm^{256} for spontaneous fission, which competes so strongly with neutron capture that no detectable amounts of heavier nuclides can be made. Further, Fm^{258} is expected to have a similarly short spontaneous-fission half-life, and a much higher neutron flux will be needed to reach Fm^{259} , which is confidently predicted to be the lightest (negative) beta-emitting isotope of fermium.

The High Flux Isotope Reactor (HFIR), now under construction at Oak Ridge, will provide a neutron flux of about 5×10^{15} n/cm²/sec, greater by an order of magnitude than that of MTR. The forthcoming availability of this high flux prompted the present calculations.

An earlier report(1) gave calculations of the yields of Cf^{252} and intermediate nuclides to be expected in high-flux irradiations of Cm^{244} . Up to this point, the main competing processes resulting in loss of atoms from the build-up chain are neutron-induced fission and competing neutron capture at the beta-decay steps. Both of these processes are dependent only on neutron flux and time, and all competing decay half-lives are long enough to be ignored. With these assumptions, comparatively simple calculations give the yields of build-up products as functions of total neutron irradiation (nvt), independently of neutron flux. Above Cf^{252} , however, competition from decay processes becomes important and, eventually, the limiting factor. The yields of the heaviest nuclides therefore become highly dependent on neutron flux.

The present calculations were accomplished by means of a more general computer program which can handle any number of competing decay processes in a build-up chain, with no inherent limit to the chain length. The availability of this program, together with some new nuclear data and developments in nuclear systematics, made it useful to re-calculate yields for various starting materials in neutron fluxes available at the present time, and to attempt predictions of yields of the heaviest nuclides, some unknown at present, in the higher neutron flux which will become available

in HFIR. Calculations have also been made for Cm^{244} and Cf^{252} as starting materials in a flux of 1×10^{16} n/cm²/sec, in order to estimate the advantage which might be gained by a two-fold increase in flux over HFIR. The neutron fluxes and starting materials considered in the present calculations are shown in Table I.

Table I

STARTING MATERIALS AND NEUTRON FLUXES

Neutron Flux (n/cm ² /sec)	Starting Materials
4×10^{13} (NRX)	Pu^{239}
3×10^{14} (MTR)	Pu^{239} , Am^{241} , Cm^{244}
5×10^{15} (HFIR)	Pu^{242} , Cm^{244} , Cm^{248} , Cf^{252}
1×10^{16}	Cm^{244} , Cf^{252}

II. METHOD OF CALCULATION

The members of the chain are indicated by subscripts 1, 2, ..., n, ..., where subscript 1 indicates the starting material. Let a_n and b_n denote the rate-determining constants for the formation and destruction, respectively, of the nth member of the chain, defined in the same way as the decay constant λ in the familiar first-order equation

$$\frac{dN}{dt} = -\lambda N \quad ,$$

N representing a number of atoms.

If the process producing the nth member is a radioactive decay, a_n is the decay constant of the parent, $\lambda_{(n-1)}$, or the partial decay constant if the decay is branched. If the process is neutron capture, a_n is the product $\sigma_{(n-1)}F$, where $\sigma_{(n-1)}$ is the capture cross section of the precursor and F is the neutron flux.

The b_n value includes all processes which result in the destruction of the nth member, including the process which produces the (n+1)th member: decay by all processes, as well as neutron capture and neutron-induced fission. Therefore, b_n is the sum of the total decay constant λ_n and $\sigma_n F$, where σ_n is the total destruction cross section (capture plus fission).

The computer program evaluated the relative yield Q_{nt} of the n th member:

$$Q_{nt} = \frac{\text{Number of atoms of } n\text{th member at time } t}{\text{Number of atoms of starting material at time zero}},$$

by means of the well-known solution of the differential equations, originally due to Bateman,⁽²⁾ which may be written:

$$Q_{nt} = (a_2 a_3 a_4 \dots a_n) \sum_{i=1}^n \left[\frac{e^{-b_i t}}{\prod_{\substack{j=1 \\ j \neq i}}^n (b_j - b_i)} \right]. \quad (1)$$

To obtain this solution it is assumed that at zero time only one species is present and that no two b values are identical. Alternative solutions for repeated b values have been derived, but in practice with the present program an arbitrary 1% difference between any two b values eliminates the difficulty; few cross sections or half-lives are known more accurately than this.

