S 74. *The Yields by Fast and Slow Neutrons in a Szilard–Chalmers Reaction.*

By Engelbert Broda and Werner Rieder.

Szilard–Chalmers reactions are known in which the yields are not quantitative even when the neutron-capturing molecules are present in dilute solution. This effect may be attributed (1) to an insufficiency of the available excitation energy to bring the chemical reaction to completion in all cases, or (2) to the ability of the unstable primary product to undergo reactions which re-form the original (target) molecule. If the primary product undergoes these reactions after all the kinetic energy derived from the nuclear reaction has been expended, the yield is not expected to depend on the energy of the nuclear process.

In order to decide whether the yield, in at least one case, does in fact depend on the energy of the nuclear reaction, a Szilard–Chalmers reaction of permanganate ion was carried out with fast (radium-beryllium) and with slow neutrons. In the fast-neutron experiments the crystals were protected against stray slow neutrons by boron and cadmium shields, and the absolute activity produced was consistent with the capture cross-section of manganese for fast neutrons ($1{\cdot}5 \times 10^{-27}$ barns at 1 Mev.; Hughes, private communication). After irradiation the crystals were dissolved in water at pH 4 (moderate changes of pH did not affect the result) and the Mn^*O_2 was separated from the solution by filtration through sintered or paper filters. Various checks excluded exchange of quadri- with hepta-valent manganese and the possibility of the finely divided manganese dioxide running through the filters.

The part of the recoil energy available for chemical reactions after capture of slow neutrons is about 150 ev. provided that all γ-energy in the case of manganese is emitted as one single ray as found by Fleischmann (*Ergeb. exakt. Naturwiss.*, 1936). With neutrons of about 1 Mev., this energy would be of the order of 10,000 ev. (Broda, *J. Chim. physique*, 1949, **45**, 196). Nevertheless, the yields (80% of the activity present as Mn^*O_2) were not found to be significantly different in the two cases. This result shows that the final valency of the Mn* is not determined by the energy available for the primary reaction, and supports Libby's idea (*J. Amer. Chem. Soc.*, 1940, **62**, 1930) that the Mn* is obtained in the heptavalent state from the "explosion." To explain its reactivity one has to assume that it is present as $Mn^*O_3^+$ rather than $Mn^*O_4^-$. This cation may, after being slowed down, either oxidise water (with reduction to Mn^*O_2) or else re-form $Mn^*O_4^-$ by

$$Mn^*O_3^+ + OH^- = Mn^*O_4^- + H^+ \quad \text{or} \quad Mn^*O_3^+ + H_2O = Mn^*O_4 + 2H^+$$

or

$$Mn^*O_3^+ + MnO_4^- = Mn^*O_4^- + MnO_3^+$$

This mechanism, then, involves dissociative removal of an oxygen ion rather than an oxygen atom in the primary reaction.

Some experiments were also performed with solutions of calcium and potassium permanganate with quite similar results, but owing to the inevitable presence of some slow neutrons in these cases interpretation is not conclusive.

The University, Vienna. [*Read, March 30th*, 1949.]

S 75. *The Production by the Cyclotron of Some Useful Radio-nuclides.**

By John W. Irvine, Jun.

The production of sodium, manganese, iron, and zinc radio-nuclides by use of 10—20-Mev. deuterons produced in a cyclotron is described.

Although the nuclear chain reactor now bears the brunt of producing radio-nuclides for research in chemistry and the other sciences, the cyclotron by its versatility is still essential to the production of some useful radio-nuclides. With certain elements the (n, γ) reaction yields only isotopes with relatively short half-lives (^{24}Na, ^{56}Mn). With other elements the

* The work was assisted by the joint programme of the Office of Naval Research and the Atomic Energy Commission.

specific activity of the product is too low for many experiments (^{65}Zn). Occasionally mixed isotopes are produced when a radio-isotopically pure activity is desired (^{55}Fe, ^{59}Fe). Fission products in the middle of the Periodic Table and (n, p) or (n, α) products from elements with atomic number less than 20 strongly supplement that group of elements produced by the (n, γ) reaction, but the nuclear chain reactor furnishes few radio-nuclides which decay by positron emission or by orbital-electron capture. A cyclotron operating with deuterons in the energy region of 10—20 Mev. can complete a radio-nuclide production programme by making available nuclides not adequately prepared by the nuclear chain reactor.

