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*CAMBRIDGE MONOGRAPHS ON PHYSICS*

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ADVANCES IN RADIOCHEMISTRY



ADVANCES  
IN  
RADIOCHEMISTRY

*and in the  
Methods of Producing Radioelements  
by Neutron Irradiation*

BY

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## GENERAL PREFACE

The Cambridge Physical Tracts, out of which this series of Monographs has developed, were planned and originally published in a period when book production was a fairly rapid process. Unfortunately, that is no longer so, and to meet the new situation a change of title and a slight change of emphasis have been decided on. The major aim of the series will still be the presentation of the results of recent research, but individual volumes will be somewhat more substantial, and more comprehensive in scope, than were the volumes of the older series. This will be true, in many cases, of new editions of the Tracts, as these are republished in the expanded series, and it will be true in most cases of the Monographs which have been written since the War or are still to be written.

The aim will be that the series as a whole shall remain representative of the entire field of pure physics, but it will occasion no surprise if, during the next few years, the subject of nuclear physics claims a large share of attention. Only in this way can justice be done to the enormous advances in this field of research over the War years.

N. F.  
D. S.





TO  
PAUL



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## AUTHOR'S PREFACE

This book was planned in the summer of 1946 when the writer was working in the Department of Natural Philosophy of the University of Edinburgh as Wilkie Scholar. The selection of the subject matter is largely based on the practical experience gained when he was radiochemist to the Department of Atomic Energy (formerly Directorate of Tube Alloys) of the Ministry of Supply, in the Cavendish Laboratory, Cambridge, in the years 1941-1946. Thanks to the unfailing helpfulness and patience of the staff of the Cambridge University Press, it has been possible to bring the account roughly up to December, 1949.

The author's thanks are due to Professor N. Feather, F.R.S., and particularly to Dr N. Miller, Senior Lecturer in Radiochemistry in the University of Edinburgh, for most valuable advice whilst the book was being written. He is also grateful to Professor M. Haissinsky, who very kindly criticized one of the Chapters.

E. B.

*Vienna*

14 APRIL 1950



## CHAPTER I

### INTRODUCTION

This monograph deals primarily with advances since the appearance of the last comprehensive works on radiochemistry, namely, Paneth's *Radioelements as Indicators* (1928) and Hahn's *Applied Radiochemistry* (1936). Earlier work has been considered only where it has been of fundamental importance, but references to early literature have been given wherever practicable. Even in the treatment of recent research emphasis must lie on general results rather than on the properties of individual bodies.

The term 'radiochemistry' was introduced by Cameron (1910) and Soddy (1911) at a time when it was felt that the developing new branch deserved coherent treatment and a name of its own. Cameron held that 'the science of radioactivity has developed to such an extent as to make it justifiable and convenient to divide it', and stated: 'Here it is treated from a chemical standpoint: the physical side is introduced only so far as is necessary to explain the special experimental methods.' Soddy spoke of radiochemistry (or 'the chemistry of the radioelements', i.e. the elements emitting radiations) as being 'concerned largely with the nature of the products of these (radioactive) changes, their isolation and separate identification'. This definition was no doubt adequate in the first stage when the main task was to apply to the new materials the well-established processes of inorganic chemistry. This approach was reflected in the titles and generally in the plans of the earlier books on radiochemistry, Makower's *Radioactive Substances* (1908), Cameron's *Radiochemistry* (1910), Soddy's *Chemistry of the Radioelements* (1911, 1914), Henrich's *Chemie und chemische Technologie radioaktiver Stoffe* (1918), and Russell's *Introduction to the Chemistry of the Radioactive Substances* (1922).

However, it was pointed out by Paneth (1928), even before the discovery of artificial radioactivity, that the field of radiochemistry increasingly tends to be defined by the working method. Being chemically dissimilar, the radioelements cannot be treated jointly from a chemical standpoint in the same way as, for example, the



platinum metals. The common quality is rather that the enormous power of the radiations from the radioelements makes assay methods based on ionization absolutely predominant. Indeed, already Soddy had stated in his book: 'Just in proportion as the rapidity of the change is the greater and the quantities of material in consequence become inappreciable to the older methods of study, the newer methods become applicable... The more evanescent the material, the less can be worked with... A special branch of chemistry, which may be appropriately termed radiochemistry, has come into existence, the scope and methods of which are largely peculiar to itself.' Clearly as long as macroscopic quantities ('macro-quantities') of material are available, the ordinary chemical methods can still be applied. It was possible for a hundred years to study the chemistry of uranium and thorium without even being aware of their activity. But radiochemical detection of extraordinarily small—invisible and unweighable—amounts of matter is possible and often needed. Before the advent of radiochemistry little was known about the chemistry of what are now known as tracer quantities, and most of our present knowledge is based precisely on radiochemical results. Following Paneth, it may be useful to define radiochemistry as the chemistry of bodies, which are detected through their nuclear radiations. In our day, after we have succeeded in making active isotopes of all elements, Paneth's considerations have even more force. We may now add that the radiations may be spontaneous or induced, though even this distinction is a practical rather than a fundamental one.

The working method enables the radiochemist not only to detect tracer quantities, but also to discriminate between radioactive isotopes. Because of the chemical near-equality of isotopes, ordinary chemistry is not concerned with isotopic composition. In radiochemistry, isotopy is of crucial importance. First, the method of isolation must vary with the lifetimes of the isotopes and their radioactive parents and daughters. The couple protoactinium and  $UX_2$ , both isotopes of element 91, is a striking example. Protoactinium (half-life 34,300 years) is extracted in milligram quantities from tons of ore in a lengthy procedure, while  $UX_2$  (half-life 1.14 mins.) is separated by rapid adsorption methods

from pure solutions of its parent  $UX_1$ . Secondly, the method of detection depends on the quality of the radiations. Thirdly, the radiochemist is expected not only to prepare his substances pure chemically but also pure in respect of their radiations, and generally their nuclear properties, as well. Often the exclusion even of stable isotopes of the element may be desirable. Though a mixture of isotopes cannot be resolved chemically, the introduction of the 'wrong' isotopes can often be prevented.

This monograph deals with the production as well as the chemical properties of radioelements. Though the transmutation of nuclei is held to be part of physics, a strict division between the production and the use of radioelements agrees neither with laboratory practice nor with the practice of previous authors. The author feels the more justified in dealing with some aspects of transmutation, as no survey of the radiochemical implications of fission or of the synthesis or discovery of the elements 43, 61, 85, 87 and 93-96 has yet been given. The artificiality of a rigid separation between the production and the chemistry of the radioelements appears especially clearly in the consideration of the specific chemical excitation due to nuclear reactions (Chapter IX). However, transmutation is treated here only in so far as it is used in planned nuclear synthesis.

Applied radiochemistry, where the radioelements are not the objects but the tools of research, has been left out. This includes the elucidation of reaction mechanisms, particularly mechanisms of exchange reactions, i.e. the contribution of radiochemistry to chemical kinetics. A number of very useful reports on applied radiochemistry are available. The older results are found in the books by Paneth (1928) and Hahn (1936), and the article by Seaborg (1940). Exchange reactions have been surveyed by Haissinsky and Daudel (1947). The application of radiochemistry to biology has been treated by Hamilton (1941), Kurbatov and Pool (1942), Radin (1947, 1948), Sacks (1948), Kamen (1948), and in a *Symposium* of the University of Wisconsin, to nutrition by Comar (1948), to metallurgy by Stanley (1947) and Harwood (1948), to friction studies by Burwell (1947) and to industry generally by Irvine (1949) and Guest (1949). Hevesy (1948) has published a book, and Sue (1948) a bibliography, on tracer work.

Radiation chemistry, i.e. the investigation of the ('generalized') chemical actions of ionizing radiations (see Smyth *Report*, p. 75; Burton, 1947; Dainton, 1948; Allen, 1949) has also been excluded. These chemical actions can be produced by external irradiation as well as by radioelements as parts of reacting systems. The field is sometimes misleadingly referred to as 'radiochemistry'. Radiation chemistry is clearly a separate branch of science.

A knowledge of the basic facts of radioactivity has been presumed. The classical reference works on natural radioactivity are, of course, those by Rutherford, Chadwick and Ellis (1930), Meyer and Schweidler (1927) and M. Curie (1935). The recent book by I. Curie (1946) is also confined to the natural radioelements. Individual natural radioelements are dealt with exhaustively in the volumes 'Uranium', 'Protoactinium', 'Actinium', 'Radium' and 'Polonium' of Gmelin's *Handbuch der Anorganischen Chemie*. In the *Manual* by Hevesy and Paneth (1938) and the semi-popular book by Pollard and Davidson (1945), artificial radioactivity is also considered. Introductions to nuclear physics have been written by Feather (1936), Rasetti (1937) and Stranathan (1945). The reference book by Mattauch and Flügge (1942) consists of a theoretical introduction and extensive tables. It has been newly edited by Mattauch and Flammersfeld (1949). The three monographs on nuclear physics by Bethe and Bacher (1936), Bethe (1937) and Livingston and Bethe (1937) are still extremely useful.

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\* For brevity, work published by more than three authors will be referred to by the name of the first-named author only in the text, while all names will be found in the lists of references.

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## CHAPTER II

# THE ROLE OF THE CHEMICAL DIFFERENCES BETWEEN ISOTOPES IN RADIOCHEMISTRY

### 2.1. The chemical near-equality of isotopes

It is one of the main results of earlier radiochemical research that to a good approximation all isotopes of an element show identical chemical behaviour, i.e. that the chemical properties of nuclear species are independent of their mass numbers  $A$ , and depend only on the parameter, which is constant in every family of isotopes, namely, the nuclear charge or atomic number  $Z$ . Chemical properties depend on  $A$  to a noticeable extent only for the very lightest elements. For medium-heavy and heavy elements, differences of this nature are beyond the precision of the usual chemical or radiochemical methods. Indeed, their smallness is expected on the basis of the Rutherford-Bohr theory of the atom.

In particular, the independence of the chemical properties, among the isotopes of a given element, of the degree of nuclear stability of those isotopes has been proved abundantly in the early days of radioactive research, and has been confirmed again with artificial radioelements. For instance, the many attempts to separate chemically the isotopes\*  ${}^{232}_{90}\text{Th}$  (ordinary thorium) and  ${}^{230}_{90}\text{Th}$  (ionium), or  ${}^{228}_{88}\text{Ra}$  (mesothorium 1) and  ${}^{226}_{88}\text{Ra}$  (radium) have failed completely (McCoy and Ross, 1907; Boltwood, 1907; Keetman, 1909; Auer von Welsbach, 1910; Marckwald, 1910; Soddy, 1911). Of course, this is again exactly what accepted nuclear theory demands: unstable nuclei are distinguished by a finite probability of nuclear disintegration per unit time, but as long as the nucleus does not actually disintegrate, its field of force is the same as if it were stable, and therefore radioactive isotopes

\* The mass number  $A$  of each nuclear species is appended to the chemical symbol as a superscript. Often the atomic number (nuclear charge)  $Z$  is also given as a subscript, though this is redundant in the presence of the chemical symbol. Each member of a natural radioactive series has its own name, e.g. ionium, but artificially produced active species are usually referred to by names like 'radiophosphorus' (Joliot). In case of doubt it must be specified which artificially produced isotope is meant.

are chemically just as similar to one another and to stable isotopes of the same element as stable isotopes are to each other. Consequently, there can be no purely chemical experiment indicating the degree of stability of a nucleus.

As the chemical differences between isotopes are both very small and quite unconnected with nuclear stability, there is no reason why they should be considered further in a monograph on radiochemistry.

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## THE DISTRIBUTION OF TRACER QUANTITIES BETWEEN SOLIDS AND LIQUIDS

### 3.1. Solubility products in radiochemistry

Precipitation reactions in radiochemistry are of special interest from a practical point of view, because precipitation is the principal method in preparative and analytical chemistry, and from a theoretical point of view, because at the prevailing dilutions the solubility products even of very poorly soluble salts may not be reached. Table I shows by way of examples how small tracer quantities are when expressed as grams, gram-atoms or numbers of atoms, though the standard source strength chosen for the table (1 micro-curie [ $\mu\text{c.}$ ], i.e.  $3.7 \times 10^4$  disintegrations/sec.\*) is fairly large from the standpoint of detection. The values of the half-lives are those listed by Seaborg (1944).

Table I. *Amount of substance per unit source strength*

Radioelement	Half-life	Grams/ $\mu\text{c.}$	Gram-atoms/ $\mu\text{c.}$	Atoms/ $\mu\text{c.}$
<sup>232</sup> Th	$1.39 \times 10^{10}$ years	8.73	$3.77 \times 10^{-2}$	$2.3 \times 10^{22}$
<sup>238</sup> U	$4.51 \times 10^9$ years	2.84	$1.20 \times 10^{-2}$	$7.2 \times 10^{21}$
<sup>226</sup> Ra	$1.59 \times 10^3$ years	$1.00 \times 10^{-6}$	$4.42 \times 10^{-9}$	$2.7 \times 10^{15}$
<sup>210</sup> Po	140 days	$2.4 \times 10^{-10}$	$1.1 \times 10^{-12}$	$6.9 \times 10^{11}$
<sup>210</sup> Bi(RaE)	5 days	$8.6 \times 10^{-12}$	$4.1 \times 10^{-14}$	$2.5 \times 10^{10}$
<sup>212</sup> Pb(ThB)	10.6 hr.	$7.6 \times 10^{-13}$	$3.6 \times 10^{-15}$	$2.1 \times 10^9$
<sup>56</sup> Mn	156 min.	$1.9 \times 10^{-13}$	$3.4 \times 10^{-15}$	$2.0 \times 10^9$

Lead sulphate, with a solubility at 25° C. of  $4.25 \times 10^{-3}$  g./l.  $\sim 1.4 \times 10^{-5}$  mol/l., may serve as an example. At a concentration of 1  $\mu\text{c.}$ /l., ThB sulphate will weigh only  $\sim 1.1 \times 10^{-12}$  g./l. Nor would a moderate excess of sulphuric acid be expected to precipitate the ThB sulphate. Assuming the lead sulphate to be fully

\* Condon and Curtiss (1946) of the U.S. Bureau of Standards recommend the use of a more rational unit instead of the curie: 1 'rutherford' (rd.) is defined as the strength of a source of  $10^6$  disintegrations/sec., i.e.  $1 \mu\text{c.} = 0.037$  rd. Though the use of such units offers a great advantage, it appears desirable to keep the association of the name of the Curies with the basic unit of radioactive strength.

dissociated, its solubility product is  $\sim [1.4 \times 10^{-5}]^2 \sim [2.0 \times 10^{-10}]$ , but the ion product of the ThB sulphate at the stated strength in  $M/10-H_2SO_4$  would be only  $\sim [3.6 \times 10^{-15}][0.1] \sim 3.6 \times 10^{-16}$ . Precipitations are possible, however, with the help of the processes of unspecific adsorption, coprecipitation by specific adsorption or by mixed crystal formation, and radiocolloid formation.

### 3.2. The unspecific adsorption of radioelements

Adsorption plays a main part in the chemistry of tracer quantities. The importance of adsorption is due to the large surfaces offered to tracer quantities by any material (Soddy, 1911*a, b*). It is useful to draw a distinction between adsorbents which from common general experience may be considered as 'unspecific', and 'specific' adsorbents (§ 3.3).

Even smooth surfaces of glass, or of a more inert material like paraffin wax, readily adsorb ions of radioelements (Horovitz and Paneth, 1914; Leng, 1927; Hensley, Long and Willard, 1948). Titanium dioxide strongly adsorbs polonium from  $N/10$ -nitric acid (Horovitz and Paneth, 1914). The thorium isotope  $UX_1$  is efficiently removed from solutions of uranyl nitrate by shaking with charcoal (Ritzel, 1909; Freundlich, Neumann and Kämpfer, 1915). The action of charcoal on dilute radioelements has also been utilized by Roginsky and Gopstein (1935), Erbacher and Philipp (1936), Erbacher (1941), Erbacher and Beck (1944), and Melander (1947). Manganese dioxide is another powerful unspecific adsorbent.

Unspecific adsorption of tracer quantities generally may be described, within wide limits, by adsorption isotherms of the Freundlich type

$$A = Bc^{1/n},$$

where  $A$  is the amount adsorbed,  $c$  the concentration, and  $B$  and  $n$  ( $> 1$ ) are constants (Berry, 1910 [ $UX_1$  on  $BaSO_4$ ]; Germann, 1921 [radium on  $BaSO_4$ ])—not strictly a case of 'unspecific' adsorption). However, clearly  $n$  cannot remain constant, but must decrease to unity, when the value of  $c$  becomes small, i.e. when only a small fraction of the surface of the adsorbent is covered. With  $n \rightarrow 1$ , the adsorption isotherm degenerates into Nernst's law describing the distribution of a solute between immiscible



solvents (Ritzel, 1909 [UX<sub>1</sub> on charcoal]; Brown, 1922 [UX<sub>1</sub> on basic iron acetate]; Brennen, 1925 [polonium on sand]). The absolute concentration of a radioelement, or of an element containing an active isotope, can be derived from the experimental value of  $n$  with a standard adsorber, if  $n$  is a known function of concentration in the range concerned (Kurbatov and Kurbatov, 1947). It has been reported that the amount of stable nuclear species formed in disintegrations may be determined in this way.

Chemically similar ions may sometimes be separated from each other by treatment with an unspecific adsorbent. Separation is often marked even in single-stage processes, but it is much improved in multi-stage processes analogous to fractional distillation. The method is known as 'chromatography' (first having been applied to organic pigments) and consists in practice in the pouring of the solution through a column filled with adsorbent, followed by 'development' with an 'eluting' agent. Sharp separations of tracer quantities of the rare earths and many other elements are possible. Alumina may be used as adsorber (Erämetsä, 1940; Lindner, 1944, 1947). The column may consist, instead of an adsorbent in the narrow sense, of a cation exchange resin (see many authors in the November, 1947, number of the *J. Amer. Chem. Soc.*; Cohn, Parker and Tompkins, 1948; Duncan and Lister, 1948). Separation factors between individual rare earths, as well as between barium and radium (Reid, 1948), are 1.2 to 1.6 per stage. The resins require ions for elution (see Kunin, 1949). In the case of the rare earths, ammonium ion is used as an eluant. In addition, citrate ion is added during elution as a complexing agent. This reduces, to an extent varying for the different ions, the concentrations of the free cations in the solution. Thus separation is enhanced. Adsorbability is found to increase with valency and with ionic radius. Chromatography also works well with macro-quantities of the rare earths (Spedding *et al.* 1947). Regarding the application of paper chromatography to tracer work, see Consden (1948). Calvin and Benson's (1949) determination of the path of radiocarbon in photosynthesis is a remarkable example. Isotope separation by chromatography is considered as promising (see Duncan and Lister, 1948).

The adsorption of colloidal radioelements (§ 3.4) on container

walls, paper (Godlewski, 1914; Kurbatov and Kurbatov, 1942, 1945), resins (Schubert and Conn, 1949), etc., is especially intense. However, the adsorption of radiocolloids is not readily reversible, and it is not suppressed by addition of ions.

There are several distinct mechanisms through which foreign ions present in solutions may influence adsorbability. First, as in the example of the citrate ion, they may effectively reduce the concentration of the ions of the radioelement through formation of complexes. Secondly, the foreign ions may displace the ions of the radioelement on the adsorbing surface. Ions capable of such action are sometimes referred to by the unsuitable name 'hold-back carriers'. Among the most efficient displacers are the ions isotopic with those of the radioelement. A minute quantity of ordinary thorium will prevent the adsorption of  $UX_1$  by charcoal (Ritzel, 1909). The addition of little inactive strontium makes it possible to precipitate radiochemically pure radiobarium as the nitrate or chloride in presence of radiostrontium. If, however, isotopic dilution must be avoided, a chemical homologue will often serve; e.g. zirconium will also reduce the adsorption of  $UX_1$  (Freundlich and Kämpfer, 1915). Even dissimilar substances may be effective, when present in large excess, e.g. methylene blue, benzoic acid, and strychnine nitrate in the displacement of  $UX_1$  (Freundlich and Kämpfer, 1915). Thirdly, adsorptive power depends on the electric charge on the adsorbent, which in turn is dependent on the foreign ions present (§ 3.3).

### 3.3. The use of carriers

The 'specific' precipitation of tracer quantities of a particular ion as an easily handled solid is ensured by addition before precipitation of a sufficient quantity of a suitable material as a 'carrier'. Broadly speaking, suitability as a carrier depends on chemical similarity with the tracer, as expressed in at least one precipitation reaction. After carrier and tracer have been isolated together from the rest of the material through this reaction, they may be separated from each other in a reaction which discriminates between carrier and tracer. Carrier action may be based (1) on specific adsorption, or (2) on the formation of mixed crystals.

The requirements for specific adsorption have been explored

by Fajans, Paneth and Hahn (Fajans and Beer, 1913, 1915; Fajans and Beckerath, 1920; Horovitz and Paneth, 1914; Hahn and Imre, 1929; see Paneth, 1914, 1928; Fajans, 1931; Hahn, 1936). The rules developed by these authors have been harmonized (Fajans and Erdey-Gruz, 1931) to read: 'An ion is appreciably adsorbed from its aqueous solution on a precipitated or precipitating salt if it forms a poorly soluble or poorly dissociating compound with the ion of opposite charge in the salt. The adsorption of a cation is enhanced (diminished) by the presence of adsorbed anions (cations), i.e. by a negative (positive) charge on the precipitate, and vice versa.' Most acids are examples of poorly dissociating compounds. The charge on the precipitate is determined by the manner of its production, depending upon whether the salt has been thrown down in presence of an excess of the cation or of the anion (Lottermoser, 1905, 1906). It is seen then that specific adsorption is conditioned by at least two independent parameters, namely, solubility and electric charge. Ion size and polarizability probably also play their parts. A further complication lies in the existence of a time factor (Imre, 1931).

An example of coprecipitation by surface adsorption: tracer quantities of radiomanganese in hydrochloric acid may be recovered by adding ferric ion, ammonia and excess ammonium sulphide. Manganese, which, like iron, forms a very poorly soluble sulphide, will be precipitated along with the iron sulphide. The excess sulphide ion will ensure a negative charge on the iron sulphide. In the end, after conversion of the sulphides into chlorides with hydrochloric acid, the iron can be separated from the manganese by extraction with an organic solvent (see § 3.6).

As an alternative to simultaneous precipitation, the radioelements may be adsorbed on pre-formed precipitates—in the example given by preformed iron sulphide. Naturally, the efficiency of this variant is less, but the speed may be superior. In this way, the short-lived eka-tantalum (protoactinium) isotope  $UX_2$  was isolated rapidly from its parent  $UX_1$  (thorium) by adsorption on pre-formed tantalum oxide (Hahn and Meitner, 1913).

In agreement with the adsorption rule, readily soluble salts of radioelements are not adsorbed by precipitating salts. The reten-

tion of radioelements in solution as soluble salts during precipitations is, of course, a feature of many routine operations. Polonium solutions are freed from silver by precipitation of silver chloride, polonium chloride remaining in solution (I. Curie, 1925).  $UX_2$  (protoactinium) is kept in solution when  $UX_1$  (thorium) precipitates as the fluoride (Fajans and Göhring, 1913).  $UX_1$  is held in solution by ammonium carbonate while iron precipitates as the sulphide (Bachelet, 1941). Radiosodium made by irradiation of magnesium metal with fast neutrons can be recovered by conversion of the magnesium into the hydroxide, or into the magnesium-ammonium double carbonate, and extraction of the sodium with water (Drehmann, 1946; Irvine and Clarke, 1948). Radiobarium remains in solution when iron, after having served as its carrier, is precipitated at pH 5.4 (Kurbatov, Yu and Kurbatov, 1948). More examples are collected in a paper by Erbacher (1941).

The distinction between carrier action by adsorption and by formation of mixed crystals is due to Escher-Desrivières (1926) and Hahn (see Hahn, 1936). As an example we may note that the adsorption rule alone does not explain why tracer quantities of radium are brought down far better by barium than by calcium sulphate (see Table II). Obviously at tracer concentrations, as in systems containing macro-quantities of radium, consideration of ion size and lattice structure are important; the formation of mixed crystals of  $BaSO_4$ - $RaSO_4$  is allowed, but not of those of  $CaSO_4$ - $RaSO_4$ . However, Hahn has shown that occasionally tracer quantities of one component may be fitted into the crystals of the other component even where macro-quantities of the two components do not give mixed crystals (radiolead chloride- $BaCl_2$ ). Whether or not such mixed crystals form, largely depends on experimental procedure (Grahl, 1944). An extreme case of mixed crystal formation obtains when the stable isotopes of a radioelement are used as its carrier (e.g. ThB-Pb).

Distinction between surface adsorption and mixed crystal formation is possible in various ways, as indicated by Hahn (1936). In the first place we may study the behaviour of analogous systems (Ca[Ba]Ra sulphate). If these systems differ markedly in behaviour it is probable that mixed crystal formation is in question. Secondly, we may study reversibility: surface adsorption is more

easily reversed than is mixed crystal formation. Thirdly, in a given chemical system and at a given temperature, adsorption will be affected more strongly if conditions of precipitation are varied (see, however, Grahl, 1944). Fourthly, with macro-crystals the distribution of the radioelement may show up directly in autoradiographs (§ 10.6). However, Hahn himself has recognized the difficulty of drawing a really sharp line between surface adsorption and mixed crystal formation by introducing the not too clearly defined concept of 'internal adsorption'.

### 3.4. Radiocolloids

Soddy (1911*b*) observed that tracer quantities (without addition of carriers) behave chemically in a manner better defined than one would expect. The case of the hydroxides of the heavy metals lead, bismuth and polonium, obtained by addition of ammonia to the solutions of their salts, or by letting the emanations decay in water, is typical; it is also historically important because active isotopes of these elements (e.g. ThB, RaE and RaF) became available at an early stage. The carrier-free precipitates can be obtained in the absence of an adsorbent by sedimentation (Lachs and Herszfinkiel, 1921; Lachs and Wertenstein, 1922) or by centrifuging (Chamié and Guillot, 1930; Guillot, 1930, 1931; Blau and Rona, 1930; Korvezée, 1933; Chamié and Haissinsky, 1934), notwithstanding the fact that solubility products may not be reached (Paneth, 1913*a, b*; § 3.1). These substances separable in tracer quantities are considered as colloids and are called 'radiocolloids' (Paneth, 1913*a, b*, 1914, 1928; Godlewski, 1913; Haissinsky, 1934). The radiocolloids diffuse only slowly compared with ions (Hevesy, 1913; Paneth, 1913*a, b*), and they do not diffuse readily through membranes (Paneth, 1912, 1913*a, b*). They migrate cataphoretically with a sign of charge which is not characteristic, but imposed by the foreign ions present (Godlewski, 1913; Lachs, 1917; Hahn and Imre, 1929). They betray their state of aggregation by producing distinct microscopic specks of blackened area rather than uniform blackening of photographic plates if the latter are exposed directly to the liquid, or to inert surfaces previously treated with the liquid (Chamié, 1929, 1939, 1946*a, b*; Herszfinkiel and Jedrzejowski, 1929; Wilkins, 1940; Bouissières, Chastel and

Vigneron, 1947). Particle size may be much inferior to the size of other colloidal particles (Hevesy, 1913; Paneth, 1913*a, b*). However, size is not uniform (Guillot, 1931), and the state of aggregation is influenced by the age (Imre, 1930, 1931; Korvezée, 1933; Chamié and Haissinsky, 1934; Bouissières, Chastel and Vigneron, 1947) and the concentration of the radiocolloid (Chamié and Marques, 1939; Kurbatov and Kurbatov, 1942, 1945), by the presence of electrolytes (Lachs and Herszfinkiel, 1921; Hahn and Werner, 1929; Werner, 1931; Kurbatov and Kurbatov, 1942, 1945) and by the nature of the solvent (Bouissières, Chastel and Vigneron, 1947). Complex formers, e.g. mannitol in case of bismuth hydroxide (Hahn and Werner, 1929), and sulphate ions in case of zirconium hydroxide (Schubert and Conn, 1949), prevent the formation of radiocolloids by increasing solubility. Recently, the technique of the direct precipitation of tracer quantities without adsorbents (§ 3.2) or carriers (§ 3.3) has been applied to the preparation of artificial radioelements of high specific activity,\* including titanium, scandium, yttrium, zirconium and the rare earths, by the Ohio school (Kurbatov, 1932; Kurbatov, Pool and Law, 1940; Allen *et al.* 1941; Kurbatov and Pool, 1944; Pool and Kurbatov, 1945; Kurbatov and Kurbatov, 1942, 1945). Schubert and Conn (1949) have investigated the radiocolloidal behaviour of fission products and plutonium. The concept of the radiocolloid has also been introduced into mineralogy (Yagoda, 1949).

The Fajans-Hahn-Paneth adsorption rule (§ 3.3) must break down when the radioelement is present as a radiocolloid in the solution from which adsorption takes place. As the radiocolloids are largely un-ionized, their adsorbability is mainly governed by their 'cataphoretic' charge, which is imposed by the medium, and by particle size. The radiocolloid must be adsorbed 'as a whole', and the solubilities of individual ions in the medium are irrelevant. The adsorption of the colloids is usually very pronounced (§ 3.2).

