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New Isotopes of Neptunium*

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Evidence is presented for three new, light neptunium isotopes formed by deuteron bombardments of U^{233}, U^{235}, and U^{238}. The isotope Np^{231} has a half-life of 50±3 min. and emits alpha-particles of 6.28-Mev energy; the proportion of decay by electron-capture has not been determined. The isotope Np^{233} decays predominantly by electron-capture with a 35±3-min. half-life; it has an alpha-decay half-life roughly determined to be *ca.* 10 yr. corresponding to a K/α-branching ratio of 1.5×10^5 and the alpha-particles have an energy of 5.53 Mev. A 13±3-min. period with electromagnetic radiation, indicating orbital electron-capture, is attributed to Np^{232}. Approximate cross sections for formation of various neptunium isotopes by deuterons of energy from 15 to 100 Mev have been determined. The cross sections are low, of the order of 10^{-26} cm², possibly because most of the excited nuclei undergo fission.

1. INTRODUCTION

A NEW field, that of the synthetic transuranium elements, was opened with the discovery in 1940 of an isotope of neptunium, element 93, by McMillan and Abelson.[1,2] Concurrently with investigations of other transuranium isotopes, a rapid advance in knowledge of the nuclear properties of neptunium isotopes was made during the next several years. By 1945 six neptunium isotopes of mass numbers 234–239 inclusive were known and well characterized.

A prerequisite to research in the transuranium field was the determination of some of the chemical properties of neptunium so that it could be separated from other elements, particularly its neighbors, uranium and plutonium. On the basis of the chemical properties, Seaborg, McMillan, Wahl, and Kennedy[3,4] were thus enabled to identify as a new neptunium isotope, a two-day negative beta-particle emitter formed in the deuteron bombardment of uranium. The assignment of this isotope as Np^{238} was proved by the use of separated isotopes and yield considerations.[5]

A very long-lived, alpha-particle emitting neptunium isotope was found a year later.[6] This was Np^{237}, formed by the β^--decay of U^{237}. The isotope Np^{237} may be produced in macro-amounts in uranium piles by the $(n, 2n)$ reaction on U^{238} and hence is the most important isotope for chemical studies of the element.[7–10] The possibilities for identifying new neptunium isotopes as the result of irradiating natural uranium were virtually exhausted at this point since the 16-Mev deuterons of the 60-in. Berkeley cyclotron were not energetic enough to remove more than three neutrons in a (d, xn) type reaction on U^{238}. Deuteron bombardment of U^{235} was expected to produce light neptunium iso-

* This paper is based on work done under the auspices of the AEC.
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[1] E. M. McMillan, Phys. Rev. **55**, 510 (1939).
[2] E. M. McMillan and P. H. Abelson, Phys. Rev. **57**, 1185 (1940).
[3] Seaborg, McMillan, Wahl, and Kennedy, Phys. Rev. **69**, 366 (1946); *The Transuranium Elements: Research Papers* (McGraw-Hill Book Company, Inc., New York, 1949), Paper No. 1.1, National Nuclear Energy Series, Plutonium Project Record Vol. 14B.
[4] Seaborg, Wahl, and Kennedy, Phys. Rev. **69**, 367 (1946); National Nuclear Energy Series, Plutonium Project Record Vol. 14B, Paper No. 1.4.
[5] Kennedy, Perlman, Segrè, and Wahl, National Nuclear Energy Series, Plutonium Project Record Vol. 14B, Paper No. 1.9.
[6] A. C. Wahl and G. T. Seaborg, Phys. Rev. **73**, 940 (1948); National Nuclear Energy Series, Plutonium Project Record Vol. 14B, Paper No. 1.5.
[7] L. B. Magnusson and T. J. LaChapelle, J. Am. Chem. Soc. **70**, 3534 (1948); National Nuclear Energy Series, Plutonium Project Record Vol. 14B, Paper No. 1.7.
[8] Hindman, Magnusson, and LaChapelle, J. Am. Chem. Soc. **71**, 687 (1949); National Nuclear Energy Series, Plutonium Project Record Vol. 14B, Paper Nos. 15.1, 15.2, 15.3, 15.4, 15.6, 15.8, 15.11.
[9] S. Fried and N. Davidson, J. Am. Chem. Soc. **70**, 3539 (1948); National Nuclear Energy Series, Plutonium Project Record Vol. 14B, Paper No. 15.5.
[10] J. J. Katz and D. M. Gruen, J. Am. Chem. Soc. **71**, 2106 (1949).

topes, but the small abundance of U^{235} (less than one percent) in natural uranium complicated any identification of the products over the background activity of the heavier neptunium isotopes produced from U^{238}.

Milligram quantities of both U^{233} and U^{235} became available for cyclotron bombardment in 1944. James, Florin, Hopkins, and Ghiorso[11] identified Np^{236}, Np^{235}, and Np^{234} as products of deuteron bombardments of U^{235}. The isotope Np^{234} was also made by deuteron bombardment[12] of U^{233}. The radioactive properties of these neptunium isotopes were summarized in a recent review.[13]

At the beginning (June, 1948) of the research reported in this paper, trends in stability with mass number were clearly apparent. Neptunium, of course, exhibits the general instability characteristic of elements of odd Z, in this case only one isotope, Np^{237}, being stable toward both electron-capture and β^--decay. Neptunium isotopes with mass numbers above 237 are β^--unstable, and those with mass numbers below 236 are unstable toward electron-capture. The observed mode of decay of Np^{236} is by β^--emission but decay by electron-capture is undoubtedly also possible. The data on these isotopes, however, reveal little about the effect of mass number on the energies (and half-lives) for decay by alpha-particle emission. Alpha-particles had been observed only from two isotopes of neptunium. The Np^{237} emits alpha-particles of 4.77-Mev energy and James[14] has found that Np^{235} has an alpha-branching decay of about *ca.* 0.005 percent emitting alpha-particles of 5.06 Mev. Much work in this laboratory has been directed toward the correlation of the systematics known to exist for the alpha-decay energies and half-lives for heavy elements.[15] It was hoped that new light neptunium isotopes could be produced which might decay by alpha-particle emission and thereby yield data for extension of the alpha-particle energy, half-life, and mass number relations for this region, and this hope was realized in that some such data were obtained for the isotopes Np^{231} and Np^{233}.