The a and b constants have the dimensions of reciprocal time, and the time unit chosen is immaterial, provided that the same unit is used for t in Equation (1). If seconds are used, the a and b values are mostly very small, and errors may be introduced due to the generation of both very large and very small numbers in the course of the calculation. The unit 10^6 sec (11.6 days) has been found useful. In those units, the a and b values ranged from about 10^{-4} to 10^2 . It should be noted that there is no a_1 in Equation (1) because the starting material is not being formed by any process.

The most important build-up paths from Pu^{239} to Md^{259} are shown in Fig. 1, the starting materials considered in the present calculations being underlined. The major route is shown by solid arrows, and minor routes by dotted arrows. These minor routes were generally considered insignificant, but in two cases a minor route was calculated separately and the yields added to those of the major route where appropriate (see discussion).

The cross sections and half-lives used in the calculations are shown in Table II. Only decay half-lives short enough to compete appreciably with neutron capture and fission are considered. The cross sections of the lighter nuclides, especially of the plutonium isotopes, have been measured with reasonable accuracy for "pile" neutrons in NRX or MTR. The cross sections for the heavier curium isotopes and the known transcurium nuclides are much less certain. They are, in general, values which have given calculated

yields consistent with experimental measurements in past irradiations, but, individually, they may be in error by as much as a factor of two. The capture cross section of Cm^{248} has been taken as 3 b rather than the more generally used value of 6 b, because the lower value gives better agreement with berkelium and californium yields in recent irradiations of Cm^{244} .

Figure 1
Main Build-up Path

Table II

HAZARD LIVES AND CROSS SECTIONS USED IN CALCULATIONS

Nuclide	τ	$\sigma(n, \gamma)$ b	σ_{fiss} b	Nuclide	τ	$\sigma(n, \gamma)$ b	σ_{fiss} b
Pu^{239}		340	810	Bk^{249}	310 d	800	
Pu^{240}		530	0	Bk^{250}	3.2 hr		2 000
Pu^{241}	13 yr	350	1 100	Cf^{250}		1 330	0
Pu^{242}		30	0	Cf^{251}		500	3 300
Pu^{243}	5 yr	100	200	Cf^{252}	2.6 yr	9	0
Am^{241}		$\begin{cases} 50^{(a)} \\ 750^{(b)} \end{cases}$	0	Cf^{253}	19 d	2	0
Am^{242}	16 hr ^(c)		3 000	Es^{253}	20 d	$\begin{cases} 250^{(d)} \\ 7^{(e)} \end{cases}$	0
Am^{243}		110	0	Es^{254}	$\begin{cases} 37 \text{ yr} \\ 480 \text{ d} \end{cases}$	40	2 000
Am^{244}	26 min		2 000	Es^{255}	24 d	40	0
Cm^{242}	162.5 d	30	0	Fm^{254}	3.24 yr		
Cm^{243}	35 yr	250	590	Fm^{255}	20 hr	100	100
Cm^{244}	18 yr	30	0	Fm^{256}	3 hr (S.F.)	20	0
Cm^{245}		150	2 000	Fm^{257}	10 d (a)	100	100
Cm^{246}		15	0	Fm^{258}	5 hr (S.F.)	5	0
Cm^{247}		200	200	Fm^{259}	10 d (b)	100	50
Cm^{248}		3	0	Md^{259}	3.5 d (a)	250	0
Cm^{249}	64 min						

(a) to Am^{242m} (long)

(b) to Am^{242} (short)

(c) 181 to Cm^{242}
119 to Pu^{242}

(d) to 37 yr Es^{254}

(e) to 480-d Es^{254}

estimated value

For the heaviest, unknown nuclides, estimates of half-lives have been made from nuclear systematics based on observed trends in lighter nuclei, and using alpha- and beta-decay energies from the mass equation of Cameron.⁽³⁾ Neutron capture and fission cross sections have been estimated from the approximate correlations between capture cross section, capture-to-fission ratio, and the binding energy of an added neutron.^(4,5) Neutron binding energies were also taken from Cameron's tables. The spontaneous fission half-life for Fm^{258} is the value predicted by Johansson.⁽⁶⁾ All of these figures must be regarded as only order-of-magnitude estimates. The extrapolations to higher neutron fluxes in new reactors may also be in error because of differences in neutron-energy distribution.