It has been claimed that the appearance of radiocolloids is due to adsorption on minute ever-present quantities of impurities like dust, fibres, etc. (Zsigmondy, 1913; Hahn and Imre, 1929; Werner,

\* Several definitions of the 'specific activity' have gained currency. Paneth (1948) defines it as 'number of disintegrations/second/gram'. Seaborg (1948) means by it the ratio of the numbers of active and inactive atoms.

1931). Certainly Werner (1931) and Rosenblum and Kaiser (1935) showed that extreme purification of the liquids improves the stability of the solutions against the formation of radiocolloids. However, radiocolloid formation is not entirely suppressed. Rather, a great many tests of widely varying kind suggest that the formation of radiocolloids, though facilitated by impurities, is not dependent on their presence (Paneth and Horovitz, 1913; Haissinsky, 1934, 1935). Haissinsky points out that radiocolloids have been observed only with the hydroxides and sulphides of heavy metals. Though the values given in the literature for the solubilities of these substances (see Haissinsky, 1935) would not necessarily justify their precipitation as radiocolloids, it should be recalled that these highly insoluble substances are generally amorphous, ill-defined and subject to complex ageing processes (Kolthoff, 1932). Different methods yield widely discordant values for their solubilities, and Haissinsky doubts whether these values have any significance: 'One should not apply the ordinary concepts of solubilities and solubility products, which imply the possibility of a complete separation of a liquid and a solid phase. . . . The solutions in question constitute rather poly-disperse systems containing simple and complex ions as well as micelles of variable dimensions—all in a process of evolution.' Possibly the solubilities of these heavy-metal hydroxides, etc., have, so far as the truly ionic form is concerned, been grossly overestimated. But undoubtedly the position in this field is still unsatisfactory.

### 3.5. Fractional precipitation and crystallization

Generally, in all incomplete precipitations the ratio carrier: radioelement will be different for the solid and the solution. Consequently, 'fractional precipitations' can be used for the enrichment of the radioelement either in the solid or in the solution. The mechanism can be surface adsorption or mixed crystal formation. E.g. radium can be enriched in mixed crystals with barium by fractional precipitation of the sulphates (see Table II). In practice, fractional crystallization is mostly preferred. One reason is that the results are more easily reproduced because the slow rate of crystallization—which essentially is precipitation from a very slightly supersaturated solution—facilitates the exchange

between the phases so that local irregularities can heal. Further, the greater solubility of the salts and the larger size of the crystals depress adsorption. The following brief account is based on an important paper by B. Goldschmidt (1940; see also Erbacher, 1930; Marques, 1936).

The enrichment in one component of the crystals, in given conditions of concentration, temperature, structure of the crystals (degree of hydration), etc., is measured through a 'fractionation coefficient'  $f$ , defined as the ratio of the concentration ratios of the two components in the two phases.  $f$  must refer to a differential deposit so that the composition of the mother liquor does not change. The fractionation coefficients are found to be independent of the concentration as long as one component is present in tracer quantity only. For instance, in the system  $\text{Ra}(\text{ClO}_3)_2$ - $\text{Ba}(\text{ClO}_3)_2$ ,  $f$  is constant at least for concentration ratios between  $10^{-5}$  and  $10^{-11}$ . Some values of  $f$  for tracer quantities of radium are listed in Table II, values of  $f > 1$  indicating enrichment of the

Table II. *Fractionation coefficients (micro-component: radium)*

Macro-component	Temperature, ° C.	Fractionation coefficient
$\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$	25	9
$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	20	0.1
$\text{BaSO}_4$	20	1.8*
$\text{Ba}(\text{CH}_3\text{COO})_2$	40-100	~ 1
$\text{Ba}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	25- 40	~ 0.4
$\text{Ba}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$	0- 25	~ 0.25
Ba tartrate laevorotatory	25	0.85
Ba tartrate dextrorotatory	25	0.85
Ba tartrate racemic	25	1.5
$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	20	0.015
$\text{SrSO}_4$	20	340*
$\text{CaSO}_4$	20	0.02*
$\text{PbSO}_4$	20	11*
$\text{PbCO}_3$	20	0.06*

\* Fractional precipitations.

solid. It is found that  $f$  generally tends towards unity with increase of temperature. There is only a crude correlation, in many individual cases breaking down, between the value of  $f$  and the ratio of the solubilities of the two salts.

The integral distribution of the two components at a given



constant value of  $f$  will still depend on whether exchange between the two phases during the crystallization of a finite quantity is facilitated or inhibited (Doerner and Hoskins, 1925; Henderson and Kracek, 1927; Chlopin, 1931; Mumbrauer, 1931; Polesitsky, 1932; Käding, Mumbrauer and Riehl, 1932). In the former case the Berthelot-Nernst distribution law applies, i.e.

$$\frac{x}{y} = f \frac{a-x}{b-y},$$

where  $a$  and  $b$  are the quantities of the two components in the initial solution, before the beginning of crystallization, and  $x$  and  $y$  the quantities of the components in the crystals. This law also describes the partition of a solute between two ideal immiscible solvents. Equilibrium exists at any moment between the liquid and the whole crystals. The condition of full exchange is approximated if the crystals have a large surface and are well stirred with the mother liquor. Though diffusion in solids is slow, the constant repetition of re-solution and re-crystallization will lead to uniform distribution over the volume of the crystals. Where the experimental conditions are the opposite, and exchange is impeded, the integral equation of Doerner and Hoskins applies:

$$\log \frac{a}{a-x} = f \log \frac{b}{b-y}.$$

In this case, equilibrium is established, at any moment during crystallization, only between the surface layer of the crystals and the mother liquor. Therefore, with  $f > 1$  ( $< 1$ ), the interior of the crystals contains more (less) radioelement than the surface parts. Hahn has compared the layers to the shells of an onion.

### 3.6. The partition between solvents

Grahame and Seaborg (1938) investigated the partition of various radioelements between solvents. They found that, in agreement with Nernst's law, the partition coefficient of  $\text{GaCl}_3$  between 6N-HCl and ether is the same at concentrations  $10^{-12}$  and  $10^{-3}$  M. Also the partition coefficients of  $\text{Co}(\text{SCN})_3$  between amyl alcohol and aqueous  $\text{NH}_4\text{SCN}$  at  $10^{-12}$  and  $10^{-5}$  M are identical (see also McCallum and Hoskovsky, 1948). In these experiments the total ionic strength in the aqueous medium was kept constant by the large excess of ions from the hydrochloric

acid or the  $\text{NH}_4\text{SCN}$ . Therefore, the thermodynamic activities of the ions of the radioelements were proportional to their individual concentrations so that the constancy of the partition coefficients is understood. The result also shows that adsorption does not interfere in these systems.

Grahame and Seaborg used partition in practice for the separation of radiogallium from its parent material zinc after irradiation of the latter, and for the separation of radiocobalt and radiomanganese from parent iron. Enormous amounts of iron can be removed from aqueous solution by ether extraction of the chloride without any loss of radiocobalt (Broda, Feather and Wilkinson, 1947). The iron thiocyanate also lends itself to ether extraction (Erbacher, Herr and Wiedemann, 1944).  $\beta$ - $\beta'$ -dichloro diethyl ether is another suitable solvent for ferric chloride (Coryell, 1949).

The solubility of uranyl nitrate, and the insolubility of thorium nitrate, in ether is used to separate  $\text{UX}_1$  (thorium) from uranium. During the extraction the  $\text{UX}_1$  remains in the aqueous layer derived from the water of crystallization of the uranyl nitrate (Crookes, 1900; Smyth *Report*, p. 55; see Bachelet and Cheylan, 1948). In the application of this process to neutron-irradiated uranium, most fission products also go into the water. Complexing agents may assist extractions by solvents (see Cohn, 1948). For instance, uranyl benzoyl methane and the analogous compound of  $\text{UX}_1$  both go into organic solvents from water, and can both be separated from fission products in this way (Götte, 1946). For complex compounds of plutonium, soluble in organic solvents, see Purkayastha (1948). Haissinsky (1933) suggests solvents to separate the nitrates of radium (insoluble in alcohol and pyridine), actinium (soluble in alcohol and pyridine) and thorium (soluble in alcohol, but not in pyridine).

The halogens lend themselves to extraction by partition. Extraction of fission bromine and iodine from solutions of irradiated uranium in water by shaking with carbon tetrachloride or toluene is a standard method (Libby, 1939; Langsdorf and Segrè, 1940; Dodson and Fowler, 1940; Hahn, Strassmann and Seelmann-Eggebert, 1946; Broda and Wright, 1946; Snell *et al.* 1947; Arnold and Sugarman, 1947).

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## TRACER QUANTITIES IN GASES

**4.1. Volatilizations at low temperatures**

The recovery of the emanations from solutions or porous solids holding the radioelements can be regarded as a distillation. In agreement with the law of Henry-Dalton, the partial pressure of radon in a gas in contact with a liquid is proportional to its concentration in the latter (Mache, Rausch von Traubenberg, see Meyer and Schweidler, 1927, p. 427; Szeperowicz, 1920). Outlines of standard techniques for the recovery of radon from solutions of radium salt are found in the monograph by Jennings and Russ (1948), as well as in the works by Rutherford, Chadwick and Ellis (1930), Meyer and Schweidler (1927) and I. Curie (1946). The determination, after distillation, of minute quantities of the emanations, and therefore of their radioactive parents, in gases, liquids and solids, is described by Evans (1935). For modern work on 'highly emanating' solids of suitably open structure, employing appropriate ratios between the carrier and the radioelement, the book by Hahn (1936) and the papers by Strassmann (1934), Erbacher (1941) and Erbacher and Radoch (1944) may be consulted. Hahn and his school have developed as a special field of applied radiochemistry the investigation of the 'emanating power' of solids with the object of following structural changes (see Zimens, 1943; I. Curie, 1946; Perey, 1947; Hahn, 1949).

Similar techniques as for the preparation of the emanations are used for the extraction from liquids or porous solids of active noble gases made artificially, including the rapid recovery (in a few seconds) of the short-lived isotopes of krypton and xenon, which occur as fission products (Hahn and Strassmann, 1939, 1940, 1943; Götte, 1940; Seelmann-Eggebert, 1940; Dodson and Fowler, 1940; Brown, Irvine and Livingston, 1944; Wu and Segrè, 1945; Hahn, Strassmann and Seelmann-Eggebert, 1946; Sugarman, 1949*a*; see § 9.2). Götte and Radoch (1947) claim up to 100% emanating power for fission products of certain ill-defined solid uranates of organic bases, e.g. methyl or butyl amine. Moist air seems

essential for good emanating power. Langsdorf and Segrè (1940) obtained  $^{83}\text{Kr}$  from  $\text{AgNO}_3$  impregnated silica gel, to which  $^{83}\text{Br}$  had been admitted. Hahn and Strassmann (1940) point out that in contrast to the emanations, the yield of fission produced krypton and xenon, after the end of irradiation, is determined solely by diffusion, and not by recoil (§ 9.2). Sugarman (1949*b*) has shown that the yield of the noble gases rapidly decreases during the setting of silver bromide containing the radioactive parent.

Bromine and iodine also are readily removed at room temperature from solutions of the elements by a current of gas (Hahn, Strassmann and Seelmann-Eggebert, 1946). Their higher homologue astatine needs elevated temperature (§§ 4.2, 8.5).

Surface effects with tracer quantities of gases are marked. Small quantities of radon condense on cold surfaces at pressures far below the saturation pressures as derived from experiments with larger amounts (Soddy, 1914). The adsorption occurs either on the walls themselves or on particles of water, mercury, etc., precipitated in the cold (Wertenstein, 1935). Cold charcoal is a powerful adsorbent for radon; on re-warming, the bulk of the radon is released again. Radiokrypton and radioxenon may be separated with carbon cooled with ice-sodium chloride, which adsorbs only xenon; carbon cooled with liquid air condenses krypton as well (Hahn and Strassmann, 1940).

#### 4.2. Volatilizations at high temperatures

The distillation (volatilization) at high temperatures of tracer quantities—not large enough to cover the supporting surfaces—of radiolead ( $\text{ThB}$  and  $\text{RaB}$ ), radiobismuth ( $\text{RaC}$ ) and polonium, in its dependence on temperature, duration of heating, mode of deposition, nature of the support and the gas, was studied by Russell (1912), Wood (1915), Loria (1915), Bonet-Maury (1929), Walchshofer (1929), Holesch (1931), Rona and Hoffer (1935) and Karlik and Bernert (1942). This work produced the not unexpected result that at any given temperature only a certain fraction of the radioelement can be volatilized, i.e. that the volatility depends on the extent to which the surface is covered. Apparently the individual atoms of the radioelements on the surface are attached to centres of different activities. Different supporting

surfaces show different affinities for the atoms. For example, evaporation of polonium from platinum begins at  $350^{\circ}$ , but from palladium only at  $500\text{--}600^{\circ}$  (Jedrzejowski, 1929; Rona, 1932). Similarly, astatine (§ 8.5) is far less strongly held on a surface of glass than on one of gold or platinum (Johnson, Leininger and Segrè, 1949). The volatilities of the A-, B- and C-bodies are less in an oxidizing than in an inert atmosphere or in a vacuum (Russell, 1912). Finally, the volatility decreases with the age of the preparation (Rona, 1932). The atoms volatilize singly rather than in groups (Jedrzejowski, 1929). More data on the disappearance of polonium from hot surfaces will be found in § 9.3.

Volatilization has been used for the purification and the transfer of radiobismuth and polonium (Russell, 1912; Russell and Chadwick, 1914). Polonium can be concentrated by condensation of the vapour on a very small area of a cold surface (Paneth and Hevesy, 1913; Rona and Schmidt, 1928; Rona, 1932). In this process the polonium adheres particularly to platinum or palladium. Astatine sticks best to platinum and silver. The relative ease of adhesion of different radioelements, volatilized together, depends so much on the condition of the collecting surface that selective deposition is feasible (Frauenfelder *et al.* 1948). The tendency of the condensing atoms to form groups on the collector seems to be less than that of the same atoms deposited from emanations (Jedrzejowski, 1929; Herszfkinkel and Jedrzejowski, 1929; see § 4.3). An interesting process is the recovery of tracer quantities of isotopes of lead and thorium by distillation of the chlorides in a current of  $\text{HCl} + \text{CCl}_4$  at  $500\text{--}800^{\circ}$  from the sulphates of their radioactive parents (Nikitin and Polessitsky, 1941).

Among artificial radioelements, cadmium and astatine were isolated from their parents silver and bismuth by volatilization (Alvarez, Helmholtz and Nelson, 1940; Corson, Mackenzie and Segrè, 1940; Frauenfelder *et al.* 1948). Very thin sources were made in this way (Wright, 1947). Monolayer  $^{32}\text{P}$  (by volatilization in a vacuum of iron phosphate nearly free from inactive contamination) as well as monolayer  $^{90}\text{Y}$  was prepared (Sherwin, 1948, 1949). It was found that the purity of the  $^{32}\text{P}$  condensate was enhanced by double distillation. The width of the temperature interval of volatilization was indicative of purity as measured by



the efficiency of  $\beta$ -recoil (§ 9.2) from the source. In the first stage the material was condensed on a platinum 'catcher', and only one of the fractions was employed in the second stage. Radiophosphorus mixed with inactive phosphorus was separated from iron by volatilization of the chloride after reduction of the ferric chloride to ferrous chloride (Chackett and Morgan, 1948).

### 4.3. Active deposits

The collection of the active deposits from the emanations constitutes a peculiar radiochemical problem. The standard procedures have been described in the books of Rutherford, Chadwick and Ellis, of Meyer and Schweidler and of I. Curie. Active deposits are also formed in the decay of many other  $\alpha$ - or  $\beta$ -active nuclei (§ 9.2).

The atoms of the active deposits tend to aggregate in clusters while still in the gas phase, due either to adsorption on dust or to direct solidification. It appears that the presence of polar gas molecules facilitates nucleation. Drawing analogy from the radio-colloids in liquids one might speak of radioaerocolloids or radio-aerosols. Thus Debiere found that the diffusion coefficient of the active deposit from radon decreases sharply with time. This was confirmed with ThC" by Chamié and Tsien (§ 9.2). Sedimentation is observed in gravitational (M. Curie, 1907) and centrifugal (Harrington, 1928; Harrington and Gratias, 1931) fields. Clusters exist also on the surfaces covered with the deposits. This is made clear by direct photographic evidence (Chamié, 1929, 1946; Jedrzejowski, 1929), and by the occurrence of aggregate recoil (§ 9.3). The clusters in the active deposits from radon and thoron on collodion foils have been seen with the electron microscope (Martin, Baylor and Clark, 1944; see § 9.3).

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THE ELECTROCHEMISTRY OF  
RADIOELEMENTS**5.1. Preparative electrodeposition**

The first electrochemical experiments with tracer quantities are due to Marckwald (1902, 1903, 1910) and Lerch (1903), who aimed at the isolation of the nobler members of the natural radioactive series. References to the pioneer work are found in a paper by Meitner (1911). Later preparative and theoretical work is covered in the important monograph by Haissinsky (1946*a*).

A piece of metal (electrode) in contact with the solution of a salt of a radioelement covers itself with a tiny amount of the salt through adsorption (Fleck, 1913; Hevesy and Paneth, 1915; Tammann and Wilson, 1928; Erbacher and Philipp, 1930). If the cation, at its prevailing concentration, is less electropositive (nobler) than the metal, the reaction will not stop at the formation of the adsorbed layer, but the ions will transfer their charges to the electrode, and will deposit on it as the metallic form. If the difference of the electroaffinities of the material of the electrode and the radioelement is sufficient, the 'currentless deposition' of the radioelement is in the end practically quantitative. Stirring, rotation of the electrode, bubbling of gas through the solution accelerate the process, which is much used for the isolation of the very noble metal polonium on silver or copper foil, and of bismuth on nickel (Marckwald, 1905; Meitner, 1911; Hevesy and Paneth, 1913, 1914; I. Curie, 1925; Erbacher and Philipp, 1928, 1930; Erbacher, 1932, 1933*a, b*; Haissinsky, 1936, 1937*a*, 1946*a*). Mercury surfaces are also effective for polonium (Chamié, 1947; Chamié and Haissinsky, 1947). If contamination of the solution by the material of the foil is to be avoided, polonium can be deposited on platinum saturated with hydrogen gas (Erbacher, 1931, 1932, 1933*b*). The separation of radiocopper from neutron-irradiated zinc on a lead plate is an example for the currentless deposition of an artificial radioelement (Haissinsky, 1935*a*).

Hevesy (1915; see also Hevesy and Biltz, 1929; Erbacher,

1933*b, c*; Haissinsky, 1948) found that dissolved cations (lead) exchange with the atoms contained in a fairly deep surface layer of an electrode of the same material. This is attributed to local differences of potential, which will lead to deposition on the more negative spots and simultaneous dissolution elsewhere. The process can be visualized as involving 'short-circuited local solubility piles'. Self-diffusion in lead is not fast enough to account for the result.

As an alternative to currentless deposition ordinary electrolysis is also employed. Thus both lead and polonium plate out cathodically as metals, or anodically as higher oxides, depending on the composition of the solution and the applied potential (Hevesy and Paneth, 1913, 1914; Erbacher and Philipp, 1928; Haissinsky, 1937*a*, 1946*a*). Bismuth is deposited mainly on the cathode (Haissinsky, 1934, 1946*a*; Haissinsky, Rosenblum and Walen, 1939). Recently protoactinium has been found to be amenable to cathodic and anodic electrodeposition from aqueous solution (Emmanuel and Haissinsky, 1938; Bouissières, 1941; Haissinsky, 1945, 1946*a, b*), but it is uncertain in what chemical form the protoactinium is obtained. Radium, which is even baser, has been recovered electrolytically as the amalgam in a mercury cathode by Curie and Debierne. References to electrolytical work with macroquantities of radium, uranium and thorium are given by Haissinsky (1946*a*). The artificial radioelements copper (Steigman, 1938; Ratner and Kantor, 1942), cadmium (Wright, 1947) and indium (Jacobi, 1949) are easily electrodeposited. The electrolysis of radioiron mixed with inactive iron carrier has been used in biochemical tracer work (Ross and Chapin, 1942; see P. Hahn, 1945). Finally, the new element 43 (Tc, § 8.6) has been electrolysed (Flagg and Bleidner, 1945). As in currentless deposition, stirring speeds the process; the use of a spinning cathode (Fink and Rohrman, 1930) has been recommended for work with tracer quantities (Dunning and Pegram, 1935).

Thin films of very base metals like actinium (MsTh 2), thorium (UX<sub>1</sub> and RdTh) and radium (ThX) have been made from salt solutions in water (Meitner, 1911; Baeyer, Hahn and Meitner, 1914, 1915) or in (not quite dry) organic solvents (Hevesy, 1910; Haissinsky, 1937*b*; Cotelle and Haissinsky, 1938). Yields are far

from quantitative. The complicated mechanism has been elucidated by Tödt (1924). The deposits consist not of the metals, but of insoluble hydroxides or carbonates. Experimental conditions must be chosen so as to favour the formation of an adherent coating on the cathode rather than the flocculation of the precipitate in the liquid. This is achieved with high current densities and high acidities. The role of the current consists not in the discharge of the cations of the radioelement, but in their transport to the neighbourhood of the cathode, where they are rendered insoluble in the narrow alkaline zone surrounding the cathode. The process is not suitable for large amounts of material.

### 5.2. Theoretical aspects

In work with macro-quantities, the potentials of electrochemical reactions, including the potential for the straight discharge of an ion to the metal, can be derived from the current-voltage curves. The critical potentials  $E$  read from these curves are used to calculate the standard potential  $E_0$ , i.e. the potential at unit concentration, with the help of Nernst's equation

$$E = E_0 + RT/nF \ln c.$$

(It is assumed that the activities of the ions can be replaced by their concentrations  $c$ .) With tracer quantities, however, only a vanishing fraction of the total current is transported by the ions of the radioelement, and therefore no kink will appear in the current-voltage curve at the potential value where the radioelement begins to deposit. Instead, Hevesy and Paneth (1913, 1914, 1915) found the point of beginning deposition by directly testing the electrode for acquired radioactivity. Though the potential difference electrode/solution is not influenced by the minute quantity of radioelement, the deposition of this element is governed by the applied potential, and the free energy of the discharge reaction on the particular electrode can be read from the value of the critical potential at which deposition starts. In practice, this is done best, in analogy to the taking of current-voltage curves, by plotting, in a given experimental arrangement, the rate of deposition as a function of the potential. The point of intersection with the axis of abscissa gives the value of  $E$ . Joliot (1930) has devised special

apparatus to follow the activity of the electrode without interrupting the current.

$E_0$  must be calculated from  $E$  by Nernst's equation. This is done confidently now even at very low concentrations. Confirming early results by Hevesy and Paneth, Haissinsky (1935*b*) has proved the validity of the equation for the system Bi/Bi<sup>+++</sup> in the concentration range  $10^{-5}$  to  $3 \times 10^{-12}N$ , and Coche (1947) has done the same for the system Pb/Pb<sup>++</sup> down to the concentration  $10^{-10}N$ ; see, however, the results with polonium by Heal (1944) and Haissinsky *et. al.* (1949), and with zinc by Haenny and Mivelaz (1948).

Herzfeld (1913) has pointed out that in the deposition of a metal on an inert electrode the required potential will decrease with the increase of the amount deposited as long as only part of the surface is covered by it, as the frequency of the transition metal<sub>1</sub>→ion will depend on the number of available metal atoms. The effect should be observable with tracer quantities. E.g. the radiobismuth from 10 c.c. of a  $3 \times 10^{-12}N$  solution suffices only to give  $\sim 10^{-5}$  cm.<sup>2</sup> of a monatomic layer. In such a case the electrode will become polarized during electrolysis. For any given potential, provided it is not too much below the critical potential, and at any given concentration, an equilibrium (maximum deposition) will be approached. In fact, Joliot (1930), Haissinsky (1932, 1933) and Flagg and Bleidner (1945) have observed the polarization. (N.B. The influence of ordinary concentration polarization can be excluded, for example, by stirring the solution sufficiently.) However, the experimentally found polarization far exceeds the value derived from the considerations of Herzfeld. Haissinsky contends that the polarization is increased by the fact that as deposition proceeds surface areas of less and less affinity to the depositing metal have to be covered. The difference between the most and the least active parts of the surface may be of the order of 0.15–0.2 V., i.e. 3–5 kcal./mol. The inhomogeneity of the surface also leads to curious apparent variations in the range of the  $\alpha$ -rays from electro-deposited polonium (Haissinsky *et al.* 1949).

Apparently, in general, the critical potentials do not vary greatly with the material of the electrode. For example, the potentials of deposition of ThB (lead) on gold, silver and copper are the same

(Haissinsky, 1946*c*; Coche, 1947). Occasionally, however, differences have been observed, particularly with tantalum and platinum as electrodes (Coche, 1947; Griess and Rogers, 1949). These exceptions may be due to secondary phenomena—formation of an oxidic layer on tantalum, impeding deposition, or of an alloy with platinum, facilitating deposition. This means that the adhesion of the depositing atoms to different surfaces is equally strong. Attempts to explain this puzzling result have been reviewed by Haissinsky (1946*a, c*). Haissinsky himself argues that for the most active centres on the surface of the electrode, i.e. the centres which determine the critical potential, the work function—the energy required to extract from the surface the electron needed to neutralize the ion—may be opposite and equal to the free energy of adsorption on the electrode of the adsorbed neutral atom. This hypothesis is based on certain results by Langmuir and Kingdon (1925) regarding the adsorption of caesium vapour by tungsten.

Experimental material (Tammann and Wilson, 1928; Erbacher and Philipp, 1928; Joliot, 1930; Haissinsky, 1932, 1933; Flag and Bleidner, 1945) on the kinetics of electrodeposition is fragmentary.

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## CHAPTER VI

# THE PRODUCTION OF RADIOELEMENTS BY NUCLEAR SYNTHESIS

### 6.1. Cross-sections of nuclear reactions

The members of the natural radioactive series are all isotopes of the elements 81–92, and the last part of the Periodic Table is not necessarily the most interesting part to the radiochemist. True, several isolated radioelements (Table III) are also found in nature. However, the specific activities of these elements are small. Moreover, they are constant, whatever the origin of the material, so that tracer work in presence of the element is impossible. Therefore, the introduction, during the first fifteen years of artificial radioactivity (Joliot and Curie, 1934), of more than a thousand active isotopes (see Seaborg and Perlman's Tables, 1948) has immensely widened the horizon of radiochemistry. The coming of the fission products (see Siegel's Tables, 1946) has given a new impetus, and the multiple disintegration of nuclei by ultra-high energy particles (see Seaborg, 1947) promises to do so again. 'Labelled' atoms of most elements are available now.

Table III. *Isolated natural radioelements*

Active isotope	Type of radiation	References
$^{40}_{19}\text{K}$	$\beta^-$ , $K$	Campbell and Wood (1907); Thompson and Rowlands (1943); Gráf (1948); Floyd and Borst (1949)
$^{87}_{37}\text{Rb}$	$\beta^-$	Campbell and Wood (1907); Haxel, Houtermans and Kemmerich (1948)
$^{162}_{62}\text{Sm}$	$\alpha$	Hevesy and Pahl (1932); Dempster (1948)
$^{176}_{71}\text{Lu}$	$\beta^-$ , $K$	Heyden and Wefelmeier (1938); Libby (1939); Flammersfeld (1947)
$^{187}_{75}\text{Re}$	$\beta^-$	Sugarman and Richter (1948); Seliger and Bradt (1948); Naldrett and Libby (1948)
$^{60}\text{Nd}(?)$	$\beta^-$	Libby (1934); Jha (1949)

The probability of an induced nuclear reaction is expressed in terms of a 'reaction cross-section'  $\sigma$ , i.e. the bombarded nuclei are ascribed effective target areas which must be hit for the reaction

to occur. Therefore, if a material of  $c$  nuclei per c.c., and of thickness  $dl$  is exposed to a beam of  $N$  projectiles/cm.<sup>2</sup> sec., the absorbed quantity per second ( $-dN$ ) in the layer will be

$$-dN = N\sigma c dl.$$

The intensity  $N_l$  of the beam behind a finite thickness  $l$  of the bombarded material is obtained by integration as

$$N_l = N_0 e^{-\epsilon l},$$

with  $N_0$  as the initial intensity of the beam. Obviously, this last equation can also be written as

$$N_l = N_0 e^{-\epsilon l},$$

where  $\epsilon (= \sigma c)$  can be considered as an absorption (or scattering) coefficient, but the use of cross-sections is preferable because of their independence of the density of the material.

The number of nuclei reacting per second is given by the difference of  $N_0$  and  $N_l$ , i.e. it is  $N_0 - N_0 e^{-\epsilon l}$ . If  $(N_0 - N_l)/N_0 \ll 1$ , this expression degenerates into  $N_0 \epsilon l$ .