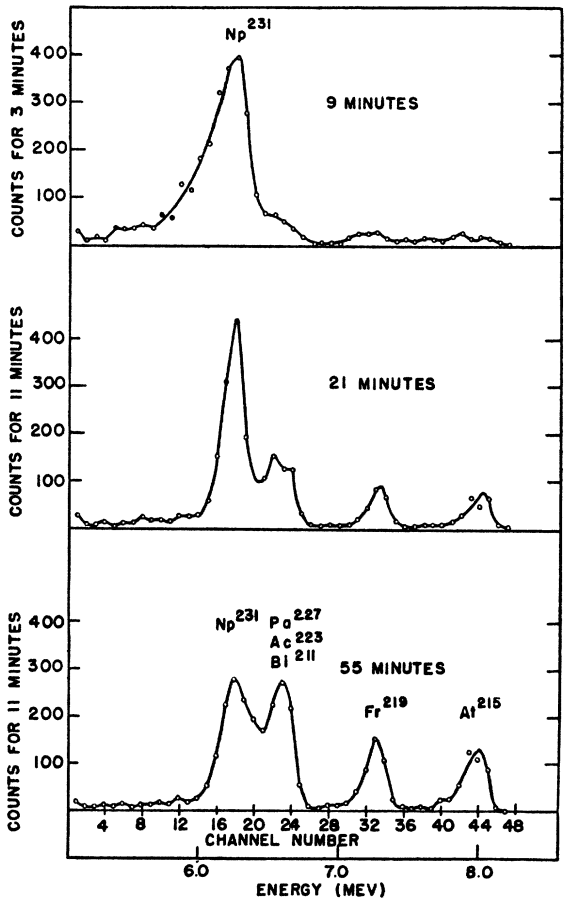

FIG. 1. Alpha-pulse analyses of Np^{231} in neptunium fraction at intervals (9, 21, and 55 min.) after separation from protactinium daughter. Sample not collimated for 9-min. reading. First reading taken 93 min. after end of 20-min. bombardment of U^{235} with 45-Mev deuterons.

The isotopes Np^{232} and Np^{233} probably had been produced in the 22-Mev deuteron bombardment of U^{233} but had not been identified.[12] The half-lives were thought to be too short for detection or possibly so close to those of Np^{236}, Np^{238}, or Np^{239} as to escape resolution.

This paper will report results obtained from deuteron bombardments at energies ranging from 15–100 Mev of U^{233}, U^{235}, and U^{238} using the 60- and 184-in. Berkeley cyclotrons. Data have been obtained for the identification of three new isotopes, Np^{233}, Np^{232}, and Np^{231}. Relative yields for a number of neptunium isotopes have been determined in many of the bombardments.

2. THE ISOTOPE Np^{231}

A process for extracting radioactively pure neptunium within an hour or two after the end of bombardment was devised (see Section 5, procedures B1 to B3) and applied to a series of 100-Mev deuteron (184-in. cyclotron) bombardments of natural uranium (metal). The neptunium fractions from these bombardments contained a new alpha-activity. Alpha-pulse analyses[16] at intervals revealed the growth of an alpha-decay series which was recognized as the collateral series of short-lived alpha-emitters[17] following the alpha-decay of Pa^{227}. The following series was indicated:

$$Np^{231} \xrightarrow{\alpha} Pa^{227} \xrightarrow{\alpha} Ac^{223} \xrightarrow{\alpha} Fr^{219} \xrightarrow{\alpha} At^{215} \xrightarrow{\alpha} Bi^{211} \xrightarrow{\beta^-} Tl^{207} \rightarrow Pb^{207}.$$

[11] James, Florin, Hopkins, and Ghiorso, National Nuclear Energy Series, Plutonium Project Record Vol. 14B, Paper No. 22.8; AEC declassified document No. 2495 (1949).

[12] Hyde, Studier, and Ghiorso, National Nuclear Energy Series, Plutonium Project Record Vol. 14B, Paper No. 22.15; AEC declassified document No. 2572 (1949).

[13] G. T. Seaborg and I. Perlman, Rev. Mod. Phys. **20**, 585 (1948).

[14] R. A. James (unpublished data).

[15] Perlman, Ghiorso, and Seaborg, Phys. Rev. **74**, 1730 (1948); **75**, 1096 (1949); **77**, 26 (1950).

[16] Ghiorso, Jaffey, Robinson, and Weissbourd, National Nuclear Energy Series, Plutonium Project Record Vol. 14B, Paper No. 17.3.

[17] Meinke, Ghiorso, and Seaborg, Phys. Rev. **74**, 695 (1948).

The parent-daughter relationship of Np^{231} and Pa^{227} was confirmed by repeated chemical separations of protactinium from the neptunium and measurement of the 38-min. decay of Pa^{227} in the protactinium fraction.

The electron and electromagnetic radiation in the neptunium fraction seemed to be largely from the known neptunium isotopes of mass number greater than 233. There was so much electron activity and electromagnetic radiation from the heavier neptunium isotopes that the ionization interfered with the alpha-particle energy determinations of Np^{231} using the differential pulse analyzer. The relatively small numbers of alpha-particle counts from Np^{231} also suggested that the yield of the $(d, 9n)$ reaction from U^{238} was very low. Increasing the energy of the deuterons did not seem to improve the relative yield of Np^{231}.

Bombardments of U^{235} with deuterons of energies varying between 45 and 100 Mev gave improved yields of Np^{231} by the $(d, 6n)$ reaction. Figure 1 shows alpha-pulse analysis data for one of the neptunium fractions from these bombardments at intervals corresponding to 9, 21, and 55 min. after separation from protactinium. A ring collimator was placed over the sample for the 21- and 55-min. readings to give sharper definition of the peaks by eliminating degraded alpha-particles scattered from the sample plate. The growth of Pa^{227} and its daughters to equilibrium with the Np^{231} is clearly apparent. Separate peaks for Pa^{227}, Ac^{223}, and Bi^{211} are not observed since the energies are about equal and the instrument was set at a low resolving power to bring the entire series within the register range. Figure 2 shows the best energy resolution obtained for Np^{231}, Pa^{227}, Ac^{223}, and Bi^{211}. The Fr^{219} and At^{215} are beyond the range covered by the instrument in this run. The Np^{231} for this measurement was produced by the $(d, 4n)$ reaction with 45-Mev deuterons on U^{233}. The energies of the alpha-particles from Pa^{227} and Ac^{223} are known to be 6.46 and 6.64 Mev, respectively.[17] From these data the energy of the alpha-particle from Np^{231} is 6.28 Mev.