Because they yield carrier-free products, deuteron reactions involving a change in atomic number are usually most important. Thus the reactions (d, n), $(d, 2n)$, and (d, α) yield a large number of radioactive products which can be separated from the target without adding a carrier. Multiple particle reactions such as $(d, p\alpha)$ and $(d, \alpha 2n)$ become important above about 15 Mev. and extend into the super-voltage range, becoming more complex as the energy increases. At present such reactions are not used extensively for production purposes. In addition to the deuteron reactions, fast neutrons generated by ^{9}Be $(d, n)^{10}$B are very useful for inducing reactions such as (n, p) and (n, α) in the elements of higher atomic number.

The reactions (d, p) and (d, H^3) yield radioactive products identical with those made by (n, γ) or $(n, 2n)$. In some cases, particularly when the half-life is short, the specific activity of (d, p)-produced nuclides is higher than the (n, γ) analogue from the nuclear reactor. In a 100-microamp. deuteron beam on a normal probe target the deuteron flux is approximately 10^{15} deuterons/cm.^{2}-sec. and (d, p) cross-sections are of the order of magnitude of 10^{-24} cm.^{2}. Of course, the deuteron beam has a very small cross-sectional area and small targets must be used.

When possible, targets should be bombarded in the outside beam of the cyclotron. When this is done the power density is reduced to a point where the cooling of the target is not difficult and volatilisation of target and product is minimised. In some cases probe bombardments are necessary. These require the use of highly refractory targets since the power density can readily be as high as 1—5 kw./cm.^{2} and the target is in a high vacuum. The yield per microamp.-hour of radio-iodine from telluride targets or of radio-sodium from magnesium targets can be increased 10—20-fold by going from probe targets to outside targets.

Production of Radio-nuclides.—(I) ^{22}Na *and* ^{24}Na. As produced by the (n, γ) or (d, p) reactions, radio-sodium is available only as ^{24}Na ($T_{1/2}$ = 14·8 hours) with a specific activity of about 5 rd/mg. (U.S.A.E.C.; "Radioisotopes Catalogue and Price List," Sept. 1947) [rd ≡ rutherford = $10^6 d/s$ (Condon and Curtiss, *Physical Rev.*, 1946, **69**, 672)]. If a carrier-free material is desired it can be obtained by bombarding magnesium or aluminium with deuterons. With 14-Mev. deuterons a yield of 8·7 rd/μah is obtained from magnesium and 1·7 rd/μah from aluminium (Clarke and Irvine, *ibid.*, 1946, **70**, 893). This last reaction gives carrier-free radio-isotopically pure ^{24}Na.

The magnesium targets also yield ^{22}Na ($T_{1/2}$ = 3·0 years). The (d, α) reaction by which the ^{22}Na is produced has a cross-section comparable to that for ^{24}Na production, but because of the longer half-life the thick target yield is only 65 mrd/μah. By ageing magnesium targets for two weeks, the ^{24}Na activity is decreased by a factor of about 10^6 and essentially pure ^{22}Na remains.

The radio-sodium can be separated from magnesium and aluminium by precipitation as sodium zinc uranyl acetate. The small amount of ^{23}Na present (~0·01%) serves as a carrier (Irvine and Clarke, *J. Chem. Physics*, 1948, **16**, 686).

(II) ^{52}Mn *and* ^{54}Mn. Neutrons on manganese produce ^{56}Mn ($T_{1/2}$ = 2·59 hours) which is too short-lived for many experiments. Longer-lived carrier-free manganese preparations can be made by bombarding iron or chromium targets with deuterons. The first target gives ^{54}Mn ($T_{1/2}$ = 310 days) by (d, α) with a yield of 37 mrd/μah at 14 Mev. (Hevesy, "Radioactive Indicators," p. 40, Interscience Publishers, N.Y., 1948). Although ^{52}Mn ($T_{1/2}$ = 6·5 days) and ^{56}Mn are also present, they soon decay away.

To make ^{52}Mn, chromium is bombarded. The $(d, 2n)$ reaction has a yield of 3 rd/μah at 14 Mev. (Clarke and Irvine, *loc. cit.*). ^{54}Mn is also made, but its yield is smaller by a power of about 10^3 and so does not interfere with the use of the ^{52}Mn for several weeks.

(III) ^{55}Fe *and* ^{59}Fe. When two radio-isotopes of the same element have radiation characteristics that allow them to be measured one in the presence of the other, and when these isotopes can be obtained radio-isotopically pure, a new field of tracer application is open for them. Double-tracing experiments utilising the two isotopes of iron have been performed in the study of the problem of preserving whole blood for transfusion purposes (Peacock *et al.*,

J. Clin. Invest., 1946, **25**, 605). The double-tracing technique permits an experimental subject to act as its own control, thus eliminating this source of uncertainty in these biological experiments.