The total cross-section can be resolved into components due to the (competing) individual reactions occurring simultaneously in the material, including scattering. In mixed elements, the cross-sections are composed of contributions by the different isotopes.

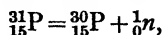
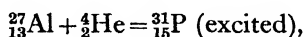
In nuclear processes cross-sections are often of the order of  $10^{-24}$  cm.<sup>2</sup>/nucleus, and this unit of the target area has become known as 1 'barn'. Experimental values of total cross-sections are obtained by measuring the transmission of the beam by the sample. On the other hand, cross-sections of individual reactions are often determined by assaying the activity induced in the sample by a beam of known strength. This 'activation method' distinguishes not only between different reactions of the same nucleus, but also between the contributions of different kinds of nuclei, including isotopes. The methods for the measurement of cross-sections with slow neutrons will be gone into in § 6.9.

## 6.2. The compound nucleus

Uncharged particles (neutrons) enter nuclei without suffering repulsion. Charged particles have to overcome the potential barrier due to the electric charge of the nucleus, before they are affected by the attraction exerted by the specific nuclear forces. This 'Coulomb' barrier is higher for the doubly charged  $\alpha$ -particles

or for still more highly charged projectiles (Alvarez, 1940; Condit, 1942; Tobias and Segrè, 1946; York *et al.* 1946) than for protons and deuterons. Deuterons are the most efficient charged transmuting agents, because a peculiar polarization effect makes possible the interaction of the neutron in the deuteron with the nucleus without actual penetration by the deuteron (Oppenheimer and Phillips, 1935; for tritons see Kundu and Pool, 1948).

Because of the intense interaction of all its constituent particles (nucleons) and its lack of a structure, the nucleus is compared to a droplet of liquid (Bohr, 1936). In the capture of the projectile by the nucleus a transient 'compound nucleus' is formed, which is excited both by the kinetic energy of the projectile and by its binding energy to the target nucleus. The life of the compound nucleus is long enough for the projectile to lose its individual energy, and therefore its identity. Consequently, the mode of the eventual disintegration of the compound nucleus is governed only by its composition and its excitation, but not by the way in which it was made. The compound nucleus ends its life with the emission of one or more photons or particles. If one particle is emitted, this may, or may not, be of the same kind as the projectile. If it is, the net reaction consists in the scattering of the projectile, and depending on whether the nucleus after scattering has its original or an increased internal energy, the scattering is elastic or inelastic. If, on the other hand, the emitted particle is different from the projectile, transmutation has taken place; e.g.



where  ${}_2^4\text{He}$  and  ${}_0^1n$  are the symbols for an  $\alpha$ -particle and a neutron. This reaction can also be described by the 'shorthand' formula  ${}_{13}^{27}\text{Al}(\alpha, n){}_{15}^{30}\text{P}$ . The formula of the compound nucleus  ${}_{15}^{31}\text{P}$  is the same as that of the only isotope of ordinary (natural) phosphorus, but the compound nucleus is highly excited. In the shorthand notation scattering is represented by formulae of the type  $(n, n)$ .

With the help of the conceptions of the potential barrier and the compound nucleus the probabilities of individual types of transmutations can be crudely estimated (see, for example, Irvine, 1948, 1949). For low excitation of the nucleus photon emission is the

only possible mechanism of de-excitation. Only when the excitation reaches the level of the binding energy of particles (ordinarily  $\sim 8$  MeV\*), can particle emission compete with photon emission; an excitation energy of this order may arise from the preceding capture of a projectile. At moderate excitation energies neutron emission is normally preferred to the emission of charged particles, which would have to penetrate the barrier when leaving the nucleus. Important reactions with emission of a neutron are  $(p,n)$ ,  $(d,n)$  and  $(\alpha,n)$ , where  $p$  and  $d$  are the symbols of proton and deuteron. At very high projectile energies (generally  $> 8$  MeV.) more than one neutron may be ejected by the compound nucleus:  $(n,2n)$ ,  $(d,2n)$ ,  $(\alpha,2n)$ . The emission of charged particles [e.g.  $(p,p)$ ,  $(n,p)$ ,  $(d,p)$ ,  $(n,\alpha)$ ,  $(p,\alpha)$  reactions] can compete with the emission of neutrons only if the charge of the nucleus is so low that the barrier is easily penetrated, or if the energy of excitation is very high. Of course, protons leave compound nuclei more easily than do  $\alpha$ -particles. Because of their small intrinsic stability (§ 6.5) deuterons are hardly ever observed in emission. Fission, which can also be regarded as a reaction involving the emission of a charged particle, will be treated in Chapter VII.

Ultra-high energy projectiles (§ 6.1) are capable of disrupting all nuclei into many fragments (Baldwin and Klaiber, 1946; Seaborg, 1946, 1947; Perlman *et al.* 1947).

### 6.3. Types of radioactive decay

De-excitation of the compound nucleus through emission of a  $\beta$ -particle is most unlikely, as  $\beta$ -decay is a very slow process according to nuclear standards. However, the de-excited nucleus is often unstable against  $\beta$ -decay. Here the term  $\beta$ -decay is meant to cover  $\beta^-$ -decay,  $\beta^+$ -decay and orbital electron capture (usually capture of a  $K$ -shell electron: ' $K$ -capture' (Yukawa and Sakata, 1936; Alvarez, 1938). The corresponding changes in the nucleus are described by the equations

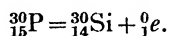
$${}^0_0n = {}^1_1p + {}^0_{-1}e, \quad (1)$$

$${}^1_1p = {}^1_0n + {}^0_1e, \quad (2)$$

$${}^1_1p + {}^0_{-1}e = {}^1_0n. \quad (3)$$

\* 1 MeV. (mega-electron-volt) =  $10^6$  eV. =  $1.60 \times 10^{-8}$  erg =  $3.83 \times 10^{-14}$  gcal.; eV./atom = 23 kcal./mol.

The other particles in the nucleus remain unaffected. Reaction (1) tends to occur in nuclei with a neutron excess, (2) and (3) in nuclei with a proton excess against a stable species of the same mass number  $A$ . Occasionally, not only (2) and (3), but (1) and (2), or (1) and (3), or even all three processes, are observed with one and the same nucleus in competition; this is due to the fact that the two isobars ( $Z$  larger and  $Z$  smaller) may be more stable than the nucleus initially present. An example of a nucleus unstable against  $\beta^+$ -decay is  ${}^{30}_{15}\text{P}$  (see above), which disintegrates with a half-life of 2.55 min. according to



This was the first example of artificial radioactivity (Joliot and Curie, 1934). In reaction (3) no detectable particle is emitted by the nucleus, and only an X-ray is emitted when the place of the captured orbital electron is filled. Practically the whole of the energy of capture is carried off by a neutrino (see Pontecorvo, 1946-47). Only if  $K$ -capture yields an excited state of the product nucleus at first, a  $\gamma$ -ray is also emitted subsequently. The rate of  $K$ -capture should be slightly influenced by the state of chemical binding of the atom (Benoist *et al.* 1948; Leininger, Segrè and Wiegand, 1949).

The body of knowledge concerning  $\gamma$ -ray emission has been reviewed by Feather (1940). Occasionally  $\gamma$ -ray emission by an excited nucleus, which on energetic grounds has no alternative mode of decay, is slow, and the excited nucleus has a 'macroscopic' life span. This happens when the level of excitation lies low (at most a few 100 keV.), and the change in nuclear spin associated with the particular  $\gamma$ -ray emission is large (Weizsäcker, 1936). It is implied that two nuclear species of identical mass and charge, namely, the excited nucleus and the nucleus in the ground state, are both capable of more than a transient existence. The two nuclei are isotopes and isobars, and are referred to as 'isomers' (see Stuhlinger, 1942; Berthelot, 1944; Segrè and Helmholz, 1949). However, in contrast to what is general in chemical isomerism, nuclear isomers can be ascribed only different energy contents, but not different structures. The first discovered case of nuclear isomerism was the couple  $\text{UX}_2\text{-UZ}$  (Hahn, 1921),

and the first case among artificial radioelements the couple  $^{80}\text{Br}$  (Kourtchatow *et al.* 1935). The isomeric nuclei may, or may not, both be unstable against  $\beta$ -decay; in the two quoted cases they are unstable. If the nucleus in the ground state is available in quantity (stable or long-lived), the excited state may be made, i.e. a spontaneous 'isomeric transition' may effectively be reversed, by irradiation with X-rays.

Fairly often the transition energy is not emitted as such, but as kinetic energy of an orbital electron ('internal conversion'). Therefore, the radiochemist must not jump to the conclusion that  $\beta$ -decay must be involved if a radiation is proved to consist of electrons. In contrast to  $\beta$ -rays the electron rays from the internal conversion of  $\gamma$ -rays have sharp line spectra (§ 10.5); the line energies are given by the differences between the sharp excitation energies and the sharp binding energies of the orbital electrons. Quite often electrons from internal conversion are distinguished from  $\beta$ -rays by a shorter half-life for a given energy.

While  $\beta$ -decay is a 'device' to adjust an unstable proton/neutron ratio in a nucleus,  $\alpha$ -decay serves to reduce the Coulomb repulsion inside the nucleus by reduction of the nuclear charge  $Z$ . Though the stabilities of individual nuclei against  $\alpha$ -decay are determined not only by their total charges, but also by their individual compositions (proton/neutron ratio), the process occurs almost exclusively with nuclei of high  $Z$ . In contrast to  $\beta$ -decay, the delay in  $\alpha$ -decay is due not to an inherent slowness of transformation of particles inside the nucleus, but to the difficulty of the heavy charged particles in penetrating the potential barrier.

#### 6.4. The importance of neutrons in radiochemistry

The efficiency of neutrons in transmutations was found by Feather (1932) soon after the discovery of the neutron by Chadwick (1932); about the history of this discovery see Feather (1938). Ultimately almost (see § 7.6) every neutron dies in transmuting a nucleus—even if it has lost practically all its kinetic energy before this happens ('slow neutrons'; Amaldi *et al.* 1935). Admittedly free neutrons themselves have to be made (except in chain reactors) by transmutations induced by charged particles at relatively low yields (§ 6.11). Therefore it might at first sight be

expected that the quantities of radioelements producible by direct bombardment with charged projectiles (from natural radioactive sources, or from high-voltage machines) are not inferior to those made with the neutrons from sources incorporating the natural radioelements, or with neutrons emitted by the targets in the machines. Actually, however, the yields are greatly improved in the 'two-stage' process. The reason is that in the first stage a target material can be chosen (§§ 6.5, 6.6), which because of a low potential barrier and suitable proton/neutron ratio gives good yields of neutrons; in the second stage the uncharged neutrons react easily even with very highly charged nuclei, while the direct penetration of such nuclei by the primary charged projectiles would require excessive energies. The advantage of good yield, however, is bought at a price. As a rule, with slow neutrons the  $(n, \gamma)$  reaction predominates, and leads to isotopes of the target material, which cannot be chemically isolated (see, however, § 9.7); fast neutron reactions, which frequently do give non-isotopic products, have poor yields because of the smaller cross-sections (§ 6.9). In contrast, in transmutations with charged projectiles, e.g. in the  ${}_{38}^{88}\text{Sr}(d, zn){}_{39}^{88}\text{Y}$  reaction, or in the important  ${}_{16}^{32}\text{S}(n, p){}_{15}^{32}\text{P}$  reaction (Erbacher and Philipp, 1939), the product can be separated chemically. Hence the ratio between active and inactive nuclei, and therefore the 'specific activities' in radioactive sources made with slow neutrons will generally be lower than in sources made by direct charged particle bombardment.

A second practical advantage of neutrons is their large range of action (§§ 6.7, 6.8), which enables the radiochemist to work without handling open radioactive material, or having to introduce the substances to be transmuted inside high-voltage machines. Instead, he can work with small capsules enclosing the natural source, or he can arrange the substances externally around the target of the machine. Again there is a drawback connected with the advantage. For good utilization of neutrons for nuclear syntheses many litres of capturing material are needed; even so, many neutrons always escape. Therefore, the distant portions contain the radioelement at great dilution, so that the specific activity is decreased still further. In radioactive equilibrium,

$$A^*/A = nf/A\lambda,$$



where  $A^*$  and  $A$  are the numbers of atoms of the active and the inactive isotope,  $n$  the neutron yield per sec. of the source,  $f$  the usefully captured fraction of the neutrons, and  $\lambda$  the decay constant of the product. If  $A \sim 5 \times 10^{24}$ ,  $n \sim 5 \times 10^6$  (natural source),  $f \sim 0.5$  (an optimistic figure), and  $\lambda \sim 10^{-5}$ ,

$$A^*/A \sim 5 \times 10^{-14}.$$

Their favourable properties—in spite of the small specific activities which are obtained—have made neutrons the principal transmuting agent in radiochemistry. There is one additional reason why neutrons, and particularly slow neutrons, will be treated here in some detail. The movements of slow neutrons—still capable of effecting transmutation—resemble the movements of diffusing chemical agents like ions, atoms and molecules. Magnitudes like the ‘diffusion length’, the ‘albedo’ and the ‘mean life’ can be treated like corresponding magnitudes in chemical dynamics, although naturally the particles vanish in nuclear reactions in the one case, and in chemical reactions in the other. It is hoped that this analogy between slow neutrons and, say, slow protons (hydrogen ions) will be followed up some time. In any case, radiochemists may owe their proven skill in handling slow neutrons partly to the ‘chemical approach’ in which they are trained.

### 6.5. Natural neutron sources

For experiments with fast neutrons, sources of well-defined neutron energy have been devised. For experiments with slow neutrons, which in any case have to be made by slowing down fast neutrons, the initial neutron energies are irrelevant, and only copiousness of emission is aimed at. Postponing the discussion of chain-reactors as neutron sources, the customary distinction between ‘natural’ and ‘artificial’ sources is here adopted. Natural sources consist of a radioelement and a suitable target material; somewhat inconsistently, the radioelement may be artificial. The technique of making sources has been described by McCallum (1949). Highest yields are obtained with beryllium, i.e.  ${}^9\text{Be}$ , as target; its efficiency is due to the abnormally low binding energy of the odd neutron in the nucleus, which otherwise consists of two  $\alpha$ -particles only. The binding energy is 1.63 MeV., compared with

2.23 MeV. in the deuteron, and four or five times as much in most stable nuclei. The energy for the release of the neutrons is supplied by the  $\alpha$ -rays or by the  $\gamma$ -rays of the radioelement. In ' $\alpha$ -sources' the radioelement, e.g. radium as the sulphate, is intimately mixed with a large excess (e.g. 50-fold) of beryllium powder. The mixture is usually kept in a metal capsule. The mixture may be pressed to save volume and keep the yield constant (Anderson and Feld, 1947). Instead of radium, radon (Rn), radiothorium (Rd'Th) or polonium may be used, the first two being most important. In every case the nuclear reaction is mainly  ${}^9_4\text{Be}(\alpha, n){}^{12}_6\text{C}$ , but the reaction  ${}^9_4\text{Be}(\alpha, n){}^4_2\text{He}$  is also observed. Ra-Be sources are permanent, but Rn-Be sources are cheap and convenient as no mechanical mixing is needed and the radon is simply introduced into a tube filled with beryllium powder. Both Ra-Be and Rn-Be sources have high yields per mc. of radioelement because each decaying nucleus (radium or radon) sets off a chain of  $\alpha$ -rays. Po-Be sources have poor yields, but are free from  $\gamma$ -rays. They may consist of polonium deposited on some powdered carrier and mixed with beryllium, or, more cleanly, of polonium deposited on a platinum foil and pressed against a beryllium surface. These sources use only one-half of the  $\alpha$ -rays. All rays are used if the polonium is deposited directly on beryllium by a chemical procedure (Haenny and Haissinsky, 1939) or by distillation (Hernegger, 1940), and this polonium surface pressed against more beryllium.

In most of these sources  $\alpha$ -rays of different energies are effective, and in any case some rays will act on the target material only after some loss of energy in traversing it. Therefore, no  $\alpha$ -source with a thick target can give monoenergetic neutrons. Experimentally it is found that the upper energy limit of the neutrons from Ra- $\alpha$ -Be as well as from Rn- $\alpha$ -Be sources exceeds 12 MeV. (Dunning, 1934) and from Po-Be sources 10 MeV. (Bernardini and Bocciarelli, 1937; Richards, Speck and Perlman, 1946), but most neutrons in the former case probably have energies of 4-5, and in the latter of 2-3 MeV. The largest  $\alpha$ -sources in radiochemical practice include about 1200 mc. of radioelement. A value for the neutron emission per mc. will be given in § 6.11.

The  $\gamma$ -rays produce neutrons through the so-called 'nuclear photo-effect', i.e. through a  $(\gamma, n)$  reaction (Chadwick and Goldhaber, 1934, 1935; Szilard and Chalmers, 1934; Wiedenbeck and Marhofer, 1945). Inevitably even in an  $\alpha$ -source some neutrons will be due to this reaction if the radioelement emits  $\gamma$ -rays. However, for good efficiency large amounts of beryllium must be exposed to the  $\gamma$ -rays. Ra- $\gamma$ -Be and Rn- $\gamma$ -Be sources consist of the radioelement in a capsule, which is surrounded by a block of beryllium. Apart from the (small) absorption of the  $\gamma$ -rays by beryllium, and the energy-degrading Compton scattering, the yield will be nearly proportional to the radius of the beryllium block. Yet with blocks of reasonable size it will still be five or ten times less than from  $\alpha$ -sources with the same amount of radium or radon. Nevertheless,  $\gamma$ -sources are useful. First, the source is easily built up and dismantled. Secondly, the neutron energies are well defined: using a radioelement for which the effective high-energy part of the  $\gamma$ -ray spectrum consists of one line only, and provided the source is small enough not to slow down the neutrons (Hughes and Egglcr, 1947), monoenergetic neutrons are obtained, the available energy, i.e. the difference between the  $\gamma$ -ray energy and the binding energy of the neutron, being shared between neutron and recoil nucleus so that momentum is conserved. If the radioelement is radium or radon in equilibrium with their short-lived descendants, practically the only effective  $\gamma$ -ray is that from RaC of 2.22 MeV. energy. In sources containing the active deposit from thoron it is correspondingly the 2.62 MeV.  $\gamma$ -ray from ThC''. Therefore, the neutron energies from Ra- $\gamma$ -Be or Rn- $\gamma$ -Be sources must be about 0.5 MeV., from RdTh- $\gamma$ -Be and MsTh- $\gamma$ -Be sources about 0.9 MeV., and from a RdTh- $\gamma$ -D source (see Allan and Poole, 1948) about 0.2 MeV. The energies of the neutrons from  $\gamma$ -sources based on artificially made  $\gamma$ -ray emitters (Pecher, 1940; O'Neal, 1941, 1946; Scharff-Goldhaber, 1941; Helmholz, 1942; Wattenberg, 1947; Hanson, 1949) vary between 0.024 ( $^{124}\text{Sb}$ -Be) and 0.83 ( $^{24}\text{Na}$ -Be) MeV. Strong Sb-Be sources have become available on a routine basis (*Science*, **110**, 223 (1949)).

### 6.6. Artificial neutron sources

The advantages of natural sources are ease of acquisition and handling, and constancy of yield, apart from calculable decay. Artificial sources, in which targets are bombarded with artificially accelerated particles, or with artificially produced electromagnetic radiation, supply neutrons more plentifully; moreover, with them monoenergetic neutrons can be obtained at higher and better adjustable energies. Among the common targets in artificial sources again beryllium and deuterium (as heavy ice, heavy phosphoric acid or heavy sodium hydroxide) are found. However, other targets can also be used here, as one is not limited to  $\alpha$ - and  $\gamma$ -rays as projectiles, i.e. to the  $(\alpha, n)$  and  $(\gamma, n)$  reactions, for which beryllium and deuterium enjoy a clear advantage as targets. Some reactions with deuterons as projectiles are listed in Table IV.

Table IV. *Neutron-producing reactions with deuterons*

Reaction	References
${}^2_1\text{D} + {}^2_1\text{D} = {}^3_2\text{He} + {}^1_0n + 3.23 \text{ MeV.}$	Livesey and Wilkinson (1948)
${}^3_1\text{T} + {}^2_1\text{D} = {}^4_2\text{He} + {}^1_0n + 17.6 \text{ MeV.}$	Colby and Little (1946)
${}^9_4\text{Be} + {}^2_1\text{D} = {}^{10}_5\text{B} + {}^1_0n + 4.2 \text{ MeV.}$	See Livingston and Bethe (1937)
${}^7_3\text{Li} + {}^2_1\text{D} = 2 {}^4_2\text{He} + {}^1_0n + 15 \text{ MeV.}$	Green and Gibson (1949)
${}^{12}_6\text{C} + {}^2_1\text{D} = {}^{13}_6\text{N} + {}^1_0n - 0.28 \text{ MeV.}$	Bonner, Evans and Hill (1949)
${}^{13}_6\text{C} + {}^2_1\text{D} = {}^{14}_6\text{N} + {}^1_0n + 5.5 \text{ MeV.}$	Bennett <i>et al.</i> (1941)

Because of the loosely bound neutron in the deuteron, deuteron-induced reactions are generally more useful for neutron generation than proton-induced reactions. In practice, the total available energy in each disintegration must be calculated from the energy of the reaction (Table IV) and the kinetic energy of the projectile. The effective kinetic energy is identical with the energy acquired during acceleration provided the target is thin. Because of the conservation of momentum only part of this kinetic energy becomes available as internal (excitation) energy of the compound nucleus, which is formed in the first stage; the rest appears as kinetic energy of the compound nucleus as a whole. In the second stage, the moving compound nucleus dissociates. The available energy is shared between the neutron and the recoil nucleus so that momentum is again conserved. Obviously those

neutrons, which happen to be emitted in the forward direction, must in the laboratory co-ordinates appear more energetic than other neutrons. If more than one product nucleus is formed in addition to the neutron (as in the  ${}^7_3\text{Li-D}$  reaction) or if the product nucleus may emerge in an excited state (as in the  ${}^9_4\text{Be-D}$  reaction), the neutron energy is indeterminate even with a thin target and in a fixed direction.

We may consider as an example the case in which deuterons of 1 MeV. are employed. Then the D-D reaction gives neutrons of about 2-4 MeV., and the (endothermic)  ${}^{12}\text{C-D}$  reaction of 0.5-0.7 MeV., according to direction. The  ${}^{13}\text{C-D}$  reaction adds some faster neutrons to the C-D spectrum, but fortunately  ${}^{13}\text{C}$  is not very abundant in natural carbon. The neutron energies and yields from the Be-D and  ${}^7\text{Li-D}$  reactions (Table V) are superior to those from the D-D and  ${}^{12}\text{C-D}$  reactions, but the neutron spectra are complex. Neutron energies up to  $\sim 10^8$  MeV. have been obtained with ultra-high energy projectiles (Helmholz, McMillan and Sewell, 1947).

Table V. *Increase of neutron yield with deuteron energy*

Reaction	Deuteron energy (MeV.)					
	0.1	0.3	0.4	0.6	0.8	1
$\text{D}_3\text{PO}_4 + \text{D}$	6	48	140	250	550	860
$\text{Li} + \text{D}$	—	40	160	800	4200	—
$\text{Be} + \text{D}$	—	9	100	700	2400	6800
$\text{C} + \text{D}$	—	—	—	10	140	680

Neutron yields increase with the energy of the bombarding particle because of improved penetration of the nuclei. In Table V some yields (expressed as the equivalent strength of a Rn-Be source in mc. per microampere ion current (i.e. for a current of  $6.3 \times 10^{12}$  deuterons/sec.) are given after Amaldi, Hafstad and Tuve (1937) and Ladenburg and Roberts (1936). The yields refer to thick targets; for thin targets see Bennett, Mandeville and Richards (1946). The figures for lithium are uncertain on experimental grounds, and the yields for deuterium are obviously far smaller than they would be with the pure element as target. Ion currents of 10-100  $\mu\text{A}$ . are often available. Consequently,

for example, the intensity of a Be-D source at 1 MeV. and 100  $\mu$ A. would correspond to that of a Rn-Be source of 680 c. Smith and Kruger (1948) have bombarded beryllium with 10 MeV. deuterons and report a neutron yield of  $3.7 \times 10^{10}$ /sec./ $\mu$ A. At only 10  $\mu$ A. this would correspond to a source strength equivalent to 25,000 c. Rn-Be and to a fast neutron flux of  $3 \times 10^{10}$  sec.<sup>-1</sup>cm.<sup>-2</sup> at 1 cm. from the source.

When beryllium is exposed to the intense beam of X-radiation from a high-energy X-ray tube (Brasch *et al.* 1934) or from a betatron, large neutron yields from the nuclear photo-effect are obtained. The X-ray source can, like  $\gamma$ -ray sources, be surrounded usefully with large quantities of beryllium, but in this case the primary radiation is not monochromatic, and the neutron spectrum must be complex.

The endothermic proton-induced reaction  ${}^7_3\text{Li}(p,n){}^7_4\text{Be}$  (see Smyth Report,\* p. 132, and Shoupp, Jennings and Jones, 1949) is a convenient source of monoenergetic neutrons. Their energy is adjusted by varying the proton energy beyond the threshold voltage of 1.88 MeV. (Herb, Snowdon and Sala, 1949). Neutrons of energies between 0.005 and 2 MeV. have been produced in this way (Daniels, 1946). Another source of monoenergetic neutrons, with a threshold of 0.99 MeV., is offered by the reaction (Taschek *et al.* 1949)  ${}^3_1\text{T}(p,n){}^3_2\text{He}$ .

### 6.7. Slowing down of neutrons

The energy of the neutrons at the time of emission is  $10^6$ – $10^9$  times the kinetic energy of particles in thermal equilibrium at room temperature (effective energy, according to Goldsmith and Rasetti, 1936, about 600 gcal./mol. =  $\frac{1}{40}$  eV./particle). Slow neutrons, including neutrons (nearly) in thermal equilibrium (thermal neutrons), can be made only by slowing down in 'moderators' the fast neutrons emitted by the sources (Amaldi *et al.* 1935). Because of their lack of charge, neutrons lose energy in matter mainly in collisions with nuclei, not by interaction with the orbital electrons, as do  $\alpha$ - and  $\beta$ -rays. According to the basic laws of mechanics, on an average most energy is lost in collisions with

\* Quotations from the Smyth Report refer to the British edition [H.M. Stationery Office, London (1945)].

particles of equal mass, and therefore hydrogen is the most efficient moderator for neutrons. In hydrogen, which is applied as water or paraffin wax, on an average neutron energy is reduced by a factor  $1/e$  in each collision, and about 14 collisions are needed to slow down a neutron from  $10^6$  to 1 eV. As soon as the remaining energy falls to the magnitude of the vibrational quanta of the O-H (water) or C-H (wax) bonds, the average energy loss per collision decreases. The hydrogen atoms cannot accept energy of less than one quantum.

Because of the small scattering cross-section of hydrogen, the mean free path of the fast neutrons from a Rn-Be source is as much as 5 cm. (Dunning, 1934; Booth and Hurst, 1936; Tuve and Hafstad, 1936). With decreasing neutron energy the scattering cross-section of hydrogen increases. At a few electron-volts the mean free path is only about 1 cm., and at thermal energy 0.3 cm. (Amaldi and Fermi, 1936; see § 6.9). During slowing down the neutron changes its direction of motion many times, but on an average some forward motion persists until thermal equilibrium is approached. Therefore, fairly large volumes of moderator are required for nuclear synthesis with neutrons (§ 6.4). The 'slowing-down length'  $L_s$

$$L_s^2 = \frac{1}{6} \bar{r}^2$$

( $\bar{r}^2$  is the mean square distance required by the neutron to be slowed down from a given initial to a given final energy), depends on the mean free path between the collisions, the average energy loss in each collision, and the average angle of scattering in each collision. In water the slowing-down length of Rn-Be neutrons to thermal energy is about 7 cm. The time needed for slowing down in water from 1 MeV. to 1 eV. is only about 1  $\mu$ sec., and from 1 eV. to thermal energy 10  $\mu$ sec. (Amaldi, 1937). In the less efficient moderators, deuterium (heavy water) and carbon, the slowing-down lengths and times are many times larger. In carbon the slowing-down length of (fission) neutrons is  $\sim 17$  cm. (Fermi, 1947). Most valuable and comprehensive accounts of the slowing-down of neutrons and the properties of slow neutrons have been given by Amaldi and Fermi (1936) and Amaldi (1937).

### 6.8. Slow neutrons

The term 'slow neutrons' is commonly applied to neutrons of energy less than 1000 eV. 'Slow neutrons', according to this definition, are absorbed chiefly when their energies are rather small, and then either in accordance with the ' $1/v$  law' (§ 6.9) over a relatively wide range of energy, or in energy bands. The nuclear reaction is, with a few exceptions, simple 'radiative capture' ( $n, \gamma$ ). Because of the small kinetic energies of the slow neutrons the excitation energies of the compound nuclei are practically equal to the neutron binding energies, and are insufficient for reactions other than radiative capture or scattering. The energy bands ('resonance bands'), first observed by Moon and Tillman (1936) and explained by Bohr (1936) and Breit and Wigner (1936), may be located in or above the thermal region. Their position with the individual nuclear species cannot be predicted theoretically, but it can be understood that the average separation of the resonance levels from each other decreases with increasing complexity of the nucleus, and is about 20 eV. in heavy nuclei. The lightest nuclei, including the nuclei in moderators, do not show resonance capture at all.