The measurement of the half-life of Np^{231} was complicated by the presence of its alpha-decay daughters. The resolution of the alpha-pulse analyzer usually proved to be too low to permit following the decay of the Np^{231} peak directly in the presence of near equilibrium amounts of the daughters. The most reliable values of the half-life were obtained from pulse analysis of aliquots of an Np^{231} solution freshly purified from Pa^{227} and daughters. The aliquot size was determined by pulse analysis for Np^{237} tracer used in all runs. Figure 3 shows plots of the decay of the alpha-activity of Np^{231}. Curves A and B are plots of the activity of Np^{231} relative to the tracer Np^{237}, and curve D is obtained from data on the decay of Np^{231} measured in the presence of its daughter by a series of pulse analyses which had unusually good resolution (as in Fig. 2). The slope of the lines is a measure of the Np^{231} half-life, the absolute values of the ratios having no significance. Included in the figure is an observed rate of decrease in recoil Pa^{227} activity from an Np^{231} sample (curve C). In this determination the Pa^{227} atoms recoiling from the alpha-decay of Np^{231}, mounted on a platinum counting plate, were caught on a second plate charged to a negative potential with respect to the first; the plates containing the recoil atoms were subsequently pulse-analyzed for Pa^{227} and daughters. The results all indicate that the half-life of Np^{231} is *ca.* 50 min.

The isotope Np^{231} is undoubtedly unstable toward electron-capture and a consideration of the alpha-systematics[15] indicates that it is probably this process

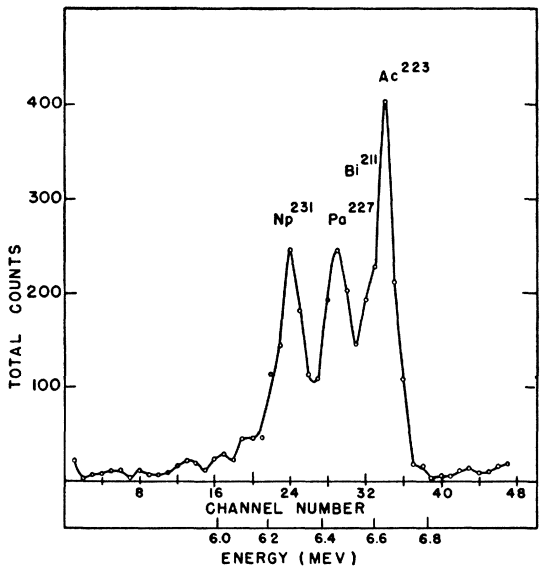

FIG. 2. Energy determination of the alpha-particle from Np^{231} (6.28 Mev) by pulse analysis. 10-min. count taken 95 min. after separation from Pa^{227} daughter and 175 min. after end of 45-min. bombardment of U^{233} with 45-Mev deuterons.

which controls the rate of decay. The electromagnetic radiations characteristic of this process were not resolvable in these experiments from the radiations resulting from the decay of the heavier neptunium isotopes. The electron-capture decay daughter of Np^{231} is U^{231}, which also decays by electron-capture with a four-day half-life. The determination of the percentage of Np^{231} which decays by electron-capture by measurement of the number of U^{231} daughter atoms is very insensitive for several reasons: namely, (1) the low Geiger tube counting efficiency for x-rays, (2) the factor of 100 in the ratio of the half-lives, and (3) as will be seen later, the low yields of Np^{231}. Uranium was separated from a neptunium fraction after complete decay of the Np^{231}, but the Geiger counter activity in the uranium fraction was only slightly above counter background and was not positively identified as U^{231}. The poor sensitivity of the method allows us to place only an upper limit of 10^3 on the ratio of electron-capture to alpha-emission from these data. From an estimate of the upper limit to the amount of x-radiation from Np^{231}

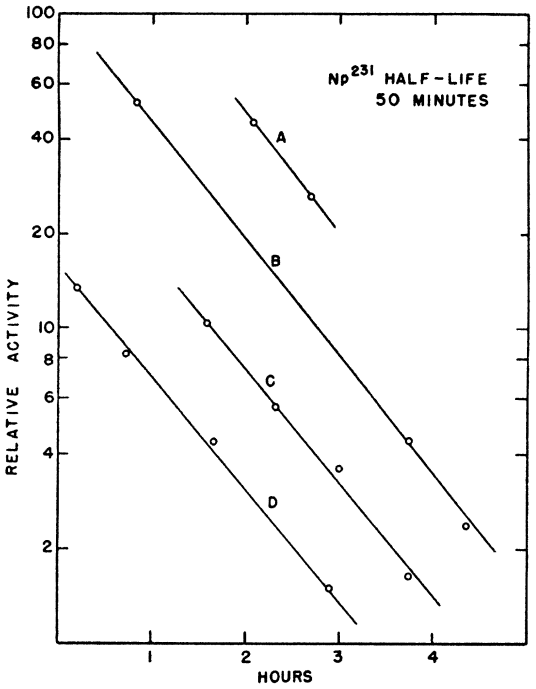

FIG. 3. Decay of the alpha-activity of Np^{231}. Curves A and B from pulse analysis of Np^{231} freshly separated from Pa^{227} and daughters. Curve C represents decaying yield of daughter Pa^{227} recoil atoms from Np^{231}. Curve D from pulse analysis of Np^{231} in presence of daughters.

which would have escaped detection, the upper limit for this ratio may be lowered to *ca.* 10^2.

3. THE ISOTOPE Np^{233}

Although the 50-min. period of electromagnetic activity expected for Np^{231} was not resolved from the decay curves, x-rays of 35-min. half-life were consistently observed in the neptunium fractions from bombardments of U^{233} and U^{235} with 45- to 100-Mev deuterons in the 184-in. cyclotron. That this activity was due to a neptunium isotope was verified by the fact that it followed precisely the same chemistry as Np^{237} tracer in separations using a chemical procedure specific for neptunium (see Section 5, procedures B1 to B3). After complete decay of the 35-min. neptunium activity, a uranium fraction containing U^{233} as a tracer was separated from this neptunium fraction in order to detect the uranium daughter produced by the electron-capture process. The amount of uranium daughter to be expected was roughly calculable by assuming that one *L* x-ray was emitted per neptunium disintegration, and that the *L* x-rays were counted with an efficiency of two percent in the argon-filled Geiger counter tube. The uranium fraction was examined in the differential pulse analyzer, and no daughter alpha-activity was observed. If the parent were Np^{232}, about three alpha-counts per minute of U^{232} should have been found; but if the parent were Np^{233}, the daughter activity should not be detectable since U^{233} has too long a half-life. The limit of detection was about 0.1 count per minute. A preliminary assignment of the 35-min. activity was therefore made to Np^{233}.

A bombardment of U^{233} with 15-Mev deuterons in the 60-in. cyclotron also yielded the 35-min. period. A different method of purification was used (see Section 5, procedures B2, B4, and B5) providing additional chemical evidence that the short-lived activity was a neptunium isotope. Since no Np^{231} was formed in this bombardment, isotopes of mass number less than 232 were ruled out. The neptunium isotopes which could be formed from the U^{233} were limited to the products of the (d, n), $(d, 2n)$, and $(d, 3n)$ reactions. The (d, n) reaction product is the 4.4-day Np^{234}, and since the 35-min. activity did not decay to U^{232} in the previous experiments, it is assigned to Np^{233}.