Neutrons on iron yield both ^{59}Fe (44 days) and ^{55}Fe (4 years). In addition to the disadvantage of low specific activity, this isotopic mixture cannot be resolved by any practicable means. These two iron isotopes can be obtained with very high specific activity and isotopically pure from two separate targets. ^{55}Fe is prepared by $(d, 2n)$ reaction on ^{55}Mn. Since this is the only isotope of manganese, and ^{56}Fe is stable, no other active isotope of iron is made. Manganese metal is a poor target material for probe targets, but an alloy containing Mn 90%, Cu 8%, and Si 2% has been fairly satisfactory. A yield of 25 mrd/μah is obtained with 14-Mev. deuterons (Peacock, *et al.*, *loc. cit.*).

Fast neutrons on cobalt give carrier-free ^{59}Fe by the (n, p) reaction. Metallic cobalt can be fastened directly behind a beryllium probe target for the maximum fast-neutron flux. The yield of ^{59}Fe under these conditions is 80 μrd/g. of Co/μah of 14-Mev. deuterons on beryllium (Peacock, *et al.*, *loc. cit.*). The simultaneous formation of ^{60}Co by (n, γ) can be minimised by covering the cobalt target with cadmium.

This (n, p) reaction can be effected by the fast neutrons in a nuclear chain reactor. The cross-section is small (5×10^{-29} calculated on the basis of a slow-neutron flux of $nv = 10^{12}$) and the large amount of ^{60}Co formed by (n, γ) complicates the separation procedure. Cadmium shielding of the irradiation sample reduces the ^{60}Co activity by a factor of 15, but the activity ratio of ^{60}Co/^{59}Fe is still 10^3. The cyclotron irradiations give an activity ratio of about 10 (Irvine, " Science and Engineering of Nuclear Power," p. 230, Addison-Wesley, Cambridge, 1949).

(IV) ^{65}Zn. This isotope is readily available from nuclear reactor bombardments. However, the specific activity is quite low (90 mrd/mg.) (U.S.A.E.C., *loc. cit.*). In biological systems zinc is usually present in trace amounts, and high specific-activity material is essential. By bombarding copper with deuterons carrier-free zinc can be made readily. The yield is 120 mrd/μah with 14-Mev. deuterons. Unless the copper is specially purified before bombardment a small amount of inactive zinc ($\sim$0·01%) will usually be present. For many purposes this is not an important dilution. Dithizone extraction into chloroform is a good method of purifying the zinc preparation after the bulk of the copper has been removed by electrolysis. An abundant supply of ^{65}Zn can usually be recovered from parts of the internal structure of the cyclotron when such parts have been removed for repair or replacement.

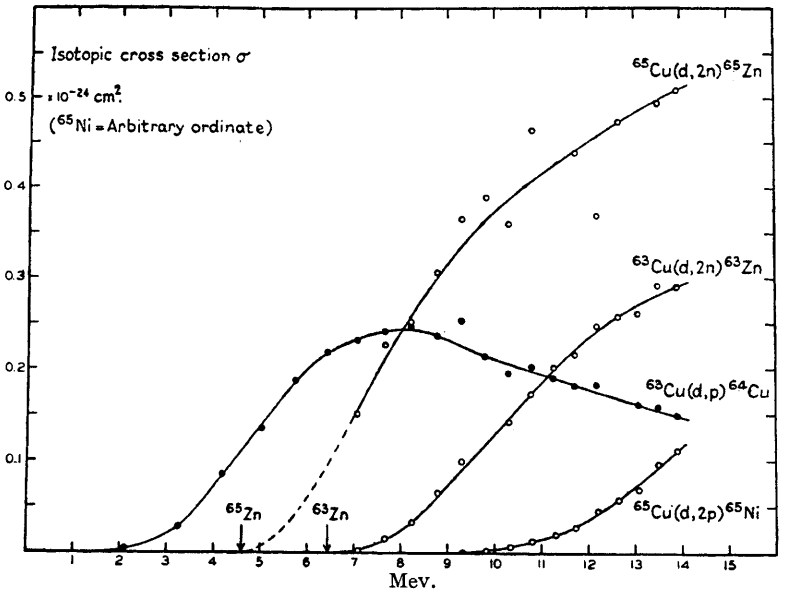
Yield Determinations from Excitation Curves.—The most practicable method of determining the yield of any radio-nuclide is to carry out a short bombardment under normal operating conditions and measure the activity obtained after careful radio-chemical purification. However, data thus obtained cannot be used for calculating yields at any other deuteron energy and they give no indication of the bombardment efficiency.