One absorption band of an isotope of cadmium happens to be effective between zero energy and about 0.30 eV. (§ 6.9). This enables crude discrimination between the effects of thermal and faster neutrons by measuring the same effect with and without shielding of the sample with cadmium sheet, i.e. by taking the 'cadmium difference'. Examples of resonance absorption bands at somewhat higher energies are:  $^{115}\text{In}$  at 1.44 eV. (Havens and Rainwater, 1946; McDaniel, 1946) and  $^{127}\text{I}$  at 20.6 eV. (Jones, 1947). The term 'epithermal' neutrons has come to refer to all slow neutrons except thermal neutrons.

Neutrons which are truly in thermal equilibrium with the moderator at any temperature must obey the Maxwell-Boltzmann velocity distribution law for that temperature. The average velocity of these 'kT-neutrons' must therefore be the same, to a close approximation, as in atomic hydrogen at the same temperature (about 2200 m./sec. at 15° C.). It has fairly recently been established that inside a large mass of material containing hydrogen 'thermal' neutrons do not in fact possess a Maxwell-Boltzmann



spectrum, but are 'hotter'. 'Thermal' neutrons produced in hydrogen are thus thermal only in the sense of having energies in the thermal region. The failure to reach true thermal equilibrium is due to the preferential capture of the slowest neutrons by hydrogen in accordance with the ' $1/v$  law' (§ 6.9). The spectrum of the 'thermal' neutrons diffusing out of hydrogen-containing media is still further distorted, because in these media the mean free path of the neutrons decreases (the scattering cross-section increases) with decreasing neutron energy (§ 6.9); therefore, the 'hotter' neutrons have a better chance than the 'cooler' neutrons of being emitted from the inside of the medium without being scattered back into the interior by the surface layer. The velocities of 'thermal' neutrons diffusing out of wax at about 300° K. fit, on the whole, a Maxwellian distribution for 400° K., with an additional excess of hot neutrons of >3500 m./sec. (Manley, Berger and Gillette, 1946; Manley, Haworth and Luebke, 1946; Rainwater and Havens, 1946; Bacher, Baker and McDaniel, 1946), but the precise form of the spectrum seems to depend upon the experimental conditions.

In heavy water and carbon (graphite) thermal equilibrium is more nearly reached (Fermi, Marshall and Marshall, 1947). The smallness of the capture cross-sections of these materials (§ 6.9) and the consequent long life of the thermal neutrons more than compensate for their lesser efficiencies as moderators. However, also in the case of carbon the spectrum of the emitted neutrons differs from the 'internal' spectrum, although for another reason than in the case of hydrogen. A diffraction effect in the graphite lattice makes for preferential emission of cold neutrons. In one arrangement an effective emission temperature as low as 18° K. has been observed. From the standpoint of radiochemistry, carbon is a useful moderator only in conjunction with a chain reactor, as otherwise the neutron density is cut down excessively by the large slowing-down length (§ 6.7).

### 6.9. Cross-sections for thermal neutrons

Except in the neighbourhood of a resonance band, slow neutrons are always absorbed with a cross-section inversely proportional to the velocity (' $1/v$  law'). This applies to radiative capture as well

as to the few processes induced by slow neutrons which involve the emission of charged heavy particles, particularly the  ${}^6_3\text{Li}(n,\alpha){}^3_1\text{H}$  (§§ 8.7, 10.2),  ${}^{10}_5\text{B}(n,\alpha){}^7_3\text{Li}$  (§ 10.2),  ${}^{14}_7\text{N}(n,p){}^{14}_6\text{C}$  (§§ 7.7, 8.8) and  ${}^{35}_{17}\text{Cl}(n,p){}^{35}_{16}\text{S}$  (§ 7.7) reactions and fission (§ 7.2). The  $1/v$  law is understood from the fact that in the absence of resonance the probability of the capture of a neutron by an individual nucleus increases with the time spent by the neutron in the vicinity of the nucleus, i.e. with the inverse of the velocity. If the cross-section for 0.025 eV. neutrons (of velocity  $v_0$ ) is  $\sigma_0$ , and for slow neutrons of velocity  $v$  is  $\sigma$ ,

$$v\sigma = v_0\sigma_0.$$

Remembering (§ 6.1) that

$$-dN = Nc\sigma dl,$$

one obtains

$$-\frac{1}{N} \frac{dN}{dl} = \frac{cv_0\sigma_0}{v},$$

i.e. what may be termed the 'capture probability per unit absorber thickness' decreases with increasing velocity. Applying the  $1/v$  law to the integral equation, one has

$$N = N_0 e^{-cv_0\sigma_0 l/v}.$$

On the other hand, it will be seen that the 'capture probability per unit time' is independent of velocity. It depends equally on the cross-section of the individual nucleus for a neutron of the given velocity, and on the thickness of the layer passed by the neutron per unit time, and can be written

$$-\frac{1}{N} \frac{dN}{dt} = c\sigma v,$$

or, after integration, as  $N = N_0 e^{-c\sigma vt}$ .

Clearly for ' $1/v$  absorbers' this expression, describing 'absorption in time', becomes

$$N = N_0 e^{-c\sigma_0 v_0 t}.$$

This means that in a medium of sufficient extent to render leakage of neutrons unimportant, i.e. in a medium in which a neutron spends all its life, the rate of capture of all slow neutrons is the same. The reciprocal value of the 'capture probability per unit time', i.e.  $1/c\sigma v$  (for  $1/v$  absorbers  $1/c\sigma_0 v_0$ ) may be considered as the 'mean life' of the neutrons in the medium, just as  $1/c\sigma$  may be considered as their (absorption) 'mean path'. This magnitude

is denoted by  $\lambda_a$ , while the scattering mean path, i.e. the mean free path, is  $\lambda_s$ . If the medium contains several kinds of absorbing nuclei, all obeying the  $1/v$  law, simple extension gives (Frisch, Halban and Koch, 1938)

$$-\frac{1}{N} \frac{dN}{dl} = (c'\sigma'_0 + c''\sigma''_0 + \dots) \frac{v_0}{v}$$

and

$$-\frac{1}{N} \frac{dN}{dt} = (c'\sigma'_0 + c''\sigma''_0 + \dots) v_0.$$

Because of the importance of boron for neutron counters (§ 10.2), the validity of the  $1/v$  law for the  $^{10}\text{B}(n, \alpha)^7\text{Li}$  reaction has been examined with special care by transmission methods (Fryer, 1942; Bacher, Baker and McDaniel, 1946; Manley, Haworth and Luebke, 1946; Rainwater and Havens, 1946; Sutton *et al.* 1947; see Dunning, 1946) and is now accepted. According to Bacher, Baker and McDaniel, the capture cross-section of natural boron for 0.025 eV. neutrons is 708 barns.

The radiative capture cross-sections of many elements for thermal neutrons have also been measured by transmission experiments (attenuation of a beam). However, the simple transmission method breaks down where the scattering cross-section (see below) is comparable with the capture cross-section. Variants of the transmission method have been devised to minimize the influence of scattering. For instance, the 'sample'—which must absorb better than water—may be dissolved in water, and the decrease in the local density of the thermal neutrons, in one selected spot, due to the presence of the dissolved absorber, is compared with the corresponding decrease due to the introduction into the solution of a standard absorber, usually boron (Lapointe and Rasetti, 1940). Instead of dissolving sample and standard, one may compare the local density decreases due to the neighbourhood of pieces of absorbers (Coltman and Goldhaber, 1946). A method, which eliminates the scattering influence more reliably, will be given at the end of § 6.10. More recently, the effect of the 'samples' on the reproduction factor of a chain-reactor ('poisoning') has been compared to the effect of a standard absorber (Anderson *et al.* 1947; Langsdorf, 1948). As an alternative to these transmission methods in the widest sense, activation

methods (§ 6.1) can be used provided every capture leads to a  $\beta$ -active nucleus. The activation of the sample by a given density of neutrons is measured against the activation of a standard absorber, e.g. manganese.

Values of the cross-sections for thermal neutrons ought to refer to a standard energy (0.025 eV.). Usually the thermal neutrons which are used have a complex spectrum with unknown average energy (§ 6.8). However, as long as the  $1/v$  law holds for the 'sample' as for the standard used for calibration, no error is introduced into the transmission or activation experiments. Since the  $1/v$  law can never hold for resonance capture, the cadmium difference has to be used instead of the total effect wherever resonance absorption above the thermal region takes place. When the resonance absorption occurs inside the thermal region, so that the  $1/v$  law does not apply even here, significant values of cross-sections for thermal neutrons can be given only for sharply defined individual energies, or for a rigidly defined neutron spectrum. For instance, for  $^{113}\text{Cd}$  (Moyer, Peters and Schmidt, 1946; Dempster, 1947), which shows resonance capture in the thermal region, the cross-section at maximum (0.18 eV.; Rainwater and Havens, 1946) appears to be about 62,000 barns. For 0.025 eV. neutrons the value is roughly 20,000, and for an ordinary spectrum of thermal neutrons 25,000 barns. The product of capture in this case is a stable species.

In Table VI the thermal capture cross-sections (almost all for radiative capture) of important nuclei, presumed to be (nearly)  $1/v$  absorbers, have been collected. They are normalized to  $\sigma_B = 708$  barns. It is seen that the cross-sections vary widely from one nuclear species to the next. As in the case of the location of the resonance bands, no theoretical explanation of individual values may be expected from current nuclear theory. Superscripts are omitted where the data refer to the natural mixture of isotopes. No half-lives are listed in these cases; such data are derived from transmission experiments. Most activation cross-sections have been selected from the results of the extensive investigation by Seren, Friedlander and Turkel (1947). Useful tables of absorption cross-sections have been compiled by Goldsmith, Feld and Ibsen (1947), and by Mattauch and Flammersfeld (1949).

Table VI. *Selected capture cross-sections for thermal neutrons*

Capturing material	Natural abundance (%)	Half-life of radioelement	Capture cross-section (barns)	Experimental method	Ref.	Remark
$^1_1\text{H}$	—	—	$\sim 0.37$	Decay of density	8	Almost all $^1_1\text{H}$
$^2_1\text{D}$	0.02	12 yr.	0.0009	Diffusion length	10	(n, $\gamma$ )
$^3_3\text{Li}$	—	—	72	Beam attenuation	9	Mostly $^6_3\text{Li}$ (n, $\alpha$ )
$^4_2\text{Be}$	100	$\sim 3 \times 10^6$ yr.	0.009	Diffusion length	11	(n, $\gamma$ )
$^6_5\text{B}$	—	—	708 (standard)	Beam attenuation	14	Mostly $^{10}_5\text{B}$ (n, $\alpha$ )
$^{12}_6\text{C}$	—	—	0.049	Diffusion length	12	Purity uncertain
$^{14}_7\text{N}$	—	—	1.4	Local reduction	2	Mostly $^{14}_7\text{N}$ (n, p)
$^{16}_8\text{O}$	—	—	very small	—	—	—
$^{19}_9\text{F}$	100	12 sec.	0.0094	Activation	1	(n, $\gamma$ )
$^{23}_{11}\text{Na}$	100	14.8 hr.	0.63	Activation	1	(n, $\gamma$ )
$^{27}_{13}\text{Al}$	100	2.4 min.	0.21	Activation	1	(n, $\gamma$ )
$^{30}_{14}\text{Si}$	3.05	170 min.	0.12	Activation	1	(n, $\gamma$ )
$^{31}_{15}\text{P}$	10	14.3 days	0.23	Activation	1	(n, $\gamma$ )
$^{32}_{16}\text{S}$	—	—	0.6	Beam attenuation	15	(n, $\gamma$ )
$^{35}_{17}\text{Cl}$	75.4	87.1 days	0.17	Activation	1	(n, p)
$^{37}_{17}\text{Cl}$	24.6	37 min.	0.56	Activation	1	(n, $\gamma$ )
$^{39}_{19}\text{K}$	—	—	3.8	Local reduction	2	(n, $\gamma$ )
$^{41}_{19}\text{K}$	6.6	12.4 hr.	1.0	Activation	1	(n, $\gamma$ )
$^{40}_{20}\text{Ca}$	97.0	8.5 days	$< 0.00012$	Activation	1	(n, $\gamma$ )
$^{50}_{20}\text{Cr}$	4.5	26.5 days	11	Activation	1	(n, $\gamma$ )
$^{55}_{24}\text{Mn}$	100	2.59 hr.	10.7	Activation	1	(n, $\gamma$ )
$^{56}_{26}\text{Fe}$	—	—	2.2	Beam attenuation	13	(n, $\gamma$ )
$^{59}_{27}\text{Co}$	100	10.7 min.	0.66	Activation	1	(n, $\gamma$ )
$^{58}_{27}\text{Co}$	100	5.3 yr.	21.7	Activation	1	(n, $\gamma$ )
$^{64}_{28}\text{Ni}$	0.88	2.6 hr.	1.06	Activation	1	(n, $\gamma$ )
$^{63}_{29}\text{Cu}$	70.1	12.8 hr.	2.82	Activation	1	(n, $\gamma$ )
$^{65}_{29}\text{Cu}$	29.1	5 min.	1.82	Activation	1	(n, $\gamma$ )
$^{64}_{30}\text{Zn}$	50.9	250 days	0.51	Activation	1	(n, $\gamma$ )
$^{66}_{30}\text{Zn}$	17.4	57 min.	1.09	Activation	1	(n, $\gamma$ )
$^{68}_{30}\text{Zn}$	17.4	13.8 hr.	0.31	Activation	1	(n, $\gamma$ )
$^{75}_{33}\text{As}$	100	26.8 hr.	4.2	Activation	1	(n, $\gamma$ )
$^{79}_{35}\text{Br}$	50.6	18 min.	8.1	Activation	1	(n, $\gamma$ )
$^{81}_{35}\text{Br}$	50.6	4.4 hr.	2.8	Activation	1	(n, $\gamma$ )
$^{81}_{35}\text{Br}$	49.4	34 hr.	2.2	Activation	1	(n, $\gamma$ )
$^{103}_{45}\text{Rh}$	100	44 sec.	137	Activation	1	(n, $\gamma$ )
$^{108}_{46}\text{Rh}$	100	4.2 min.	11.6	Activation	1	(n, $\gamma$ )
$^{107}_{47}\text{Ag}$	51.9	2.3 min.	44.3	Activation	1	(n, $\gamma$ )

Table VI (cont.)

Capturing material	Natural abundance (%)	Half-life of radioelement	Capture cross-section (barns)	Experimental method	Ref.	Remark
<sup>109</sup> <sub>47</sub> Ag	48.1	42 sec.	97	Activation	1	(n, γ) } Iso-
<sup>109</sup> <sub>47</sub> Ag	48.1	225 days	2.2	Activation	1	(n, γ)* } mers
<sup>47</sup> Ag	—	—	57	Beam attenuation	5	(n, γ)
<sup>48</sup> Cd	—	—	2,500	Beam attenuation	9	Mainly resonance
<sup>113</sup> <sub>49</sub> In	4.5	48 days	56	Activation	1	(n, γ)
<sup>115</sup> <sub>49</sub> In	95.5	13 sec.	52	Activation	1	(n, γ) } Iso-
<sup>115</sup> <sub>49</sub> In	95.5	54 min.	145	Activation	1	(n, γ)* } mers
<sup>121</sup> <sub>51</sub> Sb	56	2.8 days	6.8	Activation	1	(n, γ)*
<sup>123</sup> <sub>51</sub> Sb	44	60 days	2.5	Activation	1	(n, γ)*
<sup>127</sup> <sub>53</sub> I	100	25 min.	6.25	Activation	1	(n, γ)
<sup>138</sup> <sub>56</sub> Ba	71.7	86 min.	0.51	Activation	1	(n, γ)
<sup>64</sup> Gd	—	—	48,000	Beam attenuation	4	Slight resonance
<sup>186</sup> <sub>64</sub> Dy	27.6	140 min.	2,620	Activation	1	(n, γ) } Iso-
<sup>186</sup> <sub>66</sub> Dy	27.6	1.25 min.	120	Activation	1	(n, γ)* } mers
<sup>184</sup> <sub>74</sub> W	30.1	77 days	2.1	Activation	1	(n, γ)
<sup>186</sup> <sub>74</sub> W	29.8	24.1 hr.	34.2	Activation	1	(n, γ)
<sup>76</sup> Os	—	—	17	Beam attenuation	6	(n, γ)
<sup>191</sup> <sub>77</sub> Ir	38.5	70 days	1,000	Activation	1	(n, γ)
<sup>193</sup> <sub>77</sub> Ir	61.5	20.7 hr.	128	Activation	1	(n, γ)
<sup>77</sup> Ir	—	—	405	Beam attenuation	5	(n, γ)
<sup>197</sup> <sub>79</sub> Au	100	2.7 days	96	Activation	1	(n, γ)
<sup>80</sup> Hg	—	—	~400	Beam attenuation	9	Resonance
<sup>204</sup> <sub>82</sub> Pb	1.5	67 min.	<0.05	Activation	7	(n, γ)
<sup>208</sup> <sub>82</sub> Pb	52.3	3.3 hr.	<0.002	Activation	7	(n, γ)
<sup>82</sup> Pb	—	—	0.27	Local reduction	3	(n, γ)
<sup>208</sup> <sub>83</sub> Bi	100	5 days	0.015	Activation	1	(n, γ)*

\* May be somewhat too high owing to the presence of some resonance neutrons.

## References.

- Seren, Friedlander and Turkel (1947).
- Lapointe and Rasetti (1940).
- Coltman and Goldhaber (1946).
- Brill and Lichtenberger (1947).
- Rainwater *et al.* (1947).
- Wu, Rainwater and Havens (1947)
- Maurer and Ramm (1942).
- Stanley, Haworth and Luebke (1942).
- Havens and Rainwater (1946).
- Sargent *et al.* (1947).
- See Goodman (1947b).
- Anderson *et al.* (1947).
- Havens *et al.* (1948).
- Bacher, Baker and McDaniel (1946).
- Rainwater *et al.* (1948).

In contrast with the capture cross-sections, the scattering cross-sections for slow neutrons are almost independent of neutron velocity for most elements. Moreover, they are of the same order (mostly around 6 barns). Owing to a quantum effect connected with chemical binding, the lightest nuclei are exceptions (see Amaldi, 1937). The scattering cross-section of hydrogen in wax increases with decreasing velocity, and reaches about 58 barns for neutrons of exactly 0.025 eV. However, the effective cross-section of thermal neutrons in wax, etc., is less (Rainwater *et al.* 1948; see § 6.7).

Comparison with the capture cross-section shows that on an average a  $kT$ -neutron suffers about 150 collisions in hydrogen before capture. Its (absorption) mean path is  $\sim 50$  cm. Its mean life is  $\sim 220 \mu\text{sec.}$ , i.e. neutrons of any initial energy in water or wax spend the largest part of their lives as thermal neutrons. In heavy water and carbon the numbers of collisions before capture are of the orders of 10,000 and 1000, respectively. The two characteristic cross-sections, together with the density of the material, determine the 'diffusion length',  $L_d$ , which is defined, in analogy to the slowing-down length (§ 6.7), by

$$L_d^2 = \frac{1}{3} \bar{r}^2$$

( $\bar{r}^2$  is the mean square distance between the point where the neutron reaches thermal energy and the point where it dies in capture), through the equation

$$L_d^2 = \frac{\lambda_s \lambda_a}{3}.$$

The diffusion length is connected with the diffusion constant  $D$  by

$$L_d^2 = D/c\sigma v.$$

In water, the experimental diffusion length is about 2.88 cm. (Allison, 1948), in heavy water about 170 cm. (Sargent *et al.* 1947) and in carbon about 50 cm. (Hereward *et al.* 1947).

Another important concept determined by the capture and scattering cross-sections is the 'albedo'  $a$ , i.e. the probability of the eventual re-emergence of a thermal neutron which enters a plane surface bounding an infinite quantity of matter of a particular kind. A large thin sheet of capturing material, e.g. a 'detector' (§ 6.10), in a neutron-bearing medium, has approximately

$$1 + a + a^2 + \dots = 1/(1 - a)$$

chances of absorbing one and the same neutron, provided the probability of capture in the sheet is much smaller than in the medium. In water or wax the albedo is large (about 0.8), and therefore the sheet has about five chances of absorbing the neutron. If, however, the probability of capture in the detector cannot be neglected (case of a 'thick' detector), the number of crossings will be reduced. Therefore, the ratio of the indications of the local neutron density by thick and thin detectors depends on the albedo of the medium.

In presence of a moderator, radiative capture of thermal neutrons accounts for the bulk of the induced activity. The capture cross-sections for fast neutrons are small. They amount to  $10^{-4}$  barns with nuclei of mass  $A \sim 15$ , increase (regularly) to only  $10^{-1}$  barns with nuclei of mass  $A \sim 100$ , and remain constant with still heavier nuclei (Hughes, Spatz and Goldstein, 1949; see also Sherman, Hughes and Wallace, 1949). Much larger cross-sections are 'encountered' during slowing down in media containing resonance absorbers. For instance the cross-section of  $^{115}\text{In}$  in its resonance band is 11,000 barns (Havens and Rainwater, 1946). However, as only a fraction of the neutrons falls into these narrow energy bands (traps) during slowing down, activation by resonance neutrons is also less than activation by thermal neutrons.

In the thermal region, capture by the moderator competes with capture by the target nuclei. However, it is seen from Table VI that the capture cross-sections of the important moderators are not excessive. In practice, for instance about two-thirds of the activity induced in a solution of iodide is due to thermal neutrons. In solution of manganese 95%, and in solution of dysprosium 99% are so induced.

### 6.10. Density distributions of slow neutrons

The density distributions of slow neutrons in extended media are explored with 'point-like' detectors. These usually consist of thin sheets of substances, which are rendered  $\beta$ -active by capture of slow neutrons, or of neutron counters (boron chambers, see § 10.2). In uniform media the detector response is proportional to the local concentration of the effective neutrons, provided the absorption in the detector is small compared with the absorption



in the surrounding medium, i.e. provided the distribution remains undisturbed. With detectors obeying the ' $1/v$  law' the response is independent of velocity, and the total density of slow neutrons is directly obtained. Amaldi and Fermi (1936) investigated the distribution of slow neutrons in a sphere of water surrounding a neutron source. The detectors consisted of rhodium, silver or of an iodine salt. All these detectors show resonance absorption above the thermal region, and therefore they can be used (with cadmium shielding) to explore the distribution of neutrons of the energies corresponding to their particular resonance bands, or (by taking the cadmium difference) to explore the distribution of the thermal neutrons. For the latter purpose manganese or dysprosium detectors (§ 6.8) would be even better. The absolute values of the response are immaterial, since they depend on experimental details like the mass of the detector, the sensitivity of the  $\beta$ -ray counting device, etc.; only relative values are important. The most significant distribution curve is that drawn by plotting against the abscissa  $R$  (distance from the source) not the detector indication  $I$ , but the product  $IR^2$ , i.e. the indication times the relative volume of a spherical shell of unit thickness at the distance in question. In this way the trivial influence of the increase of the volume over which the neutrons must spread is excluded; the ordinates measure the total numbers of slow neutrons at the different distances, and not the densities.

For each slow neutron energy the  $IR^2/R$  curve is found to have a rounded maximum at a distance of a few centimetres from the neutron source. The slope on the near side is greater than on the far side. At  $R=0$ ,  $IR^2$  is zero, while for large  $R$  the values of  $IR^2$  decrease roughly exponentially. The initial increase is caused by the fact that all neutrons originate as fast neutrons in the source from which they travel a considerable distance (§ 6.7) before they become slow enough to influence the detectors. Relatively few ever diffuse back to the centre, since the diffusion length is small compared with the slowing-down length of the neutrons (§§ 6.7, 6.9). The decrease at large distances, on the other hand, arises from the gradual depletion of the fast neutrons due to slowing down. With increasing distance, the ratio of the densities of fast and slow neutrons approaches an equilibrium value. The distance from the source to the maximum ( $I < Ag < Rh$ ) is the larger the less the

energy of the resonance band, and is largest for thermal neutrons ( $\sim 10$  cm. for a Rn-Be source).

Since the distribution of the slow neutrons depends upon the distribution of the fast neutrons, the shape of the density distribution curve for slow neutrons of any energy, in a given medium, is characteristic of the particular fast neutron source. To a good approximation, addition to the medium of material, which acts as a mere absorber of neutrons, can only influence all ordinates to the same extent, and cannot change the shape of the  $IR^2/R$  curve. Hence the proof (Halban, Joliot and Kowarski, 1939) that the presence of uranium profoundly alters the shape of the curve for water by spreading it out, was equivalent to the proof that uranium cannot act as a mere absorber, but must act as a secondary source of neutrons as well (§ 7.6).

A second consequence is that no region in a volume of water, however distant from the source, may contain pure slow neutrons. This ceases to be true as soon as the primary neutrons are so slow that their slowing-down length is inferior to the diffusion length (Goldhaber and O'Neal, 1941). Another possibility of making pure thermal neutrons consists in the use of carbon or deuterium as moderators; in both media the diffusion lengths are large (§ 6.9). To eliminate the fast neutrons, either method requires work at a large distance from the source. Therefore, this must be intense. Uranium-free 'thermal columns' made of graphite or heavy water are in fact attached to chain-reactors.

The area  $A$  under the neutron distribution curve, usually determined by graphical integration (Amaldi, Hafstad and Tuve, 1937), is proportional to the total number of effective neutrons in the system. Only thermal neutrons will be considered here. The determination of the area may serve either (keeping the medium constant) to compare the yields of different sources (§ 6.11), or it may serve (keeping the source constant) to measure the average capture cross-section of the medium. If the unstarred and starred magnitudes refer to two media to be compared, clearly

$$A/A^* = (c^{*'}\sigma_0^{*'} + c^{*''}\sigma_0^{*''} + \dots) / (c'\sigma_0' + c''\sigma_0'' + \dots)$$

as the numbers of neutrons 'alive' are proportional to their absorption mean paths in the media (§ 6.9).

If a solvent (1) and a solution (2) are compared,

$$A_1/A_2 = (c'\sigma'_0 + c''\sigma''_0)/c'\sigma'_0.$$

Therefore, if the concentrations are known,  $\sigma''_0$  (cross-section of the solute) may be calculated in terms of  $\sigma'_0$  (cross-section of the solvent).

In a system of limited size, the neutron distribution curve may be followed only up to a certain point. Therefore, the neutrons escaping through the boundary must be accounted for experimentally or by calculation. This correction is applied easily with systems based on hydrogen; because of the large diffusion length, the correction is more difficult with carbon-based systems (Smyth *Report*, p. 142).

In practice, instead of measuring the densities in many places with point-like detectors, and calculating the area by graphical integration, the detecting substance may be mixed into (dissolved in) the medium, chemically isolated after irradiation and stirring, and the activity of an aliquot measured. The activity is proportional to the area under the curve ('method of physical integration'; Booth and Hurst, 1937; Fermi, Anderson and Szilard, 1939). If the specific activity of the dissolved detector is small, the Szilard-Chalmers concentration (§ 9.7) may be combined with physical integration.

### 6.11. Yields of neutron sources

Relative numerical values of the neutron yields of sources, natural or artificial, are obtained by calibration against a standard source. The common calibration method consists in slowing down the neutrons in a standard medium and measuring the area under the density distribution curve (§ 6.10). In a standard medium, the area is proportional to source strength, whatever the neutron spectrum, since practically all neutrons must sooner or later appear as detectable slow neutrons. Rn- $\alpha$ -Be sources, which require no mechanical mixing, are popular as standard sources. Bretscher *et al.* (1949) have recommended the use of the stoichiometric salt RaBeF<sub>4</sub>.