The radiations were characterized by beryllium, aluminum, and lead absorption measurements with argon- and xenon-filled Geiger tubes. All counts were corrected for the long-lived neptunium background and were corrected for decay to an arbitrary standard time. The Np^{233} absorption curves are given in Figs. 4 and 5. Although more than one sample was used to obtain these curves, the data were normalized through use of the Np^{237} tracer contents of the samples so that the figures represent equal amounts of Np^{233}. From the fact that electromagnetic radiations cause more ionization in xenon than in argon and hence are counted more efficiently, it is evident that the absorption data reveal the x-radiation characteristic of an electron-capture process. Comparison of the curves obtained with the argon- and xenon-filled counter tubes shows the presence of soft electrons which are absorbed by 100 mg/cm² of beryllium (maximum energy *ca.* 300 kev). The apparent component of 2 g/cm² beryllium half-thickness is a composite of the *K* and *L* x-rays. The composite x-radiation was counted more efficiently in the xenon-filled tube than in the argon-filled tube by a factor of five. The magnitudes of the counting rates observed through the aluminum and lead absorbers prove the electromagnetic nature of the radiations and indicate roughly the range of energies and relative abundance of the x-rays. The average half-thickness in lead for the 94–114-kev uranium *K* x-rays is 125 mg/cm². The lead absorption curves have slopes of *ca.* 230 mg/cm² indicating the presence of gamma-radiation in addition to the *K* x-rays. Gamma-radiations in these samples were not resolved in detail and will be discussed further in the section on Np^{232}. The observed electrons of 300-kev maximum energy suggest the presence of gamma-rays with some internal conversion. It is likewise likely from the lead absorption data that some gamma-radiation of energy not more than 400 kev is associated with Np^{233}. The average half-thickness in aluminum for the 13–20-kev uranium *L* x-rays is 130 mg/cm² and the aluminum absorption curves indicate the presence of x-rays of this energy over the background of *K* x-ray and gamma-radiations. The absolute counting

efficiencies for electromagnetic radiations of these energies are not well known but have been calculated to be of the order of one percent, in Geiger counter tubes containing 10 cm of argon.[14]

The absence of Np^{231} alpha-particles in the pure neptunium fraction from the low energy (15-Mev) deuteron bombardment of U^{233} permitted a sensitive detection of other short-lived neptunium alpha-activity. Figure 6 is a series of three of the alpha-pulse analyses. A small short-lived peak corresponding to an alpha-particle energy of 5.53 Mev was present, and its decay was followed by summing the counting rates recorded at this energy. The decay of counts per minute recorded under this peak is given in Fig. 7. A plot of the data following subtraction of background yielded a half-life of *ca.* 35 min. No other short-lived alpha-activity of this energy is known, so, in view of the correspondence in half-life with that observed for the radiations detected with the Geiger counter, the alpha-particles are assigned to Np^{233}. The ratio of alpha-disintegrations per minute to Geiger counts per minute (argon tube, 1.5 g/cm² Be absorber) for Np^{233} was 1.8×10^{-2}. With the assumption of one L x-ray per disintegration, an Auger coefficient of 0.5 for the L x-rays, and a counting efficiency of one percent, the partial half-life of Np^{233} for alpha-particle emission is calculated to be *ca.* 10 yr. corresponding to a K/α-branching ratio of 1.5×10^{5}. These data on the alpha-radioactivity are in good agreement with the systematics.[15]

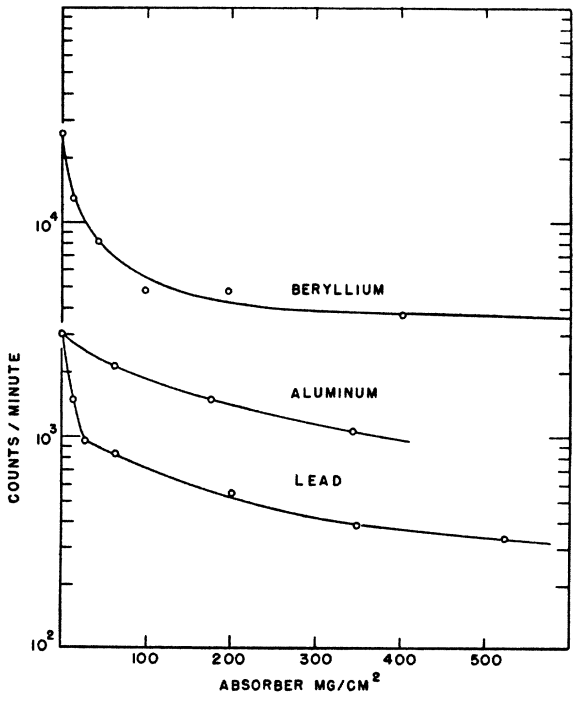

FIG. 4. Absorption of Np^{233} radiations measured with argon-filled Geiger tube. See Section 5 for placement of sample and absorbers. Data for aluminum and lead curves taken with 1.5 g/cm² beryllium next to tube window. All absorption data corrected to 90 min. after end of 30-min. bombardment of U^{233} with 15-Mev deuterons.

4. THE ISOTOPE Np^{232}

Some of the early decay curves, particularly those involving the decay of electromagnetic radiation, on the samples containing Np^{233} indicated that another period was present with half-life less than 35 min. This period was believed to be that of Np^{232}, since decay measurements on neptunium fractions from a number of bombardments in which Np^{232} was undoubtedly produced had virtually eliminated the possibility of a longer half-life for the isotope. Identification of these short-lived neptunium isotopes has been difficult since the chemical purification necessary prior to radiation measurements has required an hour or more. A better counting ratio of Np^{232} to Np^{233} was sought by shortening still further the chemical purification of the neptunium produced in another short bombardment of U^{233} in the 60-in. cyclotron. The first count of the neptunium fraction was taken 45 min. after bombardment. The decay of x-ray activity was followed with a xenon-filled Geiger tube using as alternate absorbers (a) 1.5 g/cm² of beryllium and (b) 1.5 g/cm² beryllium plus 155 mg/cm² of lead. Figure 8 gives the actual counting rates of this larger sample, although a smaller aliquot was used for the first three hours of counting. The short-lived decay can be resolved only on the basis of two activities and the half-life values, 35 min. (Np^{233}) and 13 min., give the best fit to the data.