A better method of obtaining yield data is to determine the deuteron excitation function for the particular reaction of interest. The best method of determining such functions is the stacked-foil technique (Clarke and Irvine, *Physical Rev.*, 1944, **66**, 231). Here the deuteron beam is totally absorbed in a stack of target foils and the activity induced in each foil is measured. From the energy of the deuteron beam and the range–energy relationship for deuterons in the target material the energy decrement in each foil can be calculated. A careful measurement of the total number of deuterons striking the foils permits the calculation of a cross-section value for the reaction over the energy interval corresponding to each foil. The results of such a determination from deuterons on copper are given in Fig. 1. By graphical integration of the area under each cross-section curve, thick-target yields as a function of deuteron energy are obtained. These are given in Fig. 2.*

In addition to yield data and a more detailed knowledge of nuclear energetics obtained from excitation-function determinations, new nuclear reactions can be characterised. The reaction ^{27}Al$(d, p\alpha)^{24}$Na mentioned in connection with ^{24}Na production was discovered by analysing an excitation curve (Clarke, *ibid.*, 1947, **71**, 187). Fig. 1 shows the curve for the reaction ^{65}Cu$(d, 2p)^{65}$Ni. When first observed, the nickel activity was thought to be ^{63}Ni from (d, α) on ^{65}Cu (Clarke and Irvine, *ibid.*, 1946, **69**, 680A). When the isotopic assignment of the 2·6-hour nickel activity was changed to ^{65}Ni on the basis of the (n, p) reaction on separated copper isotopes and the (n, γ) reaction on separated nickel isotopes (Conn, *et al.*, *ibid.*, 1946, **70**, 768), it was recognised that a $(d, 2p)$ reaction must be responsible for the ^{65}Ni formed in

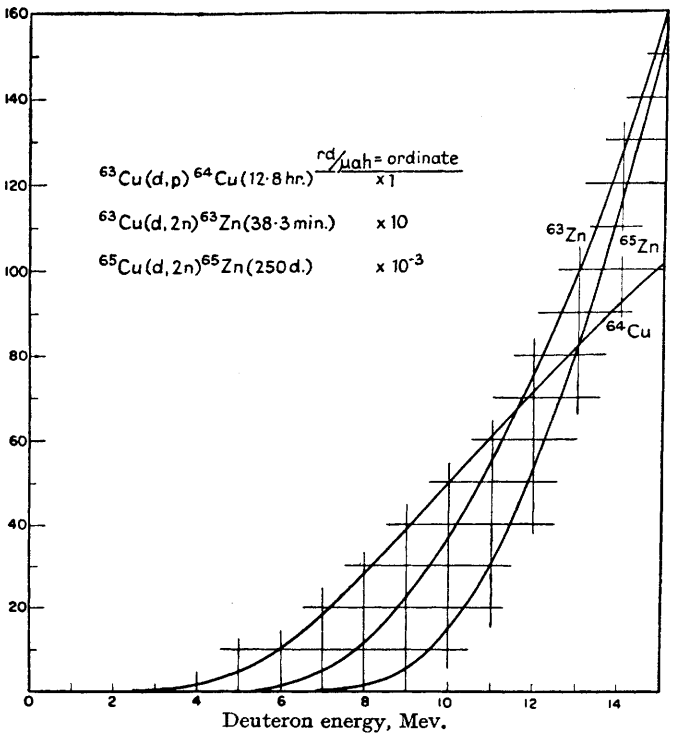
* The determination of these excitation curves and thick-target yields was carried out in collaboration with Dr. E. T. Clarke, Department of Physics, Massachusetts Institute of Technology.

FIG. 1.



Excitation curves for deuterons on copper.

FIG. 2.



Thick-target yields from deuterons on copper.

copper. Enough is known about the characteristics of (d, p) reactions to rule out the possibility of a trace of nickel impurity being responsible for this curve. Although the excitation curve for ^{64}Ni $(d, p)^{65}$Ni has not been determined, the threshold observed in Fig. 1 is much higher than would be expected for this reaction.

In order to obtain these excitation curves, rapid chemical separations were made on 24 copper foils. To save time at every step all equipment was set up in multiples of 24. Each foil was dissolved rapidly in a sulphuric acid–hydrogen peroxide solution containing 2 mg. each of zinc and nickel. The copper was precipitated by adding ammonium hypophosphite. The nickel was precipitated from the filtrate with dimethylglyoxime and ammonia, and finally the zinc was precipitated as the anthranilate. The activity in each sample was determined by measurement with calibrated counters, and the excitation function calculated. The poor data on ^{65}Zn are due to very low activities in the samples.

It should be apparent that deuteron excitation functions can play a very important role in a programme for the production of radio-nuclides by the cyclotron, and that radio-nuclides thus produced are needed in much radio-chemical research.

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