Some members of the build-up chain, Am^{243} , Cm^{244} , Bk^{249} , and Cf^{250} , are produced by the β^- decay of a parent with a half-life so short that competing capture and fission may be ignored. In these cases, the parent-daughter pair were regarded as a single step in the chain. For instance, if it is assumed that virtually every atom of 64-min Cm^{249} decays to give an atom of Bk^{249} , then the formation constant of Bk^{249} is effectively equal to that of Cm^{249} . These approximations shortened the calculations and removed the inconveniently large a and b values corresponding to the short half-lives.

The build-up curves are shown in Figs. 2 through 11 as semi-logarithmic plots of relative yield against time. Each set of curves is in two parts, (a) showing yields from unity down to 10^{-7} , and (b) showing yields from 10^{-7} down to 10^{-14} .

Figure 2a

Starting Material: Pu^{239}

Figure 2b

Flux: 4×10^{13} n/cm²/sec

Figure 3a

Starting Material: Pu^{239}

Figure 3b

Flux: $3 \times 10^{14} \text{ n/cm}^2/\text{sec}$

Figure 4a

Starting Material: Am^{241}

Figure 4b

Flux: 3×10^{14} n/cm²/sec

Figure 5a

Starting Material: Cm^{244}

Figure 5b

Flux: 3×10^{14} n/cm²/sec

Figure 6a

Starting Material: Pu^{242}

Figure 6b

Flux: $5 \times 10^{15} \text{ n/cm}^2/\text{sec}$

Figure 7a

Starting Material: Cm^{244}

Figure 7b

Flux: 5×10^{15} n/cm²/sec

Figure 8a

Starting Material: Cm^{248}

Figure 8b

Flux: $5 \times 10^{15} \text{ n/cm}^2/\text{sec}$

Figure 9a

Starting Material: Cf^{252}

Figure 9b

Flux: $5 \times 10^{15} \text{ n/cm}^2/\text{sec}$

Figure 10a

Starting Material: Cm^{244}

Figure 10b

Flux: 1×10^{16} n/cm²/sec

Figure 11a

Starting Material: Cf^{252}

Figure 11b

Flux: $1 \times 10^{16} \text{ n/cm}^2/\text{sec}$

III. DISCUSSION

The curves for Pu^{239} irradiated at 4×10^{13} and 3×10^{14} $\text{n/cm}^2/\text{sec}$ (see Figs. 2 and 3) demonstrate clearly the great advance in production of the transplutonium elements which the MTR reactor made possible. At the lower (NRX) flux, yields of transcurium elements are minute, even in irradiations enduring many years, and it is not surprising that these elements were never detected with the chemical separation and radiation-detection techniques available around 1950. However, present-day techniques would probably be able to detect the spontaneous fission activity of Cf^{252} produced by irradiating 1 g of Pu^{239} for 5 yr in NRX (a few fissions per minute).

These curves also show that Pu^{239} is a poor starting material. The high fission cross sections of Pu^{239} and Pu^{241} result in a loss of nearly 95% of the initial atoms, and a correspondingly high output of fission heat, before Pu^{242} is reached. In long irradiations, after the burnout of Pu^{239} , Pu^{242} becomes the effective starting material. For this reason, kilograms of Pu^{239} are already being irradiated at lower fluxes to provide several hundred grams of Pu^{242} for re-irradiation in HFIR.