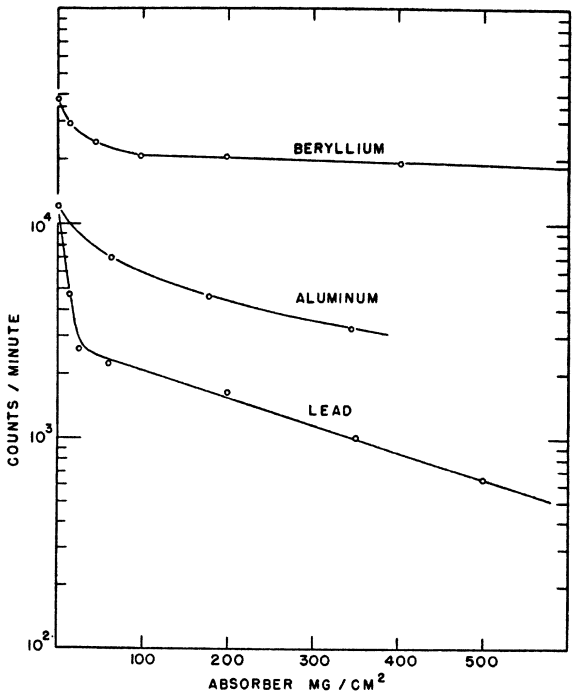

FIG. 5. Absorption of Np^{233} radiations measured with xenon-filled Geiger tube. Same conditions and amount of Np^{233} as for Fig. 4.

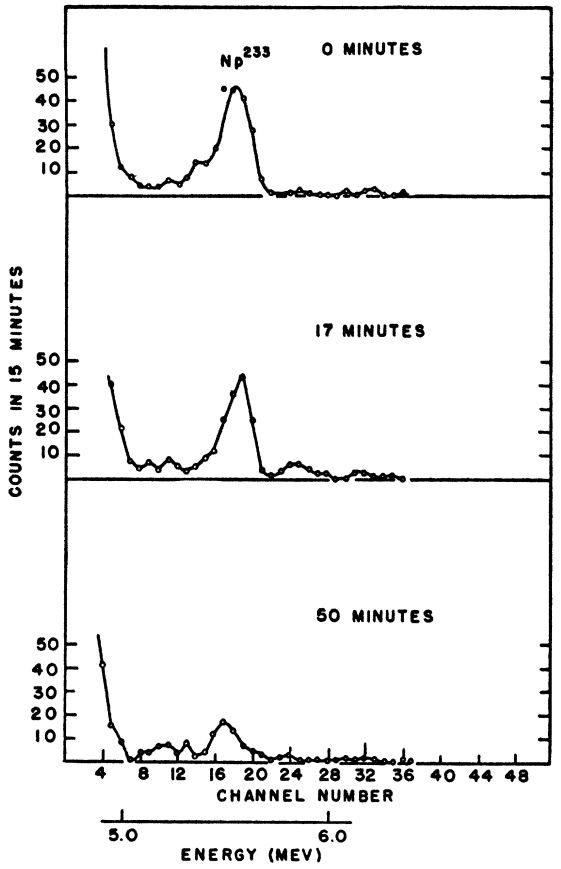

FIG. 6. Pulse analyses of alpha-particles from Np^{233} (5.53 Mev.). First measurement begun 64 min. after end of 30-min. bombardment of U^{233} with 15-Mev deuterons.

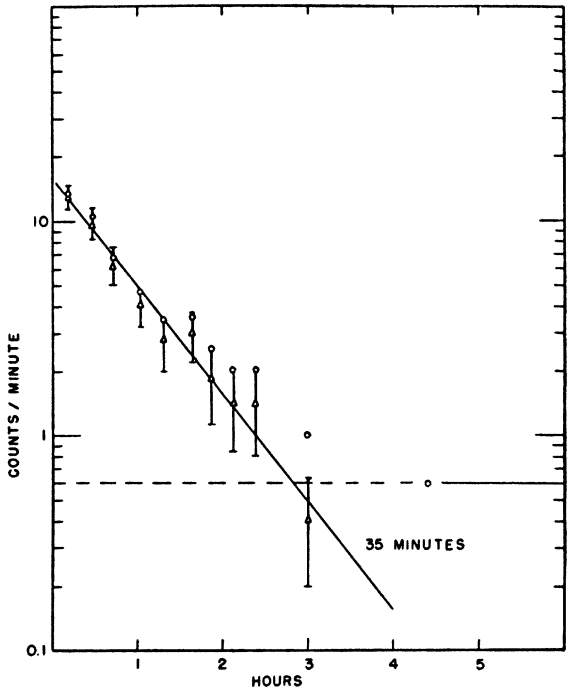

FIG. 7. Decay of Np^{233} alpha-activity. Sums of counting rates over channels 13–20 of a 48-channel pulse analyzer. Zero time is 60 min. after end of 30-min. bombardment of U^{233} with 15-Mev deuterons.

More extensive absorption measurements of the 13-min. radiations were not attempted. The close similarity to the Np^{233} x-rays in the absorption by beryllium and lead, however, leaves little doubt that the 13-min. radiations include x-rays. Measurements of the counting rates of the samples with no absorber using a thin window Geiger counter tube demonstrated the impossibility that the 13-min. electromagnetic radiation could be coming from a beta-emitting impurity since there were approximately ten to twenty times as many x-ray quanta of 13–20-kev energy as electrons.

The decay of hard electromagnetic radiation was followed with another xenon-filled tube using alternate absorbers, 1 g/cm² and 11 g/cm² of lead. Much of the hard gamma-radiation was associated with the 13-min. activity although an unequivocal resolution of the data was not possible.

A preliminary assignment of the 13-min. x-ray activity may be made to the electron-capture decay of Np^{232}. Further confirmatory experiments should produce detectable yields of U^{232} as daughter of the Np^{232}.

No alpha-particle radioactivity was observed in agreement with the systematics[15] which would predict that the degree of alpha-branching should be smaller than could be detected in experiments of the present sensitivity.

5. EXPERIMENTAL

The chemical properties of neptunium are not discussed here. The information available at the time of this research may be found in the National Nuclear Energy Series, Plutonium Project Record Vol. 14B and in the references given in the Introduction. The essential need in this research was for a process for the separation and purification of neptunium which would be much more rapid than any devised hitherto, since the objective was the identification of isotopes believed to be short-lived. This need was fulfilled largely by modification of the mechanics of previously known chemical separation processes. The most rapid isolations from the target required only 45 min., but some sacrifice in purity resulted. The methods described here required, on the average, from an hour to an hour and a half.

A. Targets

The targets in every case were uranium. A known amount of Np^{237} tracer was added to the target solvent for later measurement of aliquots and chemical yield. The Np^{231} was first found in 184-in. cyclotron bombardments of one-gram amounts of natural uranium metal. The best solvent found for quick dissolution of uranium metal targets was hot 10*M* hydrochloric acid

containing a trace of Fe(III). The resulting U(IV) solution was oxidized to U(VI) with an excess of liquid bromine.