The absolute yield of a 'natural' source was first measured by Jäckel (1934), who counted the recoil protons projected into a known solid angle from wax irradiated by the fast neutrons

emitted by a Rn- $\alpha$ -Be source. Using an experimental value of the scattering cross-section of hydrogen for neutrons of the particular average energy, Jäckel arrived at a figure of 10,000 neutrons/sec. mc. Most other workers have slowed down the neutrons before counting them. Paneth and Loleit (1935) and Paneth, Glückauf and Loleit (1936) irradiated boric acid methyl ester with the neutrons from Rn- $\alpha$ -Be sources and measured spectroscopically the helium formed in the  $^{10}\text{B}(n,\alpha)^7\text{Li}$  reaction. They could only set the lower limit at 6700 neutrons/sec. mc., since their reaction vessel was small and allowed many neutrons to escape. The Paneth method has been further developed by Seidl and Harris (1947), but no value of the standard has been given. After some pioneer experiments by Amaldi and Fermi (1936), Fink (1936) calculated an absolute value from a density distribution curve of slow neutrons in water. The local densities were measured with a lithium-coated neutron counter. Using an experimental value of the ratio of the cross-sections of lithium and hydrogen (water), the rate of neutron capture in the hydrogen at any distance from the source was derived from the rate of neutron capture in the lithium—that is, from the observed counting rate in the lithium counter—at that distance. Integration over the whole curve led to a value of 15,000 neutrons/sec. mc. Rn- $\alpha$ -Be. Although the efficiency of the lithium counter used by Fink was not well known, this value was adopted by several workers, including, for example, Booth, Dunning and Slack (1939). Bauer *et al.* (1942) later re-traced the density distribution curve, using as neutron counter a boron trifluoride chamber of efficiency almost 100%. In this experiment enough boric acid was dissolved in the water so that almost the whole of the absorption in the water was due to boron. Consequently the ratio of the counting rate to the rate of capture per unit volume of the medium was, in every place, almost equal to the ratio of the concentrations of boron in chamber and solution. In this experiment a knowledge of the ratio of the cross-sections in boron and hydrogen is needed only for a small correction. The result was 14,000 neutrons/sec. mc. Rn- $\alpha$ -Be. This value, though possibly on the low side, is on the whole supported by other experiments of different types (Rotblat, 1943; Bretscher *et al.* 1944).

Remembering that 1 mc. of radon, in equilibrium with the short-lived deposit, emits about  $1.1 \times 10^8$   $\alpha$ -particles per second, it will be found that only one out of about 8,000 projectiles disintegrates a beryllium nucleus to give a neutron. The rest lose energy completely in interaction with orbital electrons. The data of Table V have indicated an even lower efficiency for artificial sources at the energies commonly employed. In the most favourable case (Be-D at 1 MeV.) roughly one neutron is produced for every 70,000 deuterons.

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## CHAPTER VII

# THE CHEMICAL ASPECTS OF NUCLEAR FISSION

### 7.1. The fission process

The discovery of nuclear fission (for early history see Turner, 1940) opened a new era in radiochemistry. Large numbers of new active isotopes have become available as fission products, including isotopes of a previously unknown kind, namely, isotopes with large neutron excess. Moreover, the utilization of fission in chain-reactors has made it possible to transmute matter on a macro-scale.

The cohesion of a nucleus due to the specific short-range forces acting between nucleons is counteracted by the Coulomb repulsion of the positive charges of the constituent protons. The binding energy of each nucleon—so far as the specific nuclear forces are concerned—is in a crude approximation equal in all nuclei, except the lightest. Provided each nucleon makes an equal contribution, the (negative) total binding energy, so far as it is due to these forces, increases in proportion to the mass number  $A$ . Now, broadly speaking,  $A$ , for the most stable isotopes of each element, increases with rather less than the 1.2th power of the nuclear charge  $Z$ . On the other hand, the (positive) potential energy, due to mutual repulsion of all electric charges, must increase roughly with the square of  $Z$ . Consequently, highly charged nuclei must tend to break up with the emission of positively charged particles. The two variants of the break-up so far observed are (1) the emission of  $\alpha$ -particles (§ 6.3), and (2) the fission of nuclei into two nearly equal fragments.

While the energetic basis of  $\alpha$ -decay is related to that for fission, the mechanisms are different. The structure of an  $\alpha$ -unstable nucleus remains the same so long as the actual decay does not happen; the rate of decay depends on the probability of finding the  $\alpha$ -particle outside the potential barrier, due to its 'second nature' as a wave. The penetration of the barrier, known in quantum mechanics as a 'tunnel effect', does not imply preceding

nuclear deformation. By contrast, fission sets in as a consequence of the occasional formation, due to the irregular movements of the nucleons, of a sufficiently non-spherical (elongated) nucleus (Meitner and Frisch, 1939; Bohr, 1939; Bohr and Wheeler, 1939*a*; Flügge and Droste, 1939). As the cohesive forces decrease with increasing distance more rapidly than do the repulsive forces, deformation of the nucleus must reduce its stability, and may in highly charged nuclei lead to fission. The activation energy necessary to achieve deformation can be supplied either directly as  $\gamma$ -ray energy ('photo-fission'; Haxby *et al.* 1940, 1941; Baldwin and Klaiber, 1947), or through bombardment with particles, namely, neutrons (Hahn and Strassmann, 1939; Frisch, 1939), protons (Dessauer and Hafner, 1941), deuterons (Gant, 1939; Jacobsen and Lassen, 1940) or  $\alpha$ -particles (Fermi and Segrè, 1941). In fission with material projectiles, not only practically the whole of their kinetic energy, but also their binding energy is available for activation. For instance, in the exposure of  $^{235}\text{U}$  to slow neutrons (zero kinetic energy) the neutron binding energy (here 6.4 MeV.; see Table VII) suffices to activate fission before the compound nucleus  $^{236}\text{U}$  loses its excitation energy in an alternative process, e.g. photon emission or  $\alpha$ -emission. Indeed, the lifetimes of compound nuclei excited above their 'fission thresholds' are exceedingly short (Feather, 1939; Wilson, 1947*a*). Spontaneous fission also exists (Flerov and Petrjak, 1940 *a, b*; see Maurer and Pose, 1943; Pose, 1943; Flügge, 1943; Kennedy and Wahl, 1946; Scharff-Goldhaber and Klaiber, 1946; Chlopin, Gerling and Baranovskaya, 1947; Perfilov, 1947), with partial half-lives of uranium and thorium ranging between  $3 \times 10^{15}$  and  $2 \times 10^{17}$  years. However, the laws of spontaneous fission are by no means as well understood as those of induced fission.

## 7.2. Fissile nuclei

Nuclei now recognized as fissile with neutrons of a few MeV. are listed in Table VII. The calculated activation energies for fission (Bohr and Wheeler, 1939*a, b*) are given in column 3, the (crudely estimated) neutron binding energies in column 4, and the differences of columns 3 and 4 in column 5. These differences are the calculated threshold energies, i.e. the required energies of

Table VII. *Thresholds for fission with neutrons*

Absorbing isotope	Compound nucleus	Activation energy (calc.) (MeV.)	Binding energy (calc.) (MeV.)	Threshold (calc.) (MeV.)	Threshold (obs.) (MeV.)	References
$^{230}\text{Th}(f_0)$	$^{231}\text{Th}$	6.5	5.3	1.2	'Fast neutrons'	Jentschke, Prankl and Hernegger (1942); Curie and Joliot (1944)
$^{232}\text{Th}$	$^{233}\text{Th}$	6.9	5.2	1.7	1.1	Shoupp and Hill (1949)
$^{231}\text{Pa}$	$^{232}\text{Pa}$	5.5	5.4	0.1	?	Grosse, Booth and Dunning (1939); Bohr and Wheeler (1939b)
$^{233}\text{U}$	$^{234}\text{U}$	—	—	—	0	Seaborg, Gofmann and Stoughton (1947)
$^{235}\text{U}$	$^{236}\text{U}$	5.0	5.4	—0.4	?	—
$^{238}\text{U}$	$^{239}\text{U}$	5.3	6.4	—1.1	0	Ladenburg <i>et al.</i> (1939)
$^{235}\text{U}$	$^{236}\text{U}$	5.9	5.2	ref. pt.	0.7	Ghiorso and Magnusson (1946); Klema (1947)
$^{237}\text{Np}$	$^{238}\text{Np}$	—	—	—	?	—
$^{239}\text{Pu}$	$^{240}\text{Pu}$	—	—	—	0	Kennedy <i>et al.</i> (1946)

bombarding neutrons. It must be noted that Bohr and Wheeler use an experimental value of the threshold for the target nucleus  $^{238}\text{U}$  (0.7 MeV.) as reference point for their calculations; thus the absolute values of all calculated thresholds depend on its correctness. In fact, Shoupp and Hill (1949) find a value of 1.0 MeV. The observed values are listed in column 6. A zero in column 6 signifies that fission occurs with slow neutrons; calculated negative thresholds have no immediate experimental meaning, though relevant experiments have been suggested (Schiff, 1946). The experimental assignment of slow neutron fission in natural uranium to  $^{235}\text{U}$  is due to Nier *et al.* (1940) and Kingdon *et al.* (1940).

The cross-section of natural uranium for fission by thermal neutrons has been given as  $3.2 \pm 0.35$  barns, corresponding to 400–500 barns for  $^{235}\text{U}$  (Nier *et al.* 1940). The process is found to follow the  $1/v$  law (Booth, Dunning and Slack, 1939) at least approximately. Cross-sections for fast neutron fission of uranium and thorium are given as 0.5 and 0.1 barns (Ladenburg *et al.* 1939); since the cross-section for any fast neutron reaction of any nucleus, on certain theoretical grounds, cannot exceed the value 0.5 barn by orders of magnitude, and  $^{238}\text{U}$  is 140 times more abundant than  $^{235}\text{U}$ , most fast neutron fissions in natural uranium must be attributed to  $^{238}\text{U}$ . Cross-sections for photo-fission are less than 0.05 barns (Baldwin and Klaiber, 1947).

Fission into three fragments should in some cases yield more energy than ordinary binary fission (Bohr and Wheeler, 1939*a*; Present and Knipp, 1939). Evidence for three-fragment fission with an  $\alpha$ -particle as the third fragment has been obtained using the photographic plate (Green and Livesey, 1946, 1948; Demers, 1946, 1947; Wollan, Moak and Sawyer, 1947; Tsien *et al.* 1946, 1947; Tsien and Faraggi, 1947; Marshall, 1949; Titterton and Goward, 1949), and by other methods (Cassels *et al.* 1947; Farwell, Segrè and Wiegand, 1947). Third and even fourth particles heavier than  $\alpha$ -particles have been reported (Tsien *et al.* 1947; Rosen and Hudson, 1949; see Chastel and Vignerón, 1949).

No fission of less heavily charged nuclei than thorium has been demonstrated with neutrons up to a few MeV. (Borst and Floyd, 1946; Broda, 1946; Broda and Wright, 1946; Baldwin and

Klaiber, 1947; Phillips, Rosen and Taschek, 1949). Using neutrons of more than 40 MeV., Perlman *et al.* (1947) and Kelly and Wiegand (1948) have succeeded in splitting  $_{83}\text{Bi}$ ,  $_{82}\text{Pb}$ ,  $_{81}\text{Tl}$ ,  $_{78}\text{Pt}$  and  $_{73}\text{Ta}$ .

### 7.3. Different modes of fission

Contrary to the position in  $\alpha$ -decay, in fission the nucleus may break up in a multitude of different ways, and yield products of many different masses over a wide range of nuclear charges. Bohr and Wheeler (1939*a*) have drawn a semi-quantitative diagram for the binary fission of the compound nucleus  $^{236}\text{U}$ , plotting the values of  $A$  against those of  $Z$  for the fragments. Because each fission yields two fragments, it is represented in the diagram by two points which are equidistant from the point representing symmetrical fission, that for  $^{118}_{46}\text{Pd}$ . Modes of fission of equal (calculated) energy are joined by contour lines. The diagram involves important simplifications, mainly (1) that the contour lines are drawn without a fine structure, and (2) that the masses and charges are assumed to add up to 236 and 92 respectively, i.e. that the loss of mass as neutrons (§ 7.6) is disregarded. Besides, not the whole of the developed energy will appear as kinetic energy of the fragments; part will appear as internal energy of excitation, leading to the emission of photons (altogether  $4.6 \pm 1.0$  MeV. on an average; Kinsey, Hanna and van Patter, 1948), while another part will be used up to liberate and accelerate the neutrons. But broadly speaking, the kinetic energy of the fragments should be largest ( $\sim 200$  MeV.) in symmetrical fission. This prediction is borne out by experiment (§ 7.4). The modes of fission with the largest release of energy might also be expected to occur most frequently. However, all experimental evidence (§§ 7.4, 7.5) shows that this is not so, except in ultra-high energy fission (§ 7.5).

### 7.4. The physical evidence regarding modes of fission

The energy loss per unit length of path of the highly ionized (see Lassen, 1946, 1949) and comparatively slowly moving fission fragments is large. Therefore, in spite of the high initial energy, the range in air does not exceed about 2.5 cm. (Booth, Dunning and Slack, 1939; McMillan, 1939; Flammersfeld, Jensen and

Gentner, 1942; Demers, 1946), i.e. the range is less than the range of the  $\alpha$ -particles of smallest energy from the heavy radioelements. Except for slight deviations due to the 'simultaneous' emission of neutrons, the two fragments must be emitted in opposite directions. Therefore in cloud chambers (Joliot, 1939; Corson and Thornton, 1939; Bohr, 1940; Bohr *et al.* 1940; Broström, Bøggild and Lauritsen, 1940; Bøggild, 1941) or photographic emulsions (Myssowsky and Zhdanov, 1939; Green and Livesey, 1946, 1948; Demers, 1946, 1947), where the tracks of both particles are visible, they appear as one track having the combined length of the two.

The energies of individual fragments are measured in ionization chambers. The distribution of the pulse sizes due to single fragments, each arising in the fission of a separate nucleus, has been analysed, among others, by Jentschke and Prankl (1939*a, b*), Haxel (1939), Kanner and Barschall (1940), and Brunton and Hanna (1949). For the translation of the pulse sizes into fragment energies the number of ions is assumed to be proportional to the energy of the fragment, as is true for  $\alpha$ -particles (see Lassen, 1945). It appears from Brunton and Hanna's experiments, in which fission of  $^{235}\text{U}$  was induced by slow pile neutrons, that the energy spectrum of the single pulses has two distinct peaks at 59 and 93 MeV. The peaks have half-widths of 20 and 12 MeV., respectively. Only a few pulses were recorded in these experiments with energies of  $> 100$  MeV.

The combined size of the two pulses from one and the same fission act has been determined in double fission chambers with a thin uranium film between the chambers (Kanner and Barschall, 1940; Jentschke and Prankl, 1942; Flammersfeld, Jensen and Gentner, 1942; Jentschke, 1943; Brunton and Hanna, 1949). Under such conditions a single peak appears at about 152 MeV. with a large half-width, and only very few pulses of 190–200 MeV. are recorded. The differences between the amounts of energy released in the fissions of  $^{238}\text{U}$  and  $^{235}\text{U}$  by fast, and of  $^{235}\text{U}$  and  $^{233}\text{U}$  by slow neutrons are not appreciable, but the energy is less in the fission of  $^{232}\text{Th}$  (Jentschke, 1943; Fowler and Rosen, 1947; Deutsch and Ramsey, 1945; Deutsch, 1947) and especially in that of elements of still lower atomic number (Kelly and Wiegand,

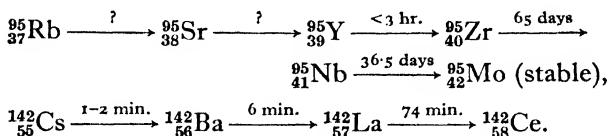
1948). On the other hand, in the fission of  $^{239}\text{Pu}$  more energy is released (Deutsch and Ramsey, 1945). The absolute value for uranium agrees reasonably well with the calorimetric determination of Henderson (1939, 1940), if allowance is made for the  $\beta$ -ray energy, etc., which is inevitably included in the latter (§ 7.5).

The comparatively low experimental value of the average fission energy already shows that symmetrical fission is infrequent. If the sizes of the two associated fission pulses are known separately, the ratio of the fragment masses can be derived from the conservation of momentum; the ratio of the masses must be equal to the inverse ratio of the kinetic energies. The necessary experimental data have been supplied by Magnan (1941, 1942), Flammersfeld, Jensen and Gentner (1942), Jentschke and Prankl (1942) and Brunton and Hanna (1949). The result is that the more symmetrical modes are those with the largest total kinetic energies, at least down to a mass ratio 4:5, and that nearly symmetrical fission is rare. This is also evident from photographic plate work (Demers, 1947). Mass ratios in the neighbourhood of 2:3 are most common. But it has also been shown that the total release of kinetic energy is not determined exclusively by the mass ratio. Nor is there, as a consequence, an unambiguous correlation between the energies of the two fragments. This spread of the total kinetic energy, at a given mass ratio, may be due to the varying energy used up for excitation, neutron emission, etc., and to the varying distribution of the charge, as considered in the Bohr-Wheeler diagram. However, the upper limit of the kinetic energy of the two fragments, at a given mass ratio, seems to agree with the Bohr-Wheeler value, provided the total charge is supposed to be distributed between the fragments in such a way that the sum of the energy contents of the fragments is a minimum, and no energy is expended otherwise than as kinetic energy of the fragments.

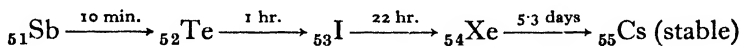
### 7.5. The chemical evidence regarding modes of fission

The radiochemical analysis of the fission products (see Siegel, 1946; Hahn, Strassmann and Seelmann-Eggebert, 1946) is based on the  $\beta$ -activity of the majority of the fission products. This activity is due to the fact that the neutron/proton ratio 'appropriate' for uranium ( $\sim 1.6$ ) is far too large for the less heavily

charged fragments, and that this ratio is not sufficiently reduced by direct neutron emission in or after the birth of the fragments. If, for instance, the compound nucleus  $^{239}\text{U}$  splits into nuclei of weights 95 and 142 and two neutrons, and the neutron/proton ratios for the two fragments are equal, the fragments must be  $^{95}_{37}\text{Rb}$  and  $^{142}_{55}\text{Cs}$ ; they are unstable. Stability is restored for each fragment by a chain of  $\beta$ -disintegrations. The elements with the lowest nuclear charges which have stable isotopes of  $A = 95$  and 142 are  $^{95}_{42}\text{Mo}$  and  $^{142}_{58}\text{Ce}$ . Hence, sequences of five and three  $\beta$ -particles respectively must follow before stability is attained in this particular case:



Since the mass does not change, except in the rare emission of delayed neutrons, it is as a rule sufficient for the identification of a sequence to establish the mass of one member. One general method of identification consists in finding a member which is also produced in a nuclear reaction which is otherwise known. For example, the important sequence

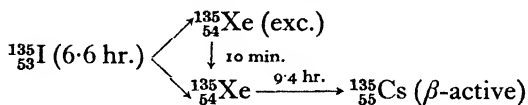


(Wu and Segrè, 1945) is assigned the mass number 133 through the independent production of 5.3 days Xe in the  $^{133}_{55}\text{Cs} (n,p)$  reaction. If a sequence does not contain known radioelements, certain regularities governing the lifetimes of successive members can be used to discriminate at least between even and odd mass numbers (Feather, 1943). A non-radiochemical method of identification has become available with the production in chain-reactors of fission products in sufficient quantity for mass-spectrographic examination (§ 10.7; Chackett, 1949). Finally, because of the (usually) smooth variation of fission yield with mass number, the latter can occasionally be deduced from the yield (Siegel, 1946).

Frequently the fission products are also  $\gamma$ -active. The mean aggregate  $\gamma$ -ray energy in each chain is estimated to be about equal to the mean aggregate  $\beta$ -ray energy ( $\sim 5.5$  MeV.; Wigner and Way, 1948). Quite often long-lived excited nuclei (isomers) are ob-



served. An example of a chain with 'isomeric transition', with a branching ratio 1:10, is given by Wu and Segrè (1945):



Comprehensive surveys of the yields as a function of  $A$  in the slow neutron fission of uranium have been given by Grummitt and Wilkinson (1946) and by Siegel (1946). The two sets of results are substantially in agreement with each other. Two 'peaks' appear, at mass numbers 95-96 and 138-139. The peak yield is about 0.06 both for the light and for the heavy fragment. The mass ratio (0.69) for the most abundant fragments agrees rather well with the corresponding ratio derived from the physical measurements. The chemical result is probably the more accurate; moreover, by the chemical method absolute values of  $A$  are obtained immediately. The masses corresponding to the peaks add up to 234; this corresponds to the mass of the compound nucleus less '1 to 3' neutrons (§ 7.6). The lowest and the highest mass numbers so far detected are 72 (yield  $1.5 \times 10^{-7}$ ) and 158 ( $2 \times 10^{-5}$ ). Again in agreement with pulse-size analysis, the yields of the products of symmetrical fission are poor. The minimum ( $\sim 10^{-4}$ ) lies at  $A = 117$ .

The radiochemical data concerning charge distribution in fission are meagre compared with the data on mass distribution. But while pulse-size analysis does not indicate  $Z$  at all,  $Z$  can be obtained from radiochemical analysis at least in principle. The analysis has to be fast enough to catch the primary fission products. One may be certain actually to have caught a primary product only where the isobar of next-lower  $Z$  happens to be stable ('shielded nuclei'). The  $\beta$ -active species  $^{82}\text{Br}$  is an example of a shielded nucleus. From the available data (Glendenin, Coryell and Edwards, 1946) it appears that for a given division of mass the most probable division of charge implies equal numbers of  $\beta$ -disintegrations. The division is, therefore, unlikely to lead to a charge distribution corresponding to maximum kinetic and minimum radioactive energy (see Wigner and Way, 1948). The probability of the occurrence of a particular value of the charge, at a given mass, falls off

smoothly but sharply with difference against the most probable value. Therefore, stable species are uncommon as primary fragments. For the same reason, it is unimportant which member of a sequence (except the first few) serves to measure the yield: later members of sequences are rarely formed directly. As a further consequence, the rarity of symmetrical fission regarding  $A$  is reflected in the poor yield of fragments of  $44 < Z < 49$ ; however, symmetrical charge numbers must be better represented than symmetrical mass numbers if the descendants of the primary fragments are also considered. The elements whose stable isotopes have masses somewhat less than the masses corresponding to the peaks in the yield curve are particularly abundant, e.g.  $^{36}\text{Kr}$  and  $^{52}\text{Te}$  with 17 and 15 known isotopes and isomers, respectively. Altogether, i.e. counting primary fragments and descendants, charge numbers 30–65 have been found among the 87 known sequences. The most rapid chemical identification has been possible with noble gases (§ 4.1). It is significant in this connexion that the longest known chains (seven members each) are derived from noble gases as ancestors.

Radiochemical analysis gives information about masses and (in principle) charges, but not about fission energies. Pulse-size analysis gives information about masses and energies, but not about charges. Interesting attempts to get all three parameters in one experiment have been made, after preliminary tests by McMillan (1939), by Joliot (1944), Meitner (1945) and Katcoff, Miskel and Stanley (1948). A thin uranium film, which is covered with a stack of thin absorbing foils, is irradiated, and the activation of the different foils due to the absorption of individual kinds of fragments is measured separately. If a plutonium film and the neutron flux from a pile can be used, one may restrict the observation to a collimated beam of fragments. The penetrating power of fission products of given mass and charge is a measure of their energies, and can in principle be determined in calibration experiments. Conversely, after calibration the energies can be deduced from the measured penetrations. However, because of the great experimental difficulties only the first steps in this direction have been taken. From a preparative point of view, the method has proved useful in the separation of short-lived yttrium from the

rare earths. On account of the mass difference, penetrations are quite unequal (Katcoff and Brown, 1949).

Little has been published about differences between the yields in the fission of different nuclei, or of the same nuclei at different degrees of excitation. Nishina *et al.* (1940, 1941) have shown that the products of symmetrical fission, regarding both  $A$  and  $Z$ , are much more conspicuous in the fast neutron fission of  $^{238}\text{U}$  than the slow neutron fission of  $^{235}\text{U}$ . Kingdon (1949) has suggested that in fast fission the fragments lack the time to 'sort themselves out' asymmetrically so that the 'neutron binding capacities' of the fragments are utilized best. A quantitative comparison of the fission yield of one selected product ( $^{139}\text{Ba}$ ) was carried out by Broda, Kowarski and West (1948). The number of fission pulses from a thin uranium layer in a 'combined fission chamber' was correlated with the quantity of  $^{139}\text{Ba}$  produced in a large quantity of  $\text{U}_3\text{O}_8$  kept in separate compartments of the chamber. It was found that the yield of  $^{139}\text{Ba}$  per fission of  $^{235}\text{U}$  by slow neutrons amounts to about 120% of the yield per fission of  $^{238}\text{U}$  by fast neutrons. The fission products of  $^{233}\text{U}$  are much like those of  $^{235}\text{U}$  (Grummitt and Wilkinson, 1948). Some quite preliminary data on the products of photofission (Langer and Stephens, 1940), of the fission of protoactinium (Grosse, Booth and Dunning, 1939) and of thorium (Hahn and Strassmann, 1940; Polessitsky *et al.* 1941) have also been published. Perlman *et al.* (1947), Goeckermann and Perlman (1948, 1949), O'Connor and Seaborg (1948), and Wolfe and Ballou (1949) have reported very recently that yields in ultra-high energy fission (e.g. by 380 MeV.  $\alpha$ -particles) differ greatly from those in the 'ordinary' fission of uranium. The masses of the products of  $^{238}\text{U}$  spread very widely ( $55 < A < 180$ ), with a single peak of abundance near 115; for bismuth,  $45 < A < 139$ , with the peak at  $\sim 100$ . It is not yet clear which products are derived from binary fission, and which from more complete types of disintegration. A peculiar feature is the formation of neutron-deficient fragments, e.g. K-capture-active  $^{131}\text{Ba}$ , unknown in 'ordinary' fission, due to the evaporation of many neutrons from the highly excited system before or after fission. Also in the fission of thorium with 38 MeV.  $\alpha$ -particles the central dip in the yield curve is little pronounced (Newton, 1949).

## 7.6. The emission of neutrons in fission

Substantial neutron emission in fission ( $3.5 \pm 0.7$ /fission) was first reported by Halban, Joliot and Kowarski (1939; see Dodé *et al.* 1939). The figure is given as 2.3 by Goodman, 1947 (see Zinn and Szilard, 1939; see Boyer and Tittle, 1949), and as '1 to 3' in the Smyth *Report*. Neutrons of up to 11 MeV. energy have been observed, but the majority are much less energetic (average  $\sim 2$  MeV.; Halban, Joliot and Kowarski, 1939; Bothe and Gentner, 1942; Wilson, 1947*a*; see Boyer and Tittle, 1949). Most neutrons are emitted isotropically by the fragments before they are stopped (Wilson, 1947*b*; Benedetti *et al.* 1948). The 'delayed' neutrons (Roberts, Meyer and Wang, 1939) amount to only 0.75% of the total, but are essential for the control of chain reactions (Smyth *Report*, p. 140). The emission of delayed neutrons decays with a composite period which can be resolved into at least six individual periods between 0.05 and 55.6 sec. (Hughes *et al.* 1948). The emitting fragments are distinguished from each other by different ranges (Campbell, Good and Strauser, 1949). Delayed neutron energies vary from about 250 to 620 keV. Because of the absence of a potential barrier the delay in neutron emission cannot be caused by any difficulty which the neutron experiences in escaping from the nucleus, provided such escape is possible energetically. The periods must rather be those of the  $\beta$ -active parents of the neutron emitters. Two of the parents have been identified radiochemically (Snell *et al.* 1947) as bromine (for the 56 sec. period) and iodine (for the 22 sec. period). Possibly they are the species  $^{87}\text{Br}$  and  $^{137}\text{I}$ , to which similar half-lives have been attributed (Sugarman, 1947, 1949). If this is so, the neutron emitters are  $^{87}\text{Kr}$  and  $^{137}\text{Xe}$ . The neutrons must be emitted from excited states since the ground states of the nuclei decay by  $\beta$ -emission. (Delayed neutrons are also emitted by the excited nucleus  $^{17}\text{O}$ , not formed in fission, with the period of parent  $^{17}\text{N}$  [see Hayward, 1949]). A third period (4.5 sec.) is also said to be due to an isotope of bromine (Sugarman, 1947). The same periods of delayed neutrons as with  $^{235}\text{U}$  have been found with  $^{239}\text{Pu}$  and  $^{233}\text{U}$ , but the relative yields of the delayed emitters vary. Moreover, in both cases the delayed contribution to total neutron emission is  $< \frac{1}{2}\%$  (Hoffman and Feld, 1947; Redman and Saxon, 1947;

Hughes, 1946*a*; Hughes *et al.* 1948). In the fission of  $^{232}\text{Th}$  the ratio of the 56 sec. to the 22 sec. activity is 76% larger than in the fission of  $^{235}\text{U}$  (Creveling, Hood and Pool, 1949).

Many neutrons per fission are emitted in the bombardment of uranium with ultra-high energy projectiles (Cunningham *et al.* 1947; Goeckermann and Perlman, 1949; Jungerman and Wright, 1949; § 7.5).

The number of neutrons produced in chain reactors of a given power can roughly be estimated. If the power of a  $10^5$  kW. chain-reactor is supplied by fissions of an overall energy (including  $\beta$ - and  $\gamma$ -ray energy, binding energy of neutrons captured in carbon, etc.) of 200 MeV. ( $= 9 \times 10^{-18}$  kWh.) each, and if each fission gives two neutrons, about 1 g.-atom, i.e. 1 g., of neutrons must be generated per day. This is an increase by a factor  $10^7$ , for the neutron production of a single device, as compared with the most powerful cyclotrons. Of course, the increase in the optimum flux is much less. However, a flux of  $2 \times 10^{13}$  cm. $^{-2}$  sec. $^{-1}$  has been reported (Yaffe *et al.* 1949). A definite drawback is constituted by the fact that in a pile neutron energy cannot be varied at will though fast neutron reactors exist (*Rev. Sci. Instrum.* **18**, 688 (1947)).