In the case of Pu^{239} at 4×10^{13} $\text{n/cm}^2/\text{sec}$, the secondary route via $\text{Pu}^{241} \rightarrow \text{Am}^{241} \rightarrow \text{Am}^{242} \rightarrow \text{Pu}^{242}$ -- was calculated separately, but it was found that the contribution to production of the transplutonium elements is almost negligible compared to the direct build-up via $\text{Pu}^{240} \rightarrow \text{Pu}^{241} \rightarrow \text{Pu}^{242} \rightarrow \text{Pu}^{243} \rightarrow \text{Am}^{243}$ ---.

The calculations for Am^{241} in the MTR flux were made to estimate the composition of samples already in the reactor. This isotope has a high capture cross section and burns out rapidly, producing Pu^{242} and Cm^{242} . After the burnout of Am^{241} , Cm^{242} declines quite rapidly due to decay and neutron capture. Although during the first year or so further neutron capture in Cm^{242} is the more important route to the heavier isotopes of curium, Pu^{242} and Cm^{244} eventually become the sustaining nuclides. In this case also two routes were calculated, and the yields added for nuclides produced by both routes.

Figure 5 shows the build-up of heavier nuclides in Cm^{244} irradiated at 3×10^{14} $\text{n/cm}^2/\text{sec}$. The yields are in reasonable agreement with the results of actual irradiations for up to 2 yr in MTR.

The curves for Pu^{242} irradiated at 5×10^{15} $\text{n/cm}^2/\text{sec}$ are shown in Fig. 6. It is clear that, starting with a few hundred grams of Pu^{242} in HFIR, it will be possible to make many grams of curium isotopes, milligram quantities of Cf^{252} , and hundreds of micrograms of Es^{253} in an irradiation lasting but a few months. In such short irradiations, the curium fraction will consist mainly of Cm^{244} . This could be separated and re-irradiated.

Figure 7 shows the build-up of heavier nuclides in Cm^{244} at HFIR flux. Starting with tens of grams of Cm^{244} , many more milligrams of Cf^{252} could be produced. It may be noted that although Cm^{244} is burned out fairly rapidly at this flux, Cm^{246} and Cm^{248} are produced in considerable quantities. After a year or so of irradiation, Cm^{248} becomes the important nuclide which sustains the higher members of the chain. Thus, in spite of the burnout of Cm^{244} , curium samples actually become more valuable for repeated irradiations, as the Cm^{248} concentration builds up. For this reason, calculations were made for Cm^{248} as the starting material. The results are shown in Fig. 8.

Figures 6, 7, and 8 demonstrate that after several years of operation, it would be possible to accumulate stocks of Cf^{252} of the order of a gram. Short irradiations of Cf^{252} would then produce the heaviest nuclides, as shown in Fig. 9. Due to their short decay half-lives, the transcalifornium nuclides grow in quite rapidly, reach maximum yields in a few months, and then decline in equilibrium with the burnout of Cf^{252} . If the nuclear properties assumed for these nuclides are approximately correct, quite appreciable quantities of heavy fermium isotopes would be produced, up to Fm^{259} , which would decay to give Md^{259} .

If the properties quoted in Table II are taken the optimum yield of Md^{259} occurs at irradiation for about 4 months, and the amount of this nuclide present in an initial 1-g Cf^{252} sample would be about 10^{-14} g, i.e., about 2×10^7 atoms or 2000 alpha disintegrations per minute. The isolation and identification of this product would present formidable experimental difficulties. However, if the fermium fraction could be isolated fairly quickly, more mendelevium would grow into it and could be isolated more easily. The einsteinium or fermium fractions could also be re-irradiated for a few days to make more mendelevium.

The results for Cm^{244} and Cf^{252} at 1×10^{16} n/cm²/sec are shown in Figs 10 and 11. The most important conclusion to be drawn from these curves is that up to Fm^{255} little is gained, except time, by a two-fold increase in flux over HFIR. The yields of the heaviest nuclides, however, are considerably increased, and for Md^{259} the gain is nearly a factor of ten.

Finally, it must be emphasized that these calculations are highly speculative. The authors can only hope that future experience will not prove them to be grossly erroneous.

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