The targets for the bombardments of U^{235} in the 184-in. cyclotron were 100-mg amounts of U_3O_8 sealed in thin-walled Pyrex tubes. After bombardment the tube was dropped into a centrifuge tube containing solvent and crushed with a glass rod. Hot 8*M* nitric acid with a trace of Fe(III) was a rapid solvent for the uranium oxide. The 45-Mev bombardments of U^{238} and U^{233} also employed oxides held in Pyrex tubes. The bombardments of U^{233} in the 60-in. cyclotron were made using milligram amounts of UO_3 prepared by drying uranyl nitrate solution in platinum interceptor boats or troughs.

The bombardment energy in the 184-in. cyclotron was varied by adjusting the distance of the target probe from the center of the cyclotron.

B. Neptunium Separations

Neptunium was isolated from all other radioactive species by combinations of co-precipitation and solvent extraction techniques. The procedures may be outlined as follows.

1. Lanthanum Fluoride

A few mg of MnO_2 is precipitated from the 1*N* HNO_3 solution of uranyl nitrate by adding a solution of $KMnO_4$ followed by enough $NaNO_2$ solution to reduce all the permanganate. The $KMnO_4$ ensures that all the uranium is U(VI) and the MnO_2 is an effective decontaminant, particularly for protactinium, usually present in large yield. The MnO_2 precipitate is discarded. The nitrite reduces Np(VI) to Np(V). A milligram or less of La(III) is added followed by the addition of HF to precipitate LaF_3 which carries the neptunium. The uranium remains in the supernatant solution. The LaF_3

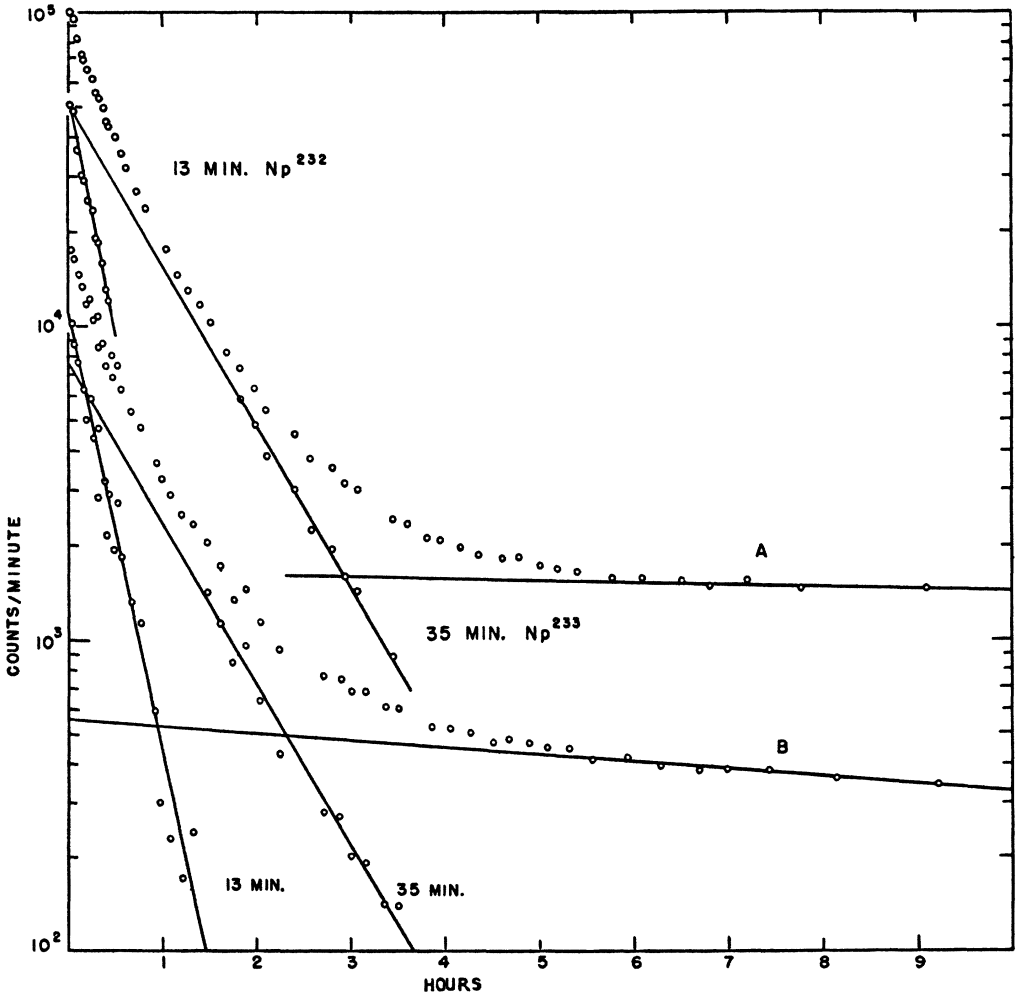

FIG. 8. Decay of electromagnetic radiations in neptunium fraction from 15-min. bombardment of U^{233} with *ca.* 17-Mev deuterons. Zero time is 45 min. after end of bombardment. Curve A with 1.5 g/cm² beryllium absorber between sample and counting tube window. Curve B with 1.5 g/cm² beryllium absorber plus 155 mg/cm² lead absorber over sample.

precipitate is metathesized to $La(OH)_3$ by heating and stirring with concentrated KOH solution. The $La(OH)_3$ is dissolved in HNO_3 and the solution is diluted with H_2SO_4 to give a solution of approximate composition: $1M$ H_2SO_4, $1M$ HNO_3. The solution is made about $0.1M$ in $NaBrO_3$, heated, and LaF_3 is precipitated and separated following the addition of HF to a concentration of about $0.1M$. The supernatant containing Np(VI) is then diluted a factor of five by the addition of excess SO_2 solution so that all bromate is reduced to bromide. More La(III) is added and precipitated as LaF_3, which carries the neptunium as Np(IV), from a solution which has been made 1–$3M$ in HF.