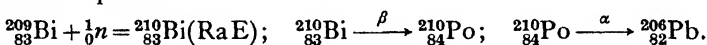
An experiment of basic radiochemical interest, which becomes a practical possibility now, is the investigation of the radioactivity of the only known isotope of element zero, i.e. of the neutron itself. The neutron should be  $\beta$ -active with a moderately long period (Hughes, 1946*b*; Snell and Miller, 1948), but the rapid loss of neutrons by capture or diffusion has so far prevented experimental proof. Perhaps it will now be feasible to collect electrically the protons formed in the decay of the neutrons, or to measure them as hydrogen (Cockcroft, 1946; Shrader, Saxon and Snell, 1946).

### 7.7. The manufacture of radioelements in chain reactions

The products of non-fission capture in uranium and thorium will be considered in Chapter VIII. The other chain-reactor-produced radioelements can be divided into two classes, namely, the fission products, and the products of capture in non-fissile elements. The 'availability' (ARI, 1946; RSI, 1949; see Aebersold, 1948) is governed by nuclear yield, ease of chemical separation, convenience of period, and demand.

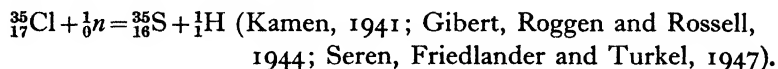
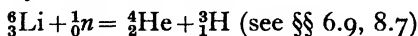
Fairly many fission products with half-lives ranging between 1 week and 30 years are currently isolated on a routine basis. Apparently the radiation hazard in the treatment of waste solutions from the recovery of plutonium is prohibitive, and the fission products are always extracted from material introduced into special irradiation shafts. The quantities offered lie between  $10^{-5}$  and 1 curie, depending on yield and period. The fission products are supposed to be free from inactive contaminants or carriers. Mostly the products cannot be made in alternative processes because of their high neutron excess.

A larger number of radioelements is being made available by irradiation of non-fissile elements. When the radioelements are made by radiative capture, the material is not treated chemically after irradiation, and contains much inactive matter. The half-lives lie between several hours and  $10^6$  years ( $^{36}\text{Cl}$ ), and the activities between  $10^{-5}$  and 1 curie.  $\beta^-$ ,  $\beta^+$ - and capture-active bodies are made, and for  $Z > 82$   $\alpha$ -decay must eventually follow neutron capture:



The quantities of polonium are sufficient for crystal analysis (Beamer and Maxwell, 1949).

In a few cases the irradiation of non-fissile elements with slow neutrons leads not to radiative capture, but to changes in  $Z$ . The active products of such reactions are obtained free from carrier by chemical isolation:



The capture of neutrons by elements consisting of several isotopes must progressively remove the isotopes with the highest cross-sections. Alternatively, pure isotopes can be obtained in the decay of chain-reactor-produced radioelements. These stable materials of unnatural isotopic composition, along with the products of isotope separation plants, will no doubt be employed in future, not only in nuclear science and technology, but also in other fields of pure and applied science (see § 10.8).

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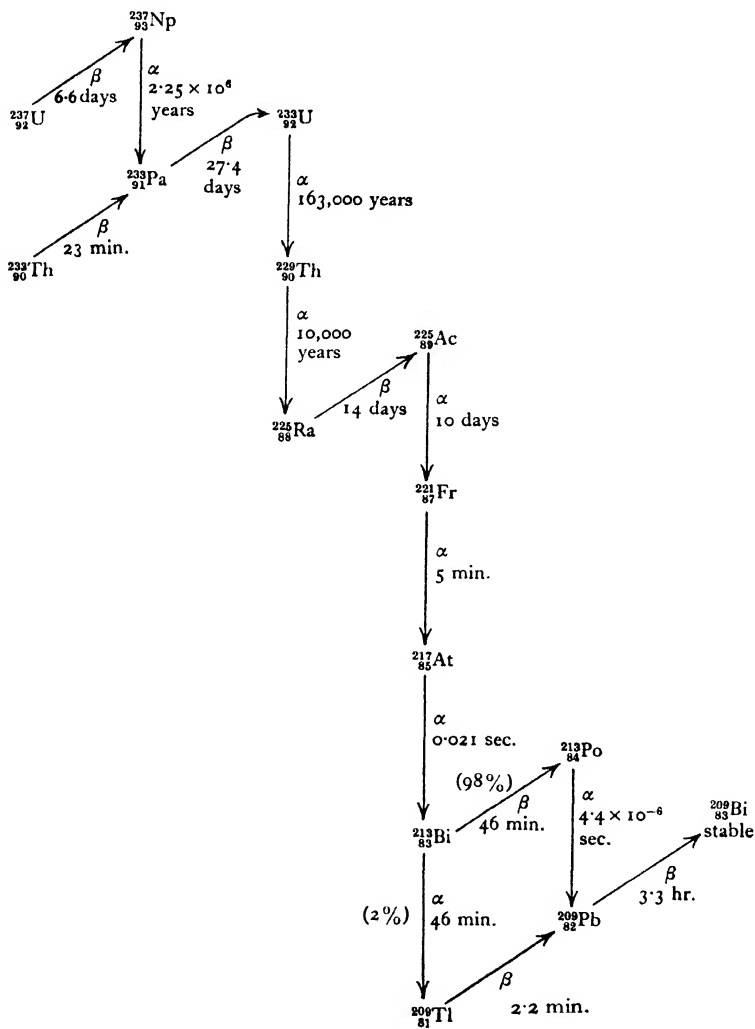
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## NEW RADIOELEMENTS OF SPECIAL INTEREST

**8.1. The  $(4n + 1)$  radioactive series**

Four, and only four, distinct radioactive series can exist, provided only  $\alpha$ - and  $\beta$ -disintegrations are permitted, i.e. if the mass may change only by four units, or, alternatively, not at all. Only three series have been found in nature, namely, the thorium series for which mass numbers are of the type  $4n$ , the uranium ( $4n + 2$ ), and actinium ( $4n + 3$ ) series. All three series owe their continued existence to the longevity of one and only one of their members ( ${}_{90}^{232}\text{Th}$ ,  ${}_{92}^{238}\text{U}$  and  ${}_{92}^{235}\text{U}$ ). There is no other member in any of these series with a half-life of more than 267,000 years ( ${}_{92}^{234}\text{U} = \text{U II}$ ; Goldin *et al.* 1949). It will be seen that the  $(4n + 1)$  series (discussed by Russell, 1923; Russell and Widdowson, 1924; Curie, Halban and Preiswerk, 1935; Turner, 1940; Ponisovsky, 1943) does not happen to contain a really long-lived member, and therefore has decayed by now in nature. Furthermore, the absence of bismuth from thorium or uranium minerals shows that the thorium and uranium isotopes belonging to the series had decayed at the time of formation of the minerals. However, members of the missing series may be made artificially. For example,  $(n, \gamma)$  reactions with members of the thorium series, and  $(n, 2n)$  reactions with those of the uranium series must lead to members of the  $(4n + 1)$  series. In this way,  ${}_{90}^{233}\text{Th}$  was made by radiative capture of neutrons by ordinary thorium (Amaldi *et al.* 1935). The decay product of this body,  ${}_{91}^{233}\text{Pa}$ , was identified by Meitner, Hahn and Strassmann (1938) and further investigated by Hahn and Strassmann (1941), Seaborg, Gofmann and Kennedy (1941), and by Grosse, Booth and Dunning (1941). Using more abundant sources of neutrons (chain-reactors) it was possible later (English *et al.* 1947; Hagemann *et al.* 1947) to trace the new series down to the stable end-member  ${}_{83}^{209}\text{Bi}$ . Alternatively,  ${}_{92}^{238}\text{U}$  can be converted into  ${}_{92}^{237}\text{U}$  by the  $(n, 2n)$  reaction with very fast neutrons (Nishina *et al.* 1940; McMillan, 1940; Melander and Slätis, 1948*a, b*). The series is known as the 'neptunium series', after its

longest-lived member. In the following diagram the members of the main sequence, beginning from  $^{237}_{92}\text{U}$ , are included, but more will be said about the transuranic members in the following sections. For further information the reader may be referred to the forthcoming volume of the present series of monographs by Paneth and English.



## 8.2. Production and nuclear properties of neptunium and plutonium

During four years the fission products were mistaken for transuranic elements (see Fermi, 1934). Only after fission was recognized in 1938 did the exploration of matter beyond the end of the sequence of the natural elements become possible. Thus in 1939 it became clear that the 23 min.  $^{238}_{92}\text{U}$  (Hahn, Meitner and Strassmann, 1937) is the only genuine product of non-fission capture of slow neutrons by  $^{238}_{92}\text{U}$ . Its  $\beta$ -decay must lead to the body  $^{239}_{93}$ . The ( $\beta$ -) radiation of this first-discovered isotope of a transuranic element was observed by McMillan (1939) in the non-recoiling fraction of the activity induced by neutrons in uranium. The body was radiochemically investigated by Segrè (1939*b*), but mistaken for a rare earth; it was correctly identified only by McMillan and Abelson (1940). It was clear that its daughter must be  $^{239}_{94}$ , but because of its comparatively long period (24,000 years) this  $\alpha$ -ray emitter was not detected before 1941 (Seaborg *et al.* 1946*a*; Seaborg, Wahl and Kennedy, 1946; Seaborg, 1946*a, b*; Chamberlain *et al.* 1947). The elements 93 and 94 are now known as neptunium (Np) and plutonium (Pu). Thirteen reactions yielding isotopes of the two elements are listed in Table VIII. Five more reactions will be found in Table IX. All known isotopes of the elements are found in Table X. The practical importance of  $^{238}_{94}\text{Pu}$  (discovered in 1940, before the discovery of  $^{239}_{94}\text{Pu}$ ; see Seaborg *et al.* 1946*b*) lies in its short life, which made tracer work with the element possible before enough  $^{239}_{94}\text{Pu}$  was collected for such studies.  $^{237}_{93}\text{Np}$  (Wahl and Seaborg, 1942; Magnusson and LaChapelle, 1945) is of value as the only neptunium isotope of long life, i.e. the only isotope useful for ordinary chemical work, or as a target in nuclear reactions. For the fissility of neptunium and plutonium compare Table VII.

The development of the production of plutonium and neptunium, first with cyclotrons and later in chain reactors, has been described in the Smyth *Report* (pp. 60, 61, 86) and by Seaborg (1946*a, b*). In 1941 the American stocks of plutonium consisted of tracer amounts, perhaps of the order of  $10^{-8}$  g., in 1942 of  $5 \times 10^{-4}$  g., in February 1944 of 0.2 g., in March 1944 of several grams, and in 1945 of many kilograms. While the production of long-lived

$^{239}\text{Pu}$  (and of 2.3 days  $^{239}\text{Np}$ ) in chain reactors is due to the main reaction of  $^{238}\text{U}$  with slow neutrons, the long-lived  $^{237}\text{Np}$  is the product of a side reaction with fast neutrons which produces only one-thousandth as much neptunium (Seaborg, 1946c). The first visible and weighable quantities of plutonium and neptunium salts were made by Cunningham and Werner (1942) and by Magnusson and LaChapelle (1945). Exceedingly small quantities of plutonium (1 part in  $10^{14}$ ) were found in pitchblende by Seaborg and Perlman (1948a; see also Garner, Bonner and Seaborg, 1948). Probably it is constantly formed from  $^{238}\text{U}$  by the action of the ever-present neutrons, some of them derived from the spontaneous fission of uranium.

Table VIII. *Reactions yielding isotopes of neptunium and plutonium*

(1)	$^{238}_{92}\text{U}(n, \gamma) ^{239}_{92}\text{U}; ^{239}\text{U} \xrightarrow{\beta}_{23 \text{ min.}} ^{239}_{93}\text{Np};$	Refs.	
	$^{239}_{93}\text{Np} \xrightarrow{\beta}_{2.3 \text{ days}} ^{239}_{94}\text{Pu}; ^{239}_{94}\text{Pu} \xrightarrow{\alpha}_{24,000 \text{ years}} ^{235}_{92}\text{U}$	See above	
(2)	$^{238}_{92}\text{U}(d, 2n) ^{238}_{93}\text{Np}; ^{238}\text{Np} \xrightarrow{\beta}_{2 \text{ days}} ^{238}_{94}\text{Pu}; ^{238}\text{Pu} \xrightarrow{\alpha}_{90 \text{ years}} ^{234}_{92}\text{U}$	See above	
(3)	$^{238}_{92}\text{U}(n, 2n) ^{237}_{92}\text{U}; ^{237}\text{U} \xrightarrow{\beta}_{6.6 \text{ days}} ^{237}_{93}\text{Np}; ^{237}\text{Np} \xrightarrow{\alpha}_{2.25 \times 10^6 \text{ years}} ^{233}_{91}\text{Pa}$	See above	
(4)	$^{235}_{92}\text{U}(d, 3n) ^{234}_{93}\text{Np}$	} Seaborg (1946b,c); Seaborg and Perlman (1948b)	
(5)	$^{235}_{92}\text{U}(\alpha, p 4n) ^{234}_{93}\text{Np}$		
(6)	$^{231}_{91}\text{Pa}(\alpha, n) ^{234}_{93}\text{Np}$		
(7)	$^{235}_{92}\text{U}(d, 2n) ^{235}_{93}\text{Np}$		
(8)	$^{235}_{92}\text{U}(\alpha, p 3n) ^{235}_{93}\text{Np}$		
(9)	$^{235}_{92}\text{U}(d, n) ^{236}_{93}\text{Np}$		
(10)	$^{238}_{92}\text{U}(d, 4n) ^{236}_{93}\text{Np}$		
(11)	$^{235}_{92}\text{U}(\alpha, p 2n) ^{236}_{93}\text{Np}$		
(12)	$^{237}_{93}\text{Np}(d, p 2n) ^{236}_{93}\text{Np}$		
(13)	$^{238}_{92}\text{U}(\alpha, 5n) ^{237}_{94}\text{Pu}; ^{237}\text{Pu} \xrightarrow{\text{K}}_{40 \text{ days}} ^{237}_{93}\text{Np} \xrightarrow{\alpha}_{2.25 \times 10^6 \text{ years}} ^{233}_{91}\text{Pa}$		James <i>et al.</i> (1948)

### 8.3. Production and nuclear properties of americium and curium

Tracer quantities of elements 95 (americium, Am) and 96 (curium, Cm) have been made by bombarding uranium and plutonium with 40–44 MeV.  $\alpha$ -particles in a cyclotron. The induced and the consecutive spontaneous reactions are listed in Table IX. Weighable and visible quantities of americium (Cun-

ningham, 1946) and curium (Perlman, 1947) have also been reported.

Table IX. *Reactions yielding isotopes of americium and curium*

	References
(1) ${}_{92}^{239}\text{U}(\alpha, n) {}_{94}^{241}\text{Pu}; {}_{94}^{241}\text{Pu} \xrightarrow[10 \text{ years}]{\beta} {}_{95}^{241}\text{Am}; {}_{95}^{241}\text{Am} \xrightarrow[500 \text{ years}]{\alpha} {}_{93}^{237}\text{Np}$	$\left. \begin{array}{l} \text{Seaborg, James} \\ \text{and Morgan} \\ (1946) \\ \text{Seaborg} \\ (1948) \\ \text{Seaborg} \\ (1946c, 1947) \\ \text{James and} \\ \text{Seaborg} \\ (1948) \end{array} \right\}$
(2) ${}_{94}^{239}\text{Pu}(\alpha, n) {}_{96}^{242}\text{Cm}; {}_{96}^{242}\text{Cm} \xrightarrow[150 \text{ days}]{\alpha} {}_{94}^{238}\text{Pu}$	
(3) ${}_{94}^{239}\text{Pu}(\alpha, 3n) {}_{96}^{240}\text{Cm}; {}_{96}^{240}\text{Cm} \xrightarrow[27 \text{ days}]{\alpha} {}_{94}^{236}\text{Pu}$	
(4) ${}_{95}^{241}\text{Am}(n, \gamma) {}_{95}^{242}\text{Am}; {}_{95}^{242}\text{Am} \xrightarrow[16 \text{ hr.}]{\beta} {}_{96}^{242}\text{Cm}; {}_{96}^{242}\text{Cm} \xrightarrow[150 \text{ days}]{\alpha} {}_{94}^{238}\text{Pu}$	
(5) ${}_{94}^{239}\text{Pu}(\alpha, 2n) {}_{96}^{241}\text{Cm}; {}_{96}^{241}\text{Cm} \xrightarrow[55 \text{ days}]{\text{K}} {}_{95}^{241}\text{Am}; {}_{95}^{241}\text{Am} \xrightarrow[500 \text{ years}]{\alpha} {}_{93}^{237}\text{Np}$	

Nothing has been published regarding the fissility of the elements 95 and 96, but particularly the lighter isotopes would be expected to be fissile. Probably spontaneous fission will also occur. At some place among the transplutonic elements the point may be reached where spontaneous fission becomes the predominant mode of decay. In the end, spontaneous fission may set an end to the continued extension of the sequence of the elements.

Table X summarizes the available information on the modes of decay and the half-lives of elements 92–96. This table includes members of the neutron-deficient ‘collateral chains’ of the radioactive series (Studier and Hyde, 1948; Meinke, Ghiorso and Seaborg, 1949) as well as a number of other recently discovered species from Seaborg and Perlman’s (1948*b*) Tables.

#### 8.4. The chemical properties of the transuranic elements

It was predicted by Bohr (1922) and further discussed by Bohr and Coster (1923), Sugiura and Urey (1926), Goldschmidt (1931), Wu and Goudsmit (1933), and Goepfert-Mayer (1941), that a new group of elements similar to each other, and comparable to the group of the rare earths, may begin somewhere in the region of uranium. Goldschmidt (1934) selected minerals to be searched for long-lived transuranic elements on the assumption that they are chemically similar to one of the known members of the last horizontal row of the Periodic Table between actinium and uranium. It is now, in fact, found that at least the artificial elements 93 and

Table X. Modes of decay of elements 92-96

Element	Mass number														
	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242
<sup>92</sup> U	$\alpha, \kappa$ 9.3 min.	$\alpha, \kappa$ 58 min.	$\alpha$ 20.8 days	$\kappa$ 4.2 days	$\alpha$ 70 years	$\alpha$ 163,000 years	$\alpha$ 267,000 years	$\alpha$ $7 \times 10^8$ years	$\beta$ 22 hr.	$\beta$ 6.6 days	$\alpha$ 2.1 days	$\beta$ 23 min.	$\alpha$ 6,000 years	$\beta, \alpha$ 10 years	
<sup>93</sup> Np				$\alpha, \kappa$ 53 min.	$\alpha$ 22 min.		$\alpha, \kappa$ 4.4 days	$\kappa, \alpha$ 435 days	$\beta$ 22 hr.	$\alpha$ 2.25 $\times 10^6$ years	$\beta$ 2.3 days	$\alpha$ 24,000 years	$\alpha$ 6,000 years	$\beta, \alpha$ 10 years	
<sup>94</sup> Pu							$\alpha, \kappa$ 8 hr.		$\alpha$ 2.7 years	$\kappa$ 40 days	$\alpha$ 90 years	$\kappa, \alpha$ 12 hr.	$\kappa$ 50 hr.	$\alpha$ 500 years	
<sup>95</sup> Am														$\alpha$ 27 days	$\beta$ 16 hr.
<sup>96</sup> Cm														$\alpha$ 55 days	$\alpha$ 150 days



94 are chemically similar to element 92 (McMillan and Abelson, 1940; Seaborg, 1946*a, b*, 1949). However, in spite of the similarity of neptunium and plutonium to uranium, Seaborg suggests that the typical valency of the transuranic elements is three. Actinium would be, then, the first 'actinide' in the sense in which lanthanum is the first 'lanthanide' (Goldschmidt, 1925; Hevesy, 1925). It must be admitted that the chemical similarity of  $^{89}\text{Ac}$ ,  $^{90}\text{Th}$ ,  $^{91}\text{Pa}$  and  $^{92}\text{U}$  is by no means striking. In particular, the characteristic valency seems to increase just as markedly from three to six as among their lower homologues  $^{57}\text{La}$ ,  $^{72}\text{Hf}$ ,  $^{73}\text{Ta}$ ,  $^{74}\text{W}$ .

The formation of the rare earths is associated with a tendency to accept the newly added electrons into a deeper (the  $4f$ ) shell. Calculations certainly show that the binding energies of the last electron in the  $4f$ ,  $5d$  and  $6s$  shells do not differ greatly. Emission spectroscopy, the only method offering conclusive evidence as to the configuration of the free atoms, confirms that the  $4f$  shell is filled gradually. However, this is not a smooth process. Table XI, after Meggers (1947), gives the presumed development of the shell structure of the first lanthanides and actinides from spectroscopical evidence. Configurations merely inter- or extrapolated are marked by asterisks. Absorption spectra of the cations of the elements 92-95 also display many narrow lines attributed to  $5f$ -electrons (Freed and Leitz, 1949; see Seaborg, 1949).

The formation of compounds of the three-valent rare earths, except lanthanum and gadolinium, as well as of compounds of six-valent uranium, etc., must, in part, involve  $f$ -electrons. The pronounced shift towards tervalency among the heavier actinides, then, is explained through an increase in the stability of the  $f$ -group as the condition of being half-filled is approached. An analogous explanation of the increasing tendency towards formation of ions of low valency among the lanthanides is generally accepted.

Wherever the transuranic elements are four-valent, their compounds resemble those of thorium and  $\text{U}^{++++}$ , and where they are six-valent, those of  $\text{UO}_2^{++}$  (McMillan and Abelson, 1940; Hahn and Strassmann, 1942; Seaborg and Wahl, 1942). For example, the fluorides of six-valent neptunium and plutonium (neptunyl and plutonyl fluoride) are soluble in water like uranyl fluoride, while

the fluorides (or iodates) of the four-valent elements (neptunous and plutonous compounds) are insoluble like the analogous thorium and uranium salts. Sodium neptunyl and plutonyl acetate are insoluble like sodium uranyl acetate. Plutonyl nitrate, like Table XI. *Distribution of the orbital electrons in the first members of the lanthanides and actinides*

Element	Shell											
	1	2	3	4				5				6
				s	p	d	f	s	p	d	f	
La	2	8	18	2	6	10	.	2	6	1	.	2
Ce*	2	8	18	2	6	10	2	2	6	.	.	2
Pr*	2	8	18	2	6	10	3	2	6	.	.	2
Nd	2	8	18	2	6	10	4	2	6	.	.	2
Gd*	2	8	18	2	6	10	5	2	6	.	.	2
Sm	2	8	18	2	6	10	6	2	6	.	.	2
Eu	2	8	18	2	6	10	7	2	6	.	.	2
Gd	2	8	18	2	6	10	7	2	6	1	.	2

Element	Shell															
	1	2	3	4				5				6				7
				s	p	d	f	s	p	d	f	s	p	d	f	
Ac*	2	8	18	2	6	10	14	2	6	10	.	2	6	1	.	2
Th	2	8	18	2	6	10	14	2	6	10	.	2	6	2	.	2
Pa*	2	8	18	2	6	10	14	2	6	10	2	2	6	1	.	2
U	2	8	18	2	6	10	14	2	6	10	3	2	6	1	.	2
Np*	2	8	18	2	6	10	14	2	6	10	4	2	6	1	.	2
Pu*	2	8	18	2	6	10	14	2	6	10	5	2	6	1	.	2
Am*	2	8	18	2	6	10	14	2	6	10	6	2	6	1	.	2†
Cm*	2	8	18	2	6	10	14	2	6	10	7	2	6	1	.	2

† See, however, Tompkins and Fred (1949).

uranyl nitrate, dissolves readily in ether. The chemistry of neptunium is the subject of a comprehensive paper by Fried and Davidson (1948). Many details concerning the chemistry of neptunium and plutonium, including oxidation levels, electrochemistry, absorption spectra and radiocolloid formation, have been collected by Purkayastha (1948) and Haissinsky (1949).

While the most stable valency of uranium is six, and of neptunium and plutonium four, the typical valency three of the actinides is fully pronounced in the later members. The separation

of neptunium from plutonium is based on its easier oxidation to valency six (Seaborg and Wahl, 1942). Curium salts in solution are always derived from the three-valent element (Seaborg, 1949). Five-valent ions of elements 92-95 (formula  $\text{UO}_2^+$ , etc.; Kraus, Nelson and Johnson, 1949; Connick, 1949) and solid oxides  $\text{NpO}$  and  $\text{PuO}$  with metallic type binding (Zachariassen, 1948) have also been reported. The industrial recovery of plutonium is based on a change of valency; the two-stage process consists of separation by precipitation of four-valent plutonium from the whole of the (six-valent) uranium and from one part of the fission products, and of separation by precipitation of the rest of the fission products from six-valent plutonium after oxidation (Smyth *Report*, p. 82). The typical valency of the transuranic elements, as of the fission products, critically determines their metabolism in animals (Hamilton, 1948).

To the extent to which the mutual similarity of the actinides increases, similarity with the 'homologues' in the Periodic Table must decrease. Thorium still resembles hafnium, and proto-actinium resembles tantalum, but the similarity of uranium and tungsten is less marked, and neptunium and plutonium are quite unlike rhenium and osmium. Among the more striking differences are that the transuranic elements are not precipitated from acid solution by hydrogen sulphide, that their higher salts are not reduced in solutions to the elements by zinc, and that their oxides are not volatile.

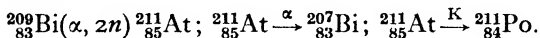
Crystal chemical evidence (Goldschmidt, 1931; Zachariassen, 1948) clearly shows that in the three series of cations,  $\text{UO}_2^{++}$ ,  $\text{NpO}_2^{++}$ ,  $\text{PuO}_2^{++}$ — $\text{Th}^{++++}$ ,  $\text{U}^{++++}$ ,  $\text{Np}^{++++}$ ,  $\text{Pu}^{++++}$ ,  $\text{Am}^{++++}$ — $\text{U}^{+++}$ ,  $\text{Np}^{+++}$ ,  $\text{Pu}^{+++}$ ,  $\text{Am}^{+++}$ , as among the corresponding lanthanides, the ionic size contracts along the series.

### 8.5. Elements 85 and 87

Both these recently discovered elements are short-lived products of rare modes of disintegration of natural radioelements. The element 85 has also been made artificially and was first identified in such a process. Element 87, first found in nature, can be prepared artificially in several ways.

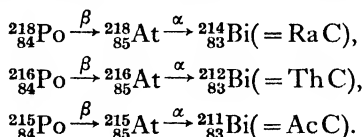
Element 85 (astatine, At) was made by Corson, Mackenzie and Segrè (1940*a, b*, 1947) by bombarding bismuth with 32 MeV.

$\alpha$ -particles. The product decays with a half-life of 7.5 hr., partly (40%) by  $\alpha$ -emission to unstable  $^{207}_{83}\text{Bi}$  (Krishnan and Nahum, 1940; Fajans and Voigt, 1941), and partly (60%) by  $K$ -capture to  $^{211}_{84}\text{Po}$  (= AcC'):



Because of its short half-life of 5 msec., AcC' is always in equilibrium with its parent.  $^{211}_{85}\text{At}$  has also been found among the products of high-energy disintegration of uranium (O'Connor, 1947). The reaction  $^{209}_{83}\text{Bi}(\alpha, n) ^{212}_{85}\text{At}$  is known as well (Weissbluth, Putnam and Segrè, 1948).

Several workers have claimed to have found element 85 among the members of the natural radioactive series (Hulubei and Cauchois, 1939; Minder, 1942; see, however, Karlik and Bernert, 1942; Labhart and Medicus, 1943). Stronger evidence has recently been presented by Karlik and Bernert (1943, 1944 *a, b*, 1946), though some difficulties of interpretation remain (Flügge and Krebs, 1944; Feather, 1945). According to Karlik and Bernert, the *A*-members of all three natural series are capable of  $\beta$ -decay, leading to  $\alpha$ -active isotopes of element 85. The branching ratios are given as  $4 \times 10^{-4}$ ,  $1.35 \times 10^{-4}$  and  $5 \times 10^{-6}$  for RaA, ThA and AcA. The two last nuclei are also members of collateral chains of the thorium and actinium series (Ghiorso, Meinke and Seaborg, 1948; Meinke, Ghiorso and Seaborg, 1949):

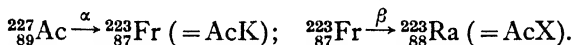


The  $\alpha$ -active body  $^{214}_{85}\text{At}$  has also been found by the American authors. According to Walen (1949),  $^{218}_{85}\text{At}$  is  $\beta$ -active as well as  $\alpha$ -active. The isotope  $^{217}_{85}\text{At}$  is a member of the artificial ( $4n + 1$ ) series (§ 8.1). Ultra-high energy disintegrations have yielded the isotopes 207, 208 and 210 (see Seaborg and Perlman, 1948 *b*).

Astatine is very interesting chemically (Leininger and Segrè, 1949). Though it is a homologue of the halogens, it has, like some of the other heaviest members of vertical groups in the Periodic Table, distinctive properties, and is not unlike its neighbour polonium. The element is soluble in carbon tetrachloride and

benzene. Astatine can be electrodeposited cathodically like a metal, or anodically. Its salt-like sulphide is insoluble in strong hydrochloric acid and co-precipitates with mercury sulphide. Silver astatide co-precipitates with silver halides, while an oxidized form comes down with silver iodate. Zinc and sulphur dioxide reduce it to the negative ion. Although astatine can be volatilized out of its parent bismuth at the melting-point of the latter ( $271^{\circ}\text{C.}$ ) and condensed on a cool surface (§ 4.2), it cannot be distilled efficiently from solutions in dilute nitric acid. Rather surprisingly it is reported that astatine concentrates along with iodine in the thyroid (Hamilton and Soley, 1940).

The first isotope (AcK) of element 87 (francium, Fr; see Paneth, 1947) was discovered by Percy (1939*a,b*, 1946*a*; see Schintlmeister, 1938) as an emitter of fairly soft  $\beta$ -rays of 21 min. half-life which grows in actinium as the product of its rare  $\alpha$ -decay. The branching ratio is about 0.012. The  $\alpha$ -activity of actinium had been observed by Hahn and Rothenbach (1913), and the range of the rays had been measured by Meyer, Hess and Paneth (1914), but these early observations had not been followed up:



The physical properties of AcK have been summarized by Percy (1946*b*; see also Guillot and Percy, 1947; Grégoire and Percy, 1947). The isotopes  ${}_{87}^{221}\text{Fr}$  (§ 8.1),  ${}_{87}^{218}\text{Fr}$ ,  ${}_{87}^{219}\text{Fr}$  and  ${}_{87}^{220}\text{Fr}$  (short-lived  $\alpha$ -rayers; Meinke, Ghiorso and Seaborg, 1949) have been made artificially. Claims that another isotope of element 87 is the product of a rare  $\alpha$ -decay of MsTh<sub>2</sub> (Cranston, 1913; Guében, 1933) have been contested (Rona and Schintlmeister, 1938). A recent search for a long-lived isotope of element 87 in the caesium-bearing mineral lepidolite was unsuccessful (Hirsh, 1943; see, however, Hulubei, 1947).

Francium is an alkali metal (see Percy, 1946*c*). The hydroxide and carbonate are soluble, while the perchlorate, the picrate and certain complex salts co-precipitate with the caesium salts.

## 8.6. Elements 43 and 61

Though the elements 43 and 61 are outside the region of the natural radioelements, neither is capable of natural existence

(Goldschmidt, 1937; see Yost, Russell and Gardner, 1947; Marinsky and Glendenin, 1948; Takvorian, 1945). However, both have been synthesized. Element 43 (technetium, Tc), located in column VII of the Periodic Table between manganese and rhenium, was made by Perrier and Segrè (1937, 1939, 1947; see Segrè, 1939*a*) in a  ${}_{42}\text{Mo}(d,n)$  reaction. By now at least nineteen different activities with half-lives between 18 sec. and 940,000 years ( ${}^{99}\text{Tc}$ ) are attributed to technetium (Seaborg and Perlman, 1948*b*; Siegel, 1946; Motta, Boyd and Larson, 1947). Fission has yielded at least six isotopes of mass numbers between 99 and 107. Weighable quantities have been made by Motta, Boyd and Larson (1947) and Fried (1948), and the crystal structure of the element has been determined by Mooney (1948).

Chemically technetium is more similar to rhenium than to manganese, as had been predicted (Perrier and Segrè, 1939; Jacobi, 1948). The hydroxide is soluble in ammonia solution as an anion, but this can be reduced into a cation by hydrochloric acid or stannous chloride. The cationic or anionic character shows in the adsorbability by 'acid' or 'basic' alumina (Flagg and Bleidner, 1945). Differences against manganese lie in the insolubility of the sulphide in dilute acid, the non-co-precipitation with manganese dioxide, and the volatility of the oxide at 400–500° C. Separations from rhenium are more difficult than from manganese. Partial separation is achieved by fractional crystallization of the potassium salts, and complete separation by the distillation of rhenium with hydrogen chloride from its solution in sulphuric acid at 200° C. Contrary to technetium, ruthenium is volatilized from its boiling solution by chlorine. Useful reactions for the removal of parent molybdenum are the precipitation of the latter with benzidine or oxin, and the extraction of molybdenum chloride with ether. Recovery from a molybdenum metal target is complete if the surface is etched with ammoniacal hydrogen peroxide. The metal is precipitated by zinc. Flagg and Bleidner have used the Hevesy-Paneth method (§ 5.2) to measure the standard potential of technetium in the reaction



Its value (–0.41 V.) lies almost midway between those for the

analogous reactions of rhenium and manganese ( $-0.15$  and  $-0.78$  V.).

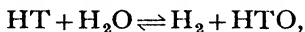
Eight half-lives of artificially made isotopes of element 61 have been listed by Seaborg and Perlman (1948*b*), and five isotopes ( $147 < A < 156$ ) have been reported as fission products alone (Siegel, 1946). Element 61 may be separated from other rare earths by chromatography (Marinsky, Glendenin and Coryell, 1947; see § 3.2). One isotope ( $^{147}_{61}$ ) has a fairly long period (3.7 years) and can be produced in weighable quantity (Coryell, 1947; Parker *et al.* 1947; Inghram *et al.* 1947; Lantz, 1948). Some X-ray lines have been observed (Peed, Spitzer and Burkhard, 1949). However, the element presents little chemical interest. The history of the discovery of element 61 was traced, and the name 'promethium' (Pm) suggested, by Marinsky and Glendenin (1948).

### 8.7. Radiohydrogen (tritium)

The knowledge of tritium (T) has been discussed in articles by Rutherford (1937) and Smith (1948). The species was discovered by Oliphant, Harteck and Rutherford (1934) as the product of the reaction  ${}^2_1\text{H}(d,p){}^3_1\text{H}$ , i.e.  $\text{D}(d,p)\text{T}$ . For a time it was doubtful which of the isobars  ${}^3_1\text{H}$  and  ${}^3_2\text{He}$  is stable, but Alvarez and Cornog established the  $\beta$ -activity of tritium, and found stable  ${}^3\text{He}$  in natural helium (Alvarez and Cornog, 1939*a, b*, 1940*a, b*; Aldrich and Nier, 1946, 1947, 1948). The half-life is about 12 years (Novick, 1947; Goldblatt, Robinson and Spence, 1947). The concentration of tritium in natural hydrogen must be less than  $1:10^{17}$  (Eidinoff, 1947*b*). The radiation is extremely soft (upper limit 18 keV.; Curran, Angus and Cockroft, 1949). Tritium is probably produced on a large scale, but with low specific activity, by radiative capture in the deuterium of chain reactors (see Smyth, *Report*, p. 82). Pure tritium is made with cyclotrons in the reaction  ${}^9_4\text{Be}(d,t){}^8_3\text{He}$ , or with chain reactors in the reaction  ${}^6_3\text{Li}(n,\alpha)\text{T}$  (Chadwick and Goldhaber, 1935; ARI, 1946; § 7.7). Other nuclear reactions yielding tritium have been listed by Cornog and Libby (1941). The formation of tritium through various reactions of fast cosmic-ray neutrons with nuclei in the atmosphere, and the geochemistry of its decay product  ${}^3\text{He}$ , have been dealt with by Libby (1946). Fast tritons *in statu nascendi* can be used to

induce nuclear reactions (Kundu and Pool, 1947, § 6.2). The D-T reaction (§ 6.6) supplies very energetic neutrons.

Tritium is an interesting tracer, though its chemical properties must deviate markedly from those of ordinary hydrogen or deuterium. It has been concentrated by thermal diffusion and separated from inactive hydrogen in the mass spectrograph (Seaborg, Wahl and Kennedy, 1940). The partition functions of  $T_2$  and its oxide were calculated (Libby, 1943), the equilibrium  $H_2 + T_2 \rightleftharpoons 2HT$  treated (Jones, 1948), and the vapour pressures of HTO and DTO (Libby and Cornog, 1941) and of HT and HD (Libby and Baxter, 1942) measured. Black and Taylor (1943) found an equilibrium constant of  $6.47 \pm 0.12$  at  $20^\circ$  in the exchange reaction



in agreement with calculation. The electrolytic separation factor T-H on a platinum electrode in alkaline solution is 14, against 7 for D-H (Eidinoff, 1947*a*). For working methods with tritium, see § 10.4.

### 8.8. Radiocarbon

Short-lived (period 20.35 min.)  $\beta^+$ -active  $^{11}_6C$  was discovered by Crane and Lauritsen (1934) as the product of the  $^{10}_5B(p, \gamma)$  reaction, and used for tracer work (see Smith and Cowie, 1941; Kamen, 1946, 1948). The more useful long-lived  $\beta^-$ -active isotope  $^{14}_6C$  (half-life about 5700 years; Engelkemeir *et al.* 1949) was not discovered until six years later (Ruben and Kamen, 1940, 1941). This delay was due to the low specific activity, and to the softness of the radiation (upper limit  $156 \pm 1$  keV.; Langer, Cook and Price, 1948; § 10.4). The first samples were made in cyclotrons by the  $^{13}_6C(d, p)^{14}_6C$  reaction. Presumably large quantities of radiocarbon, along with inactive  $^{13}_6C$ , are produced in piles by radiative capture in the carbon moderator (natural composition 98.9%  $^{12}_6C$ , 1.1%  $^{13}_6C$ ), but this material seems to be unused. Rather, the slow neutrons from piles are employed in the reaction  $^{14}_7N(n, p)^{14}_6C$ . Radiocarbon from this reaction should be free from inactive isotopes, but in practice it still contains an excess (e.g. 30-fold) of inactive carbon. Three manufacturing methods are in use (Norris *et al.* 1946; Norris and Snell, 1947, 1949; Kamen, 1946): (1) batch processing of irradiated solid calcium nitrate,



(2) continuous extraction from 'some kind of an emanating nitrogenous substance', and (3) continuous extraction from a liquid, e.g. solution of ammonium nitrate. A factory of the last type has been operating in Clinton. The solution is circulated through the pile with a glass centrifugal pump, and the active carbon is carried out, mostly as dioxide, with the gases resulting from radiation decomposition of the liquid. The carbon is precipitated from the gas as barium carbonate. This must not be exposed excessively to carbon-dioxide-carrying air (Yankwich, 1948). Working methods with radiocarbon have been described by Miller and Price (1947), by Kamen (1948), and by Calvin *et al.* (1948).

The chemical forms of the emerging radiocarbon have been studied by Yankwich, Rollefson and Norris (1946). The recoil suffered by the newly born carbon nucleus in the emission of the proton amounts to 40 keV.; thus the carbon will combine readily with available atoms or molecule where it stops. The details depend on the nature of the irradiated substance. Where the system contains oxygen, the bulk of the activity is found as the oxides carbon dioxide and carbon monoxide. In solutions of ammonium nitrate active methyl alcohol and formic acid also appear. From dry urea, hydrazine or glycine up to 50% of the activity is recovered as hydrocyanic acid, but no hydrocyanic acid is produced in solutions of these compounds, or in ammonium nitrate or aniline. Active methane appears in the absence of oxygen. On irradiation of beryllium nitride,  $\text{Be}_3\text{N}_2$ , in presence of air, and dissolution in alkali, the radiocarbon is found as methane, carbon dioxide, carbon monoxide, methyl alcohol, formic acid and hydrocyanic acid (Yankwich, 1947).

The primary active compounds are converted in the laboratory into more complicated bodies for biological tracer work. Often biosynthesis is used. Contrary to the practice in conventional chemical synthesis, attention must now be paid to the origin of the individual carbon atoms in the product, and no doubt many standard processes of organic chemistry will have to be 'duplicated' with 'marked' carbon. Synthetic work with radiocarbon is treated by Miller and Price (1947), by Melville (1948), by Calvin *et al.* (1948) and by Arrol and Glascock (1949).

Cosmic-ray neutrons make radiocarbon from atmospheric

nitrogen. Anderson *et al.* (1947) state that 'biological' carbon (from city sewage) gives about 10 disintegrations/g. min. Contrariwise, carbon in mineral oil from deep wells is inactive. The age of carbonaceous matter, e.g. bones, can thus be determined from its specific activity. This decreases from the point when exchange with atmospheric carbon came to an end (Arnold and Libby, 1949).

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## CHAPTER IX

# SPECIFIC RADIOCHEMICAL EFFECTS (CHEMICAL EXCITATION DUE TO NUCLEAR REACTIONS)

### 9.1. Definition of the 'specific radiochemical effects'

A fraction of the energy released in nuclear reactions is always available to the affected atoms and their immediate neighbours as kinetic or excitation energy. This energy as a rule suffices to raise the 'local temperature' to a level at which chemical changes are observed. The changes involve tracer quantities and can be followed radiochemically. In this chapter only these 'local' or 'specific' effects will be treated. Coryell (1948) calls them 'chemical phenomena associated with nucleogenesis'. Generalized 'indiscriminate' action of radiation beyond the immediate neighbourhood of the spot of the nuclear reaction, i.e. the subject of radiation chemistry, is excluded. The specific radiochemical effects have been reviewed by Maddock (1949).

### 9.2. Recoil collection

In the emission of an  $\alpha$ -particle the product nucleus recoils. This recoil was observed by Brooks (1904) in Rutherford's laboratory, and independently re-discovered and utilized by Hahn and Meitner (1909) and by Russ and Makower (1909, 1910). When the emitter is present as a thin layer, one-half of the recoiling nuclei (strictly, highly ionized atoms) are ejected from the source into space, while the rest dissipate their energy in the support. Because of conservation of momentum,

$$E_r/E_\alpha = 4/m_r,$$

where  $E_r$  and  $E_\alpha$  are the energies of recoil nucleus and  $\alpha$ -particle, and  $m_r$  is the mass of the former. Owing to the sharpness of  $E_\alpha$ ,  $E_r$  is also well defined. It is of the order of 100 keV., which is ample to break any chemical bond. However, both because the kinetic energy is smaller and because the energy loss per unit path length is greater, the range of the recoil nuclei is much less than

that of the  $\alpha$ -rays (Wertenstein, 1910, 1911, 1912; Wood, 1913; Kohlhörster, 1920; Dee, 1927). For example, in the decay of ThC, the range in air of the recoiling ThC'' nuclei is only 0.13 mm. The range of the  $\alpha$ -particles is 4.7 cm.

If a plate is arranged at a small distance in front of an  $\alpha$ -particle source, some of the product nuclei will stick to the plate. Chamié (1934) found with ThC that the collected quantity  $N$  (about 10% of all ThC'') is independent of the distance  $l$  between source and collector, so long as this is smaller than the range of the nuclei in the gas. When the distance exceeds the range, but is less than about 2-3 mm. air, the efficiency decreases in inverse proportion to distance

$$N = c/l,$$

where  $c$  is a constant. Langevin (1934) has interpreted this result in terms of competitive collection by the emitting and the 'collecting' surface. The nuclei diffuse in the intervening space like the molecules of a gas, but are adsorbed on the surfaces with high efficiency. The stationary concentration in the space remains small. Obviously, the formula is valid only when the diffusion coefficient is large compared with the decay constant of the recoiling nuclei, so that no activity is lost during the passage. Chamié and Tsien (1941) showed experimentally, again with ThC-ThC'', that at larger distances (5-25 mm. air) the rate of diffusion is much reduced, and the stationary concentration in space cannot be very small any more. This was explained as being due to adsorption of the diffusing recoil atoms on dust, etc. The particle weight of these radioaerocolloids (§ 4.3) is of the order of  $10^6$ .

Collection efficiency is much improved if advantage is taken of the ionization of the recoil atoms (Hahn and Meitner, 1909; Wertenstein, 1915; Wood and Makower, 1915; Dee, 1927; § 4.3), and the collector is negatively charged. The presence of the field prevents readsorption of the recoil atoms by the emitter. The field needed for full collection (saturation) increases with the strength of the source but is usually a few 100 V./cm. The collected atoms form clusters on the surfaces (§ 4.3). If the collector carries a positive charge, collection is observed only inside the range of the recoil atoms (Wertenstein, 1914).

Recoil collection of the products of  $\alpha$ -decay has been applied to

the practical preparation of sources of the A-, B- and C''-bodies, and of AcX and ThX (see e.g. Curie, 1946). The parents of the A-bodies are gaseous, and the limit of efficiency is unity instead of one-half. Recently, the infrequent  $\alpha$ -decay of RaE with the formation of  ${}_{81}^{206}\text{Tl}$  ( $= 4.2$  min. RaE'') has been discovered in recoil experiments (Broda and Feather, 1947).

In the investigation of the  $(4n + 1)$  series (§ 8.1) and of collateral chains of the other series (§ 8.3) it has been found useful to subject to recoil collection the active descendants of species obtained by recoil collection themselves (multiple recoil collection).

Because of the varying energy carried by the neutrino, the energy of  $\beta$ -recoil (Hahn and Meitner, 1909; for early work see the book by Rutherford, Chadwick and Ellis) is unsharp. The upper limit with all but the lightest elements is only of the order of 5–100 eV. The C- and C'-bodies have been collected by  $\beta$ -recoil, and (inactive)  ${}^{32}\text{S}$  nuclei from the  $\beta$ -decay of  ${}^{32}\text{P}$  have been counted with an electron multiplier after acceleration in a field (Sherwin, 1948; § 4.2). The low yields, which are found, may be due primarily to difficulties experienced by recoil atoms in leaving the surface. Even if the radioelement is present initially as a monolayer, the quality of the source deteriorates fairly rapidly. A further yield-decreasing factor is neutralization of the recoil ions on emission from the support; this is minimized by choosing a support of high work function (Sherwin, 1948). Hahn and Strassmann (1940, 1943) and Katcoff (1946) have applied the process to gaseous  $\beta$ -ray emitters in the isolation of short-lived daughters (alkali metals) of the fission products krypton and xenon. Katcoff swept the irradiated uranium solution with a carrier gas and measured the 'spatial decay' of the activity deposited on a negative wire at different distances (§ 4.1). Recoil nuclei have been collected or observed following  $K$ -capture (Allen, 1942; Jacobsen, 1946; Wright, 1947), where the recoil may be due to the emission of a neutrino only, and recoil energy is sharp (see Pontecorvo, 1946–7).

The valency of  $\beta$ -active products of  $\beta$ -decay and  $\alpha$ -decay has been investigated with members of the natural radioactive series (Mortensen and Leighton, 1934; Haissinsky and Cottin, 1948) and of fission chains (Burgus *et al.* 1948; Davies, 1948). This material has not yet been treated adequately from the standpoint of theory.



The very energetic fission fragments have also been collected by recoil (Joliot, 1939, 1944; § 7.5). Finally, it would no doubt be possible to collect by recoil nuclei of  $^{14}\text{C}$ ,  $^{35}\text{S}$  and  $^3\text{H}$  in the transmutation of nitrogen, chlorine and lithium with slow neutrons (§ 7.7).

$\alpha$ - and  $\beta$ -decay, fission,  $(n, p)$  and  $(n, \alpha)$  reactions change atomic numbers. Therefore, in contrast with what obtains in radiative neutron capture, isolation of the product in ordinary chemical operations is possible in principle, but the recoil method is rapid and efficient and produces clean thin films.

### 9.3. Aggregate recoil

This phenomenon (Ratner, 1909; Makower and Russ, 1910; Lawson, 1915, 1918, 1919) is only of negative practical value. Recoiling atoms may transfer some of their energy to neighbours, eject them from the source and cause them to wander and to contaminate the laboratory. The intensity of the effect, with one and the same radioelement, depends on various factors, including the nature of the supporting surface, the thickness, concentration and age of the source, and the pressure of the gas. Again, a negative potential on a collector increases the 'yield'. The effect is often noticed with polonium, where the life is short enough to make thin films very active, and long enough to keep the contamination 'alive' for long periods. When the quantity of the radioelement does not suffice to cover the available surface, e.g. with polonium sources of  $\ll 1$  mc./cm.<sup>2</sup>, or sources of ThB and its descendents of  $\ll 1$  c./cm.<sup>2</sup>, appreciable aggregate recoil is possible only if the radioelement is not distributed uniformly over the surface. It is assumed, from the fact that aggregate recoil does occur and from other (§ 4.3) evidence, that these radioelements are concentrated in patches or atom clusters. The clusters in the active deposits from radon and thoron frequently have diameters of about  $1-3 \times 10^{-7}$  cm., but, owing to aggregate recoil, the size of such clusters decreases with age (Martin, Baylor and Clark, 1944; § 4.3).

Wertenstein and Dobrowolska (1923), Rona and Schmidt (1927), Bonet-Maury (1928, 1929), Jedrzejowski (1929, 1932) and Schwarz (1934) have studied the dependence on temperature of the rate of disappearance of polonium (or its oxide?) through different pro-

cesses from various surfaces. (1) No genuine evaporation—the rate of which would be strongly affected by temperature—was found from silver, gold or platinum below  $350^{\circ}\text{C}$ . It was, however, rapid from mica. (2) Pseudo-evaporation by aggregate recoil, independent of temperature, was large. (3) Two-dimensional diffusion in the surface was observed on platinum, silver, and, to a lesser extent, on gold. It was absent on mica. (4) No volume diffusion into gold, platinum, aluminium, iron, nickel, copper, or lead was observed at room temperature, nor into silver at any temperature below  $500^{\circ}\text{C}$ . There was a positive effect with gold and platinum at  $470^{\circ}\text{C}$ . Only (2) is a specific radiochemical effect, but the other processes are easily observed with radioactive tracers.

#### 9.4. Szilard-Chalmers effect—qualitative observations

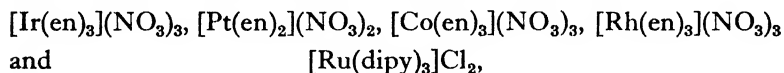
Szilard and Chalmers (1934) showed that in certain circumstances an active isotope formed in a nuclear reaction without change of atomic number can be separated chemically, at high specific activity, from the (isotopic) irradiated material. The most important nuclear reaction without change of atomic number is radiative capture of neutrons ( $n, \gamma$ ), but ( $n, 2n$ ), ( $\gamma, n$ ) and ( $d, p$ ) reactions also give isotopes of the target element. The theory of the effect will be treated in § 9.6, but it may be stated here already that at least a partial explanation is provided by a simple mechanism. Even if no heavy particle is emitted by the compound nucleus, the energy being lost as photons (radiative capture), the product nucleus (atom) suffers a recoil ('Compton recoil'). As a rule the recoil energy will be sufficient to break the chemical bond between the affected atom and the rest of the molecule. This applies *a fortiori* if the emitted neutral particle is heavy.

Szilard and Chalmers exposed ethyl iodide,  $\text{C}_2\text{H}_5\text{I}$  ( $\text{I} = {}^{127}\text{I}$ ), to neutrons and found that they could extract a part of the resulting active  ${}^{128}\text{I}$  (half-life 25 min.) with water to which some ordinary iodine had been added as a carrier. The ethyl iodide molecule itself is insoluble in water. The experiment shows that in the course of radiative capture the bond between the organic radical and the iodine is broken. Whether the iodine emerges from the parent molecule as an ion or as an uncharged atom is irrelevant in this type of experiment, since electrons are exchanged

rapidly between iodine ions and atoms. It is, however, essential for the successful 'separation of isotopes' that exchange between the target atoms in the original bound condition and the final free condition is slow. Exchange would lead to re-entry of the active isotope into the original molecule and obliterate the effect. The condition of negligible exchange is fulfilled in the non-dissociating covalent organic halides.

Further experiments with such halides were performed by Fay and Paneth (1935, 1936), Amaldi *et al.* (1935), Breshneva, Roginski and Shilinski (1936), Roberts and Irvine (1938), Erbacher and Philipp (1936*a, b*), Lu and Sugden (1939), Libby (1940), Sue (1941), Erbacher and Beck (1944), and others. The bond between the activated nucleus and the organic radical is also broken in the metal-organic compounds diethyl tellurium (Seaborg, Friedlaender and Kennedy, 1940), tetraphenyl lead and triphenyl bismuth (Maurer and Ramm, 1942), and triphenyl stibine (Williams, 1948*b*; Melander, 1948), and in cacodylic acid,  $\text{As}(\text{CH}_3)_2\text{O}\cdot\text{OH}$  (Agostino, 1935; Starke, 1940; Sue, 1943). Covalent bonds are destroyed in the production of active phosphoric acid from organic esters of phosphoric acid (Erbacher and Philipp, 1939) and of free radioarsenic from arsenic hydride (Fay and Paneth, 1935, 1936). Radioantimony is liberated from liquid pentafluoride (Williams, 1948*b*). Stable complexes, in which thermal exchange is slow, have also been widely applied. Radiohalogen in ionic or atomic form has been obtained from chlorates, perchlorates, bromates, iodates and periodates (Amaldi *et al.* 1935; Agostino, 1935; Glückauf and Fay, 1936; Hull, Shiflett and Lind, 1936; Kolthoff and Yutzy, 1937; Libby, 1940; Daudel, 1942). In work with metals, which do not readily give covalent bonds, complexes are particularly useful. Elementary radiogold has been recovered from aurates on colloidal gold carrier (Majer, 1937, 1939), and, carrier-free, from organic complexes (Herr, 1948), elementary radioselenium and tellurium from selenites, selenates and tellurates (Daudel, 1941, 1942), radiotellurite from tellurate (Seaborg, Livingood and Kennedy, 1939; Williams, 1948*a*), radiomanganese as the dioxide from permanganates (Amaldi *et al.* 1935; Agostino, 1935; Libby, 1940; Rotblat, 1942; Wilkinson, 1946; Broda, 1948), radiocopper from a complex compound with ethyl acetoacetate (Goldhaber and

Saunders, 1938), radioiron from potassium ferrocyanide (Williams, 1947, 1948*b*) and radiovanadium from organic vanadium salts insoluble in water (Sue and Yuasa, 1944).  $^{239}\text{U}$  was concentrated, after some preliminary work with inorganic uranyl salts (Irvine, 1939), from uranyl benzoyl acetate (Starke, 1942) and from uranyl salicylaldehyde-*o*-phenylenediamine (Duffield and Calvin, 1946; Melander, 1947). Uranium, thorium and zirconium separate also from complexes with dibenzoyl methane (Götte, 1948). Steigman (1941) has used 'Werner complexes', namely,



where (en) stands for ethylene diamine,  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ , and (dipy) for dipyridyl,  $\text{NC}_6\text{H}_4-\text{C}_6\text{H}_4\text{N}$ . These particular compounds were chosen by Steigman because they can be resolved into optically active enantiomorph forms, which indicates stability of the bonds, i.e. low rates of dissociation and re-combination with intermediate formation of the free ions of the central atoms. Enantiomorphy is used only as a criterion for the applicability of the process; in radiochemical practice the unresolved compound can be employed without disadvantage.

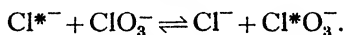
The ultimate signs of the charges of any simple ions formed, and their degrees of hydration, after the dissipation of the reaction energy, must be such that ions of the given composition are stable in the given medium, whatever their condition immediately after disruption of the original ('target') molecules. E.g., seven-valent manganese must in the end appear surrounded by four oxygen ions as a complex with a single negative charge. On the contrary, if colloidal particles are formed in liquids or gases, the ultimate charge is determined by secondary processes (see § 3.4; Fay and Paneth, 1935, 1936). The use of electrical collection after the Szilard-Chalmers reaction has been often suggested (Fay and Paneth, 1935, 1936; Amaldi *et al.* 1935; Govaerts, 1938, 1939; Capron, Stokkink and van Meerssche, 1946; Roussinow and Karamian, 1947; Goldsmith, 1948).

### 9.5. Szilard-Chalmers effect—yields

In some systems quantitative yields have been observed for the Szilard-Chalmers reaction, i.e. zero 'retention' of activity by the

target compound. Thus after irradiation of neutral or alkaline solutions of the halogenates and perhalogenates the whole of the radioelement may be recovered in the reduced form. In other systems partial retention is found. To explain why the yield should be  $< 100\%$ , in spite of the fact that sufficiency of reaction energy is indicated by the partial yield, one of the following mechanisms may be invoked.

(1) Exchange between the target compound and the (de-excited) reaction product may take place during and after exposure to the neutrons. This exchange probably accounts for retention in acid solutions of halogenates (Libby, 1940), where the radiohalogen, e.g.  $\text{Cl}^{*-}$ , may re-enter the halogenate ion



Rates of such exchange reactions can, of course, be measured independently with radioactive tracers.

(2) In undiluted target compound, or in concentrated solution, the energy of recoil may force the activated nuclei into neighbouring molecules of the target compound. In the terminology of Libby, this is an 'activated', as opposed to a 'thermal' reaction [case (1)]. According to Glückauf and Fay (1936; see, however, Libby, 1947), after irradiation of organic halides some of the radiohalogen is found in organic molecules different from the target compound. This transfer of activity is detected by chemical separation after addition of some of the newly formed body as a carrier (Table XII). If this general explanation is correct, it must

Table XII. *Activated transfer of atoms to other molecules following neutron capture* (Glückauf and Fay, 1936; see Glückauf, Jacobi and Kitt, 1949)

		Pure substances				
Target	$\text{CH}_2\text{Br}_2$	$\text{CH}_3\text{I}$	$\text{CHBr}_3$	$\text{C}_6\text{H}_5\text{Cl}$	$\text{CH}_2\text{BrCOOH}$	
Product	$\text{CHBr}_3$	$\text{CH}_2\text{I}_2$	$\text{CBr}_4$	$\text{C}_6\text{H}_4\text{Cl}_2$	$\text{CH}_2\text{Br}_2$	
		Mixtures				
Target	$\text{C}_2\text{H}_5\text{OH} + \text{I}_2$	$\text{CH}_3\text{COOH} + \text{I}_2$	$\text{C}_6\text{H}_6 + \text{CBr}_4$	$\text{C}_6\text{H}_6 + \text{CCl}_4$		
Products	$\text{C}_2\text{H}_5\text{I}$ $\text{CH}_3\text{I}$	$\text{CH}_3\text{I}$	$\text{C}_6\text{H}_5\text{Br}$	$\text{C}_6\text{H}_5\text{Cl}$		
Target	$\text{C}_6\text{H}_5\text{OH} + \text{CH}_3\text{Br}$	$\text{C}_6\text{H}_6 + \text{CH}_3\text{I}$				
Products	$\text{CH}_3\text{Br}$ $\text{C}_6\text{H}_5\text{Br}$ $\text{C}_6\text{H}_4\text{BrOH}$	$\text{C}_6\text{H}_5\text{I}$				

be assumed that another part of the radiohalogen displaces inactive halogen atoms in re-entering molecules of the target compound (see Friedmann and Libby, 1949). Figures for the total retention (here the term is used to comprise activity in the target compound and in other organic compounds [Table XII], as opposed to activity as free halogen) are reproduced in Table XIII.

Table XIII. *Retention of activity by organic halides following neutron capture* (Libby, 1940, 1941)

Target compound	Retention (%)
$C_2H_5I$	40
$C_2H_5Br$	75
$C_6H_5I$	65
$C_6H_5Br$	70
$C_2H_4Br_2$	30

Retention by activated re-entry is reduced by dilution with inert molecules. Glückauf and Fay (1936) suppressed retention by diluting carbon tetrabromide with carbon disulphide 25-fold. Libby got the same result by diluting methyl iodide with pyridine, and carbon tetrabromide with alcohol (Table XIV).

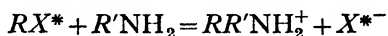
Table XIV. *Variation of retention with concentration*

Mol. % $CBr_4$ in $C_2H_5OH$	Retention (%)
100	$60 \pm 5$
1.15	$28 \pm 5$
0.74	$13 \pm 3$
0.064	$0 \pm 2$

Suess (1940; see Hamill and Young, 1949) noticed that retention by ethyl bromide is much less in the gas than in the liquid. This result is explained by Libby (1947) as follows: The velocities of the recoil nuclei are so small that they do not lose energy mainly in multiple interaction with single electrons, as do fast charged particles, but in collisions with whole atoms. On an average the loss is largest in collisions with atoms of equal weight. In collisions of this kind the knocked-on atoms may be ejected from their molecules, whereby places in these molecules become available to active atoms. The chance of bond formation is enhanced if the

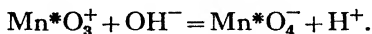
active atom is prevented from rapidly escaping the neighbourhood of the disrupted molecule by a surrounding 'cage' of other molecules. This condition is not realized in gases. Hence in gases the slowed-down atoms may still escape and lose the rest of their energy in further collisions. If the remaining energy is small, these collisions may not lead to dissociations, but to the excitation of vibrations. These general ideas on 'hot atom chemistry' have also served to explain the extent to which, in different conditions, fast radiobromine atoms substitute bromine, or alternatively hydrogen, in liquid organic compounds like propyl bromide (Willard, 1948; Friedmann and Libby, 1949).

Lu and Sugden (1939) have found a specific retention-decreasing effect of aniline and other organic bases when these are mixed with organic halides. This effect is attributed to a specific activated reaction



(3) Neither thermal nor activated re-entry can account for the finite retention of  $Mn^*$  by  $MnO_4^-$  in dilute solutions in water (Libby, 1940; Wilkinson, 1946; Rieder, 1949), while the bulk of the activity is found in reduced form as  $MnO_2$ . Thermal exchange is too slow, as shown in tests with tracers (Polissar, 1936; Mills, 1940). Activated re-entry cannot be assumed in dilute solutions. Therefore, Libby has been led to a reconsideration of the mechanism of the break-up of complex target molecules. It might be assumed that the central atoms in the complexes with oxygen are reduced in the primary stage, i.e. during their ejection from the complex. This assumption is equivalent to the idea that the ejected nuclei carry some of the electrons which had formed the bond with the (oxygen) atoms in the complex; it also means that some of the (oxygen) atoms are left behind as atoms rather than ions, i.e. in an oxidized condition. Quite possibly this notion is not correct in every case. The manganese may not recover its valency electrons during the break and may immediately after the 'explosion' still be seven-valent as any one of the fragments  $MnO_3^+$ ,  $MnO_2^{+++}$ ,  $MnO^{+++++}$  or  $Mn^{+++++++}$ , in spite of the separation from some or all of the oxygen. The reduction may occur only in a second stage during collisions of the primary fragments with molecules of water. It may be a thermal or an activated

reaction; the rate will in any case be large, because in the fragments the manganese is stripped of shielding oxygen atoms, which normally reduce its reactivity. Good reasons have been advanced why the thermal reaction is more important. The reduction reaction is predominant ( $\sim 95\%$ ) in neutral or moderately acid or alkaline media. In strongly alkaline media a different secondary reaction is more likely, namely, re-formation of permanganate in reactions of the type



In sufficiently alkaline media retention is complete, i.e. the Szilard-Chalmers effect is suppressed. In concentrated solution, the reaction  $\text{Mn}^*\text{O}_3^+ + \text{MnO}_4^- = \text{Mn}^*\text{O}_4^- + \text{MnO}_3^+$  also occurs.

The retention in crystals of permanganates decreases with increasing temperature (Libby, 1940; Erber, 1949). The retention varies also with the acidity of the solution in which the crystals are dissolved after exposure. Apparently some fragments are trapped in the crystal in an unstable condition, and complete their reaction only during dissolution. 'Annealing' of the crystals after irradiation frees some of the fragments from the trap and increases retention (Broda, Erber and Rieder, 1950). It has also been shown (Broda and Rieder, 1949; Rieder, 1950) that retention on irradiation of crystals with fast and with slow neutrons is the same. This result is consistent with Libby's mechanism.

Conditions with other oxygen complexes appear to differ from those with permanganate. It has been mentioned that retention normally is zero with halogenates and perhalogenates. With chromates (Muxart *et al.* 1947; Green and Maddock, 1949), retention in certain circumstances depends on acidity. With arsenite, arsenate and phosphate (Libby, 1940; Daudel, 1942; Sue, 1948; Broda and Müller, 1950) partial retention is found, but its value hardly depends on chemical conditions during irradiation. Incidentally, radiation chemical oxidation of the reaction product is a complicating factor in some of these systems.

(4) The result with arsenic and phosphorus seems to indicate that chemical stabilization in secondary reactions does not affect the valency of the radioelement. Possibly the finite retention, yet different from 100%, may have to be ascribed to differences in



the break-up of the individual atoms. The probability of reduction in the primary act may lie on the way between zero and unity. Correlation between the electronegativity of the central atom in the complex and decrease of valency during Szilard-Chalmers reaction has been pointed out by Daudel (1942).

### 9.6. Szilard-Chalmers effect—energetic aspects

The earliest plausible explanation of the Szilard-Chalmers effect (briefly mentioned in § 9.4) was offered by Amaldi *et al.* (1935). A  $\gamma$ -ray of energy  $E = h\nu$  has a momentum of the magnitude

$$p = h\nu/c = E_\gamma/c.$$

The recoil energy  $E_r$  is given by

$$E_r = \frac{1}{2}mv^2 = p^2/2m = E_\gamma^2/2mc^2.$$

The mass  $m$  is roughly the product of the mass  $m_H$  of hydrogen and the mass number  $A$ . Hence

$$E_r = \frac{E_\gamma^2}{A(2m_H c^2)}.$$

$E_r$  is obtained in eV. if  $E_\gamma$  and  $m_H c^2$  are so expressed. Since

$$m_H c^2 = 9.3 \times 10^8 \text{ eV.},$$

the final expression for the recoil energy is

$$E_r = 5.3 \times 10^{-10} (E_\gamma^2/A) \text{ eV.}$$

This recoil energy resides at first in the nucleus, which has actually emitted the photon. This nucleus, however, is chemically bound to the rest of the molecule (mass  $Rm_H$ ) through the orbital electrons. As the nucleus (and some, or all, of its associated electrons) is propelled in the direction opposite to the direction of emission of the photon (assuming, for simplicity, that only one photon is emitted), it exerts a pull on the rest of the molecule. Some of the recoil energy is transferred to the molecule as a whole. As long as the recoil atom still moves relatively to the remainder of the molecule, the bond is stretched to an increasing extent; therefore some of the original kinetic energy is converted into excitation energy of the molecule. If the bond is weak, it is stretched to the limit of stability, and the molecule dissociates before the velocities of the recoil atom and the remainder of the molecule are equalized.

When, however, the velocities have become equal, without dissociation having occurred, the internal excitation energy  $E_a$  has reached its maximum

$$E_a = E_r - \frac{(A+R) m_H v_f^2}{2},$$

where  $v_f$  is the final velocity. Because of the conservation of momentum

$$A m_H v = (A+R) m_H v_f.$$

Substituting for  $v_f$  in the preceding equation,

$$E_a = E_r - \frac{A m_H v^2}{2} \frac{A}{A+R},$$

i.e.

$$E_a = E_r \frac{R}{A+R}.$$

*Ceteris paribus*,  $E_a$ , the maximum energy available for chemical dissociation, increases with the mass of the attached molecule rest. In Table XV excitation energies are given for the halogen hydrides and halides with  $R = \infty$  (see Starke, 1941). In the cases of hydrobromic acid and hydriodic acid the recoil energy corresponding to single photo emission in the  $(n, \gamma)$  process should be too small

Table XV. *Energies available for dissociation*

Element	Photon energy (eV.)	Bound to hydrogen		Bound to $R = \infty$	
		Binding energy (eV.)	Available energy (eV.)	Binding energy (eV.)	Available energy (eV.)
Cl	$6.2 \times 10^6$	4.4	14.5	3.1	135
Br	$5.1 \times 10^6$	3.7	2.2	2.6	25
I	$4.8 \times 10^6$	3.0	0.8	2.0	8.3

to break the bond. The deficit would be still larger if the energy were split up among several quanta of lower energy. In that event, the quanta generally would be emitted in different directions, and, if the time intervals were sufficiently short, the effects would not only be smaller individually, but would also partially cancel out. Such cascades are quite common with the  $\gamma$ -rays from neutron capture.

The supposed insufficiency of the available energy for the dissociation of hydrobromic acid was put to test by Suess (1940). Any

free bromine formed during irradiation was taken up immediately by added acetylene gas. Contrary to expectation, the hydrobromic acid was found to dissociate on neutron capture. As an explanation it was suggested that even though the molecule does not receive enough vibrational energy for immediate dissociation, it is still sufficiently excited to react easily in collisions. Segrè, Halford and Seaborg (1939) tried to explain in a similar way, but with the help of an additional assumption, their success in separating the isomers of  $^{80}\text{Br}$ . The parent (half-life 4.4 hr.) was present as tertiary butyl bromide,  $(\text{CH}_3)_3\text{CBr}$ , dissolved in a mixture of water and alcohol. The daughter,  $^{80}\text{Br}$ , in the ground state (half-life 18 min.), is found as the free  $\text{Br}^-$  ion, although the effective decay energy amounts to 49 keV. only, and the  $\gamma$ -ray recoil energy therefore is only of the order of a few hundredths of an eV. This energy is far too small to break the C-Br bond, or even to increase markedly the velocity of the thermal reaction producing  $\text{Br}^-$ , namely, the velocity of the hydrolysis



It was pointed out that more energy becomes available through the internal conversion of the  $\gamma$ -ray. Efficient internal conversion is quite usual in slow isomeric transitions, though not in the emission of capture  $\gamma$ -rays. In  $^{80}\text{Br}$ , the efficiency is nearly 100% (Grinberg and Roussinow, 1940; Berthelot, 1944). The emission of the electron (kinetic energy  $E_e$ ) in internal conversion leads to recoil of energy

$$E_r = E_e / 1840A,$$

if for simplicity the dependence of the electron mass on velocity is disregarded\*. Comparison with the corresponding equation for the recoil energy in photon emission yields numerically

$$\frac{E_r(e)}{E_r(\gamma)} \sim 10^6 \frac{E_e}{E_\gamma^2}.$$

Therefore, if in the case of  $^{80}\text{Br}$  the binding energy of a  $K$ -electron ( $\sim 12$  keV.) is deducted from the energy of the photon,  $E_e \sim 37$  keV., and  $E_r(e)/E_r(\gamma) \sim 15$ . The internal conversion was also invoked by Vault and Libby (1939, 1941) to explain why the 18 min. activity

\* The full relativistic equation is:  $E_r = \frac{E_e^2}{2Am_Bc^2} + \frac{E_e}{2 \times 1840A}$ ;  $m_Bc^2$ , like  $E_e$  and  $E_r$  to be expressed in eV.

from bromine, present as bromate ( $\text{BrO}_3^-$ ) ion dissolved in water, is found as  $\text{Br}^-$  ion, by Willard (1940) to interpret his result that in a mixture of carbon tetrachloride and free radiobromine the same body combines with carbon, by Lu and Sugden (1939), Fairbrother (1940), Vault and Libby (1941) and Hamill and Young (1949) to account for the separation of the 18 min. body from alkyl bromides, and by Suess (1940) to explain its liberation from hydrogen bromide. Incidentally, the same separation is also obtained through preferential desorption of 18 min.  $\text{Br}^-$  ions from silver halide crystals (Imre, 1940). The case for the role of internal conversion in separations has been strengthened by the results of Seaborg, Friedlaender and Kennedy (1940). These authors compared the isomeric pairs  $^{127}\text{Te}$  and  $^{129}\text{Te}$  (as diethyl tellurium gas, or as telluric acid), which undergo internal conversion, with the pair  $^{69}\text{Zn}$  (as diethyl zinc), which does not. It was found that both pairs of tellurium isomers do, but that the zinc pair does not separate, in spite of a larger photon recoil energy in the zinc case. The essence of these findings with tellurium was reproduced by Williams (1948*a*), though yields turned out to be rather less. On the other hand, an attempt to separate the isomers of  $^{44}\text{Sc}$ , starting from scandium acetyl acetonate, failed, notwithstanding efficient internal conversion (Kennedy, 1940).

Yet it appears, as was pointed out by most of these authors, that at least in some cases all explanations based on recoil, even on electron ray recoil, must fail. The observation, that even C-Br bonds may be broken in the transition, puts an impossible strain on any recoil mechanism. The activation energy of this reaction is enormous. Several authors, while retaining the idea of the importance of internal conversion, have suggested that the rupture of the bonds need not necessarily be due to recoil at all. Segrè, Halford and Seaborg (1939), Vault and Libby (1939), Willard (1940, 1948) and Seaborg, Friedlaender and Kennedy (1940) interpret their results as meaning that the atom, deprived of an electron, transforms into an active form. Fairbrother holds that separation may be due to 'a process involving any one of a series of excited molecular states, which are produced during the gradual settling down of the Br atom after the start of internal conversion. The molecule is broken up, not merely activated, by a process, which is more in

the nature of a photo-dissociation, brought about by intramolecular quanta'. Suess (1940) stresses the role of the positive charge after the ejection of the photoelectron in the isomeric transition: 'It appears that the  $\text{HBr}^+$ , which is highly excited through the emission of the electron from an inner orbit, decomposes into a H atom and a  $\text{Br}^+$  ion during the transition into the stable ground state.' Cooper (1942) has calculated for the special and highly idealized case of bromine that a multiple Auger effect may occur. Following internal conversion and loss of an orbital electron from an inner shell an electron from an outer shell may fall into the vacant place, instead of an X-ray another electron is emitted, and so on. In each step one positive charge is added to the atom. The speed of the Auger effect compares favourably with that of the competing straight X-ray emission, so that on an average 4.7 electronic charges accumulate as the ultimate result of an internal conversion in the *K*-shell of  $^{80}\text{Br}$ . The molecule loses stability as the charges build up in the bromine atom, and Cooper concludes that the molecule must dissociate. The effect would be enhanced if the molecule were to lose binding electrons. The question has also been considered by Daudel (1943) in connexion with the isomeric transition of  $^{81}\text{Se}$ . Daudel has also pointed out that correlation between degree of internal conversion and yield should not be simple.

### 9.7. Szilard-Chalmers effect—applications

(1) The process is much used to obtain high specific activities as the result of radiative capture. Unusually high specific activities were the object of Roginski and Gopstein (1935), Erbacher and Philipp (1936*a, b*, 1939) and Erbacher and Beck (1944). Ethyl iodide and triphenyl phosphate, carefully freed from free iodine and inorganic phosphorus compounds respectively, were irradiated, and the radioelements separated either by shaking out with water, or by adsorption on carbon, without the addition of carriers. Enrichment factors of at least  $10^7$  were obtained, i.e. the active isotope was carried by not more than one part in ten million of the inactive parent element. Starke (1940) irradiated cacodylic acid,  $(\text{CH}_3)_2\text{AsOOH}$ , and recovered essentially pure radioarsenic by adsorption on magnesia. In the preparation of radiomanganese

from permanganate ion a practical limit of enrichment of  $10^5$  has been reported (Drehmann, 1943). In long irradiation, however, the specific activity of the separated sample is often observed to fall, due to the conversion of inactive material, by radiation effects, into the same chemical form as the active material (Williams, 1948*b*).

(2) The process serves to separate nuclear isomers (see § 9.6). The cases of bromine and tellurium have been mentioned. Langsdorf and Segrè (1940) separated selenium isomers. When the excited (photon-emitting) nucleus has a longer life than the nucleus in the ground state, the latter cannot be obtained pure by just waiting for the decay of the former. 'Chemical' separation must be applied.

(3) Minute neutron densities can be detected and assayed. Thus Halban, Kowarski and Magat (1939) isolated radiobromine from a large quantity of bromine compound which had been exposed to cosmic-ray neutrons at high altitude. The determination of exceedingly small neutron densities in extended aqueous media has similarly been carried out by applying the method of physical integration (§ 6.11) to a solution in which the dissolved detector gives a Szilard-Chalmers effect (permanganate; Rotblat, 1942; Broda, 1948).

(4) Activated reactions of the recoiling nuclei permit the direct rapid synthesis of chemical compounds incorporating radioelements for applied radiochemistry. Table XII shows some possibilities of the method. Its authors suggest a continuous process for the preparation of active volatile compounds involving circulation (bubbling) of a carrier gas through the parent solution during irradiation. The same idea of planned radiochemical synthesis based on the Szilard-Chalmers effect has also been put forward by Reid (1946). In § 8.8 the direct synthesis of compounds of radiocarbon has been described; the underlying idea is similar, but the recoil is due to the emission of a heavy particle.

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## CHAPTER X

# NEW DEVELOPMENTS IN THE TECHNIQUE OF RADIOCHEMICAL MEASUREMENT

### 10.1. Introductory remarks

It should be remembered that the radiochemist *counts* disintegrations, and that the qualities of the radiations are important only as far as they influence counting efficiencies, or where their identity is in doubt. Only short reference can be made to recent developments, and only the most important instruments can be considered, namely, ionization chambers, electroscopes, G.-M. counters and photographic plates. Mass spectroscopy and ultra-microchemistry will barely be mentioned in this review. Though extremely important in nuclear physics, cloud chambers (see Das Gupta and Ghosh, 1946), proportional counters (see Korff, 1946; Ballentine and Borkowski, 1949; Borkowski, 1949), coincidence counters (see Dunworth, 1940; Maier-Leibnitz, 1942) and electron multipliers (see Bay, 1941; Allen, 1947, 1948; Coltman and Marshall, 1947) will be left out of account, since none of these is in common use in radiochemistry. The counting of scintillations (see Rutherford, Chadwick and Ellis, 1930) was abandoned for a period; very recently it has been resumed with the help of the photo-multiplier tube, which responds to the light flashes, which are produced efficiently by rays, including  $\gamma$ -rays (Kallmann, 1947, 1949; Moon, 1948), in suitable transparent materials, e.g. naphthalene, anthracene or stilbene. Another effect on crystals, which may serve to measure weak sources, including  $\gamma$ -ray sources, is radioactivity induced photo-conductivity (Van Heerden, 1945; Wooldridge, Ahearn and Burton, 1947; Hofstadter, 1949). However, the solid counters of either kind are not quite ripe for application in radiochemistry.

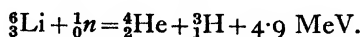
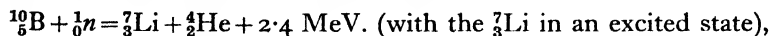
The preparation of samples for measurement, and the interpretation of numerical results, including the evaluation of errors, have been treated in a thorough paper by Kohman (1949). A full bibliography on radiation detection has been provided by Goldsmith (1949).

## 10.2. Ionization chambers

Ionization chambers count single pulses of ionization due to heavy charged particles, i.e. strongly ionizing particles, emitted by material contained in the gas filling or in thin films coating the walls. In contrast with the conditions obtaining in Geiger counters, in ionization chambers the applied electric field is too weak for ion multiplication. The small pulses to which they give rise may be observed directly with sensitive electrometers (see Neher, 1946), but it is now the usual practice to feed them into linear amplifiers, operating scaling circuits and mechanical recorders (see Lewis, 1942; Strong, 1946; Korff, 1946). If the whole energy of each ray is dissipated in the gas filling, the pulse sizes, i.e. the numbers of collected ions, are found to be very nearly proportional to the ray energies. If the rays are due to different nuclear reactions, and the pulses therefore of different sizes, the mixture of pulses can be analysed with an electronic 'discriminator', i.e. a 'bias curve' experiment is performed. The resulting sharp discrimination constitutes the main advantage of the ionization chamber over the Geiger counter. Discrimination is improved through suitable chamber design. For example, the discrimination between fission pulses and  $\alpha$ -ray pulses is enhanced in 'shallow chambers', in which only the first part of the range is utilized, because fission fragments produce most ions at the beginning of their ranges and  $\alpha$ -rays most at the end. Superposition of individual pulses is made less probable by reducing the resolving time. This is done by using suitable electronic circuits, and by filling the chamber with gases which will not interfere with the rapid collection of the free electrons which are the initial products of ionization ( $N_2$ ,  $H_2$ , noble gases). The shape of the individual pulses may be checked with the oscillograph. In the counting of heavy particles with an ionization chamber and a properly adjusted discriminator the spurious count ('background' or 'natural') is very small and is predominantly due to  $\alpha$ -rays from radioactive contamination.

Among the chief applications of the ionization chamber are the counting of  $\alpha$ -rays, fissions, and proton recoils due to fast neutrons. Slow neutrons do not supply enough energy to the knocked-on nuclei of the gas filling to be recorded, but they may be made

to induce efficiently exothermic nuclear reactions which provide large bursts of ionization. Slow neutron counters (Amaldi *et al.* 1935; Chadwick and Goldhaber, 1935) therefore contain a film of a compound of boron or lithium, e.g.  $B_4C$ , or preferably they are filled with  $BF_3$  gas. The predominating nuclear reactions are:



The efficiency of 'boron chambers' is increased fivefold by filling with pure  ${}^{10}BF_3$  gas. The slow neutron density is indicated irrespective of energy (§ 6.9). Boron chambers are often worked as proportional counters (see Korff, 1946).

Normally, light ( $\beta$ -) particles and  $\gamma$ -rays are not completely absorbed in the gas filling, and therefore produce much smaller pulses than do  $\alpha$ -rays of comparable energy. For these rays, therefore, the measurement of an average current in an 'integrating chamber' is substituted for single particle counting in a 'counting chamber'. The sensitivity of integrating chambers is improved by filling with heavy gases (e.g. xenon) or gases at high pressures. Integrating ionization chambers were used, for instance, by Langsdorf and Segrè (1940) for gaseous  ${}^{83}Br$  and  ${}^{83}Kr$ , by Smith and Cowie (1941) for  ${}^{11}C$ , and by Borkowski (1949) for  ${}^{14}C$ . Integrating chambers are also popular for the assay of the ( $\alpha$ -active) emanations.

### 10.3. Electroscopes

In radiochemistry the measurement of the current passing through an integrating ionization chamber is usually replaced by visual observation of the discharge of an electroscope. Electroscopes need no auxiliary electrical equipment. Nowadays the familiar gold-leaf electroscope has been superseded by the more sensitive Lauritsen (1937) electroscope (see Neher, 1946). In this instrument the restoring force is not gravity, but the elasticity of a low-capacity, short, thin, gold-coated quartz fibre. The movement of the fibre is followed with a microscope. The Lauritsen electroscope is rugged, and its 'natural leak' small. As with an air-filled ionization chamber, the sample is easily introduced into the sensitive space, assuring a large effective solid angle, and because

of the absence of any intervening wall, electroscopes are efficient for easily absorbed radiations. Within certain limits softness of the rays is even an advantage, since the specific ionization increases with decreasing energy. Some authors (Henriques *et al.* 1946; Henriques and Margnetti, 1946; Libby, 1947; see, however, Miller, 1947; Miller and Price, 1947) consider the electroscopic method as being among the best for the routine assay of  $^{14}\text{C}$  (upper limit of  $\beta$ -ray energy 156 keV.; see § 8.8; may be introduced as carbon dioxide),  $^{35}\text{S}$  (169 keV.; Langer, Cook and Price, 1948; introduced as solid benzidine sulphate) and  $^3\text{H}$  (18 keV.; § 8.7; introduced as hydrogen). The method is not good, however, for absolute measurements.

#### 10.4. Geiger counters

In Geiger-Müller (G.-M.) counters, as already implied (§ 10.2), the applied field is strong enough not only to collect ions, but also to accelerate them sufficiently to produce more ions through collisions with the molecules of the gas filling (gas amplification). The pulses are again fed into an electrometer, or, more often, into an amplifier with scaling circuit and mechanical recorder. Because of the increased pulse size, amplification in the circuit can be much less than with ionization chambers. Experience shows that in the 'Geiger region' of field strength (on the 'plateau') pulse size does not depend on the amount of primary ionization: the pulses from individual  $\beta$ - and  $\gamma$ -rays—the latter in so far as they produce ions at all in the counter—are registered along with the pulses due to heavy particles. Thus maximum sensitivity is reached. This has, of course, the drawback that cosmic rays and  $\gamma$ -rays from the neighbourhood contribute to the 'background'. It has been suggested to cut out the former by using anti-coincidence circuits (Berthelot, 1941, 1943; Roussinow and Igelnitzki, 1945; Hirzel and Wäffler, 1947), but the set-up is too elaborate for ordinary radiochemical work. All aspects of the Geiger counter have been well described by Korff (1946). Details of the construction and operation of the counters, including circuits, are also found in Strong's (1946) handbook and in the survey by Brown (1948). A bibliography has been supplied by Healea (1947). The standard type of counter still has its field between a cylindrical (copper or

aluminium) wall, and a central wire (tungsten) charged positively. Counters used for nuclear research are always 'fast' counters with small resolving time, and are usually filled with a mixture of argon and alcohol of a few cm. mercury pressure (see Brown, 1949; for dependence on pressure, see Rochester and McCusker, 1945).

If high efficiency in  $\beta$ - or  $\gamma$ -counting is the main object, the sample may be arranged round the counter wall. If the aim is rather to analyse the properties (energy spectrum) of the rays, or to identify them, counters with a thin flat end-window (mica) are preferred (bell-jar type counters; see Copp and Greenberg, 1943; Henriques *et al.* 1946; Yankwich, Rollefson and Norris, 1946; Dauben, Reid and Yankwich, 1947), though the solid angle is less favourable. The mica may be sealed to the metal with low-melting glass (Wu, Meaker and Glassford, 1947). If the window is thin enough, such counters will respond to  $\alpha$ -particles as well. If the radiation is exceptionally soft, the counter may be designed to receive the active film inside the casing. In this case the cathode may be a screen wall between active film and anode (Libby, 1947; see *Rev. Sci. Instrum.* **18**, 683 (1947)). Or the cathode is a thin foil between film and anode, with air pressure outside the foil kept equal to the pressure of the gas inside (Smythe and Hemmendinger, 1937; Strassmann and Hahn, 1942; Labaw, 1948). Or the cathode has a hole, through which the rays penetrate into the counter; as with the screen wall counter, the whole casing is then filled with counting gas mixture (Norris and Inghram, 1948