2. Ether Extraction

The LaF_3 is dissolved with hot, saturated $Al(NO_3)_3$ as the result of the formation of a soluble complex ion containing aluminum and fluoride, the solution is diluted and made $1M$ in HNO_3 and $0.1M$ in $NaBrO_3$, and heated 2–3 min. to oxidize the neptunium. Solid NH_4NO_3 is added to make its concentration $10M$ in the solution and the neptunium is extracted from the solution with twice its volume of diethyl ether. (The ether used for this extraction must be free from reducing impurities, e.g., alcohols and aldehydes. Effective purification is attained by shaking it with $K_2Cr_2O_7-1M$ H_2SO_4 solution followed by distilled water washes.) The ether extract of neptunium is washed once with $10M$ NH_4NO_3 solution, and may then be poured or pipetted onto platinum counting plates. The combined lanthanum fluoride plus ether extraction procedures could be carried out within a time of one hour, and yielded neptunium fractions pure with respect to alpha-activity. These fractions were usually also sufficiently pure for the measurements with Geiger counters. As confirmation of the purity, it was customary to put the neptunium through another extraction into an organic solvent involving the formation of a chelate complex with thenoyl trifluoroacetone, described as follows.

3. Thenoyl Trifluoroacetone (TTA)

The neptunium is extracted from its ether solution into water containing a little $NaNO_2$ and La(III). Lanthanum hydroxide is precipitated carrying the neptunium and separating it from nitrate. The $La(OH)_3$ is dissolved in $5M$ HCl, $0.1M$ KI, and $0.05M$ $N_2H_4\cdot 2HCl$ solution, followed by heating 1–2 min. at 90°C. The solution is diluted to $0.5M$ HCl and heated for a minute again to reduce free iodine. This reduction treatment produces Np(IV) which is then extracted into a benzene solution of thenoyl trifluoroacetone. In this procedure the $0.5M$ HCl solution of Np(IV) is agitated 20–30 min. with a $0.3M$ solution of TTA in benzene. The benzene solution is placed on a platinum counting plate and evaporated by heating the plate with an induction coil. The neptunium chelate compound is volatile and a large percentage is lost if the benzene solution is simply dried and heated strongly. It was found that a small amount of trichloroacetic acid placed on the plate before adding the benzene solution effectively prevented volatilization of the neptunium during drying and ignition. When the TTA extraction procedure is employed, an additional 45-min. time is required.

4. Zirconium Phosphate

Zirconium phosphate may be used as a carrier for Np(IV) in an oxidation cycle procedure analogous in principle to the lanthanum fluoride method. The uranium target solvent was $6M$ HNO_3, $10^{-3}M$ Ce(IV), $0.02M$ Zr(IV) with added Np^{237} tracer. The target solution is adjusted to $3M$ in HNO_3 and is made $0.02M$ in $NaBrO_3$. The solution is heated one minute to oxidize neptunium to Np(VI). The solution is made $0.5M$ in H_3PO_4 and is heated a minute to coagulate the zirconium phosphate precipitate which does not carry the Np(VI). The supernatant solution containing Np(VI) is reduced with excess $N_2H_4\cdot H_2SO_4$ to destroy bromate and is then made $0.01M$ in $N_2H_4\cdot H_2SO_4$ and $0.005M$ in Fe(II) to reduce neptunium to Np(IV). This reduction is very rapid. About 1 mg of Zr(IV) per ml of solution is added and the solution is heated and stirred. Zirconium phosphate precipitates carrying Np(IV) and the precipitate is washed with $3M$ $HNO_3-0.5M$ H_3PO_4 solution. Uranium remains in the supernatant solution. About 0.1 mg La(III) as a nitrate solution is slurred with the zirconium phosphate (about 1 mg) and the zirconium is dissolved by forming a complex ion with fluoride by the addition of a $1M$ HF, $1M$ HNO_3 solution. A precipitate of LaF_3 remains, bearing the neptunium.

5. Resin Column

A column containing the ion exchange resin, Dowex-50, has been used for the separation of trace amounts of neptunium from uranium. Neptunium as Np(V) is adsorbed[18] on a small amount of resin from a solution of low acid concentration and placed at the top of a column packed with resin and containing $13M$ HCl. The neptunium is eluted rapidly by passing $13M$ HCl through the column. The samples for counting are prepared by placing the elutriant dropwise directly on platinum counting plates.

The absorption and alpha-particle data given for Np^{233} were obtained from neptunium samples purified by the zirconium phosphate, ether extraction, and resin column procedures in that order. The data for Np^{232} were obtained by counting aliquots of the LaF_3 precipitate after employing the zirconium phosphate procedure.

C. Radioactive Measurements

Samples for radioactive assay were mounted on platinum plates of 2-mil thickness. A uniform geomet-

[18] James, Orth, and Street (unpublished work).

rical arrangement was used for all Geiger counter activity measurements. Since the principal objective of this work was measurement of electromagnetic radiations, no large general lead housing was used around the Geiger tube and sample. As a shield against general background radiation, a small lead shield was placed directly around the brass, bell-type Geiger tube. This arrangement was used to minimize spurious counting rates caused by the scattering of primary and secondary radiations around the absorbers. The sample plate was supported on a flat aluminum holder in a Lucite stand below the mica window of the counter tube. The distance from sample to counter window was 2.1 cm for all measurements. The mica windows for all the tubes used were near 3 mg/cm^2 in thickness. The Geiger tubes were filled to 10 cm mercury pressure of argon or xenon with 1 cm pressure of ethanol.

A value of 8.5 percent for the fraction of the radiation which entered the counter from the sample at the 2.1-cm distance was determined by counting the β^--particles from Pa^{234} (UX_2) in equilibrium with a known weight of U^{238} (as UO_2) mounted between cellophane sheets in the same position. The Th^{234} (UX_1) β^--particles were eliminated by a thin aluminum absorber (30 mg/cm^2).

Beryllium absorbers were used to determine the relative amounts of electron and electromagnetic radiation. The absorbers were placed in the top shelf of the Lucite stand, giving a distance of 0.4 cm between the top surface of the absorber and the counter window. The absorptions of the electromagnetic radiations in aluminum and lead were measured with the aluminum or lead absorbers resting over the sample plate holder and with a large beryllium absorber in the top shelf.

Alpha-particle activity was assayed in "50 percent geometry" argon-filled ionization chambers. The determination of alpha-particle energies and analysis of mixtures of alpha-emitting isotopes were made in a 48-channel ionization pulse analyzer[16] in which the energy range covered by the 48 channels could be varied.

6. CROSS SECTIONS

In the course of the search for radiations from light neptunium isotopes, measurements of the intensities of the radiations from previously known isotopes were also obtained. From these measurements and the times and intensities of bombardment, it is possible to calculate the atom yields and cross sections for formation. However, only in the 60-in. cyclotron bombardments of U^{233} was the absolute beam intensity known to any accuracy.

TABLE I. U^{233} cross sections (unit 10^{-24} cm^2).

	Deuteron energy (Mev) 15	50
Np^{234}	$1(10^{-2})$	$2(10^{-2})$
Np^{233}	$8(10^{-3})$	$8(10^{-3})$
Np^{232}	$2(10^{-2})$	—
Np^{231}	0	$<2(10^{-3})$

Nevertheless, very rough values for the cross sections have been calculated for the 184-in. cyclotron bombardments under the assumption of a deuteron beam of about 2 μa/cm^2. In view of the uncertainty in the beam intensities, the values determined for a given cross section in two different bombardments cannot be expected to agree better than within a factor of about three. The relative cross sections determined for the various isotopes produced in any given bombardment, however, should be nearly as accurate as the decay schemes, half-lives, and counting efficiencies are known. Aside from the uncertainty introduced by these factors, the reliability of the determinations depends on the accuracy of counting and decay resolution.

The atom yields of Np^{236} were calculated from the measured alpha-activity of the daughter, Pu^{236}, and the yields of Np^{238} from the observed Np^{238} β^--particle activity. Gross assumptions are required for the calculation of the atom yields of the electron-capturing isotopes. The number of L x-rays associated with each isotope was measured approximately; and the atom yields were calculated with the assumptions that one L x-ray is emitted per disintegration, that the counting efficiency in the argon tube is one percent, and that the Auger coefficient for the L x-rays is 0.5. Upper limits for the cross sections for the formation of Np^{231} were calculated on the basis that the ratio electron-capture/alpha-emission is 100. No 50-min. x-ray activity corresponding to the electron-capture decay of Np^{231} could be resolved from decay curves, and an upper limit of 100 for the electron-capture/alpha-emission ratio was derived from the observed x-ray activity of Np^{233} samples containing known amounts of Np^{231} alpha-activity and an estimated limit of detection for the Np^{231} x-radiations. Tables I–III list the very approximate cross sections in units of 10^{-24} cm^2. Blanks in the tables signify that insufficient data for the calculation were obtained in the experiments.

These cross sections are to be regarded as a by-

TABLE II. U^{235} cross sections (unit 10^{-24} cm^2).

	Deuteron energy (Mev) 45	70	100
Np^{236}	$2(10^{-3})$	$2(10^{-3})$	$2(10^{-3})$
Np^{235}	$2(10^{-2})$	$2(10^{-2})$	$8(10^{-3})$
Np^{234}	$1(10^{-2})$	$8(10^{-3})$	$8(10^{-3})$
Np^{233}	$4(10^{-3})$	—	—
Np^{231}	$<4(10^{-4})$	$<6(10^{-4})$	$<6(10^{-4})$

TABLE III. U^{238} cross sections (unit 10^{-24} cm^2).

	Deuteron energy (Mev) 45	120
Np^{238}	$6(10^{-3})$	—
Np^{236}	$3(10^{-3})$	$6(10^{-3})$
Np^{235}	$8(10^{-3})$	$2(10^{-2})$
Np^{234}	$8(10^{-3})$	—
Np^{233}	$<4(10^{-4})$	—
Np^{231}	0	$<4(10^{-5})$

product of the present investigation and are useful chiefly for the practical purposes of indicating the intensity of radioactivity which may be produced for each of the isotopes under the conditions outlined in this paper. The nature of such targets, namely small amounts of powdered material, and the conditions of the bombardments were not such as to lead to sufficiently accurate cross sections to enable safe deductions to be made in regard to the mechanism of these relatively high energy nuclear reactions involving heavy nuclei.

However, it can be seen that the cross sections for the (d, n), $(d, 2n)$, $(d, 3n)$, $(d, 4n)$, etc., reactions on uranium in this energy range are substantially smaller than for the same reactions on non-fissioning nuclei. Apparently, a predominant fraction of the excited intermediate nuclei undergo the fission reaction. Consideration of the results suggest that the total cross section for the formation of neptunium isotopes by (d, xn) reactions does not change greatly over the energy range investigated, which suggests that increased excitation does not markedly increase fission and competing reaction yields at the expense of (d, xn) reaction yields.

It may be noticed that the reactions involving the emission of only a small number of neutrons, such as the (d, n) and $(d, 2n)$ reactions, do not drop off very much in yield even at relatively high deuteron energies. This indicates that reactions involving only small energy transfers[19] from the high energy bombarding particles are important here as has been found also to be the case for reactions with lighter nuclei. It may also be noticed that the lightest isotope, Np^{231}, is not formed in yields as high as the other isotopes at any deuteron energy, which perhaps indicates an increasing relative yield of the fission reaction with decreasing mass of the intermediate excited neptunium nuclei, as might be expected from the simple Bohr-Wheeler picture of the fission process.

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[19] R. Serber, Phys. Rev. **72**, 1114 (1947).

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Nuclear Mass Determinations from Nuclear Q-Values

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Consistent values of the masses of the light nuclei have been calculated from the best measurements of Q-values for several nuclear reactions, and from mass spectrographic measurements. Tables are given of the Q-values and of the calculated mass values.

1. INTRODUCTION

THE Q-values for several reactions involving light nuclei have been recently measured with probable errors of 20 kev or less. In general these measurements have been made possible through the employment of high resolution electrostatic or magnetic analyzers for determining the energy of the particles involved in the reaction. These new data are sufficient to determine the nuclear masses relative to H^1 through B^{10}, independently of mass spectroscopic data. Unfortunately sufficient data are not yet available to base the masses upon O^{16} and consequently the mass spectroscopic value for H^1 is used. Furthermore some uncertainty still exists in the mass of He^4 and subsequent nuclei as discussed below.

The mass values of H^1, D^2, C^{12} and N^{14} were calculated from the mass spectroscopic doublets $2H-D$, CH^4-O, CH^2-N^{14}, and $3D-C_{\frac{1}{2}}$. In view of the discrepancies recently found in the early values of $2H-D$, it was decided to use Nier's[1] recent values for the first three doublets combined with the results of Bainbridge[2] for the last doublet.* Nier's value for $2H-D$ combined with Bell and Elliott's[3] new value for $H^1(n, \gamma)D$ leads to an $n-H^1$ difference of 788 kev compared to 782 ± 1 kev as determined at Los Alamos from threshold measurements on $T^3(p, n)He^3$ combined with the decay energy of tritium. The nuclear data have been combined with the mass spectroscopic values of C^{12} and N^{14} to yield the masses of N^{13}, C^{13}, and C^{14}.

Table I lists all the accurately determined Q-values considered in this note. The $Li^7(p, \alpha)He^4$ value is not new but was included in order to determine the mass of the α-particle and hence it influences all subsequent

[1] T. R. Roberts and A. O. C. Nier, Phys. Rev. **77**, 746(A) (1950).
[2] K. T. Bainbridge, NRC Nuclear Science Series No. 1.
* It is emphasized that a future change in the mass spectroscopic value of H^1 will change the masses for D^2 to B^{10} inclusive by the same amount.
[3] R. E. Bell and R. G. Elliott (private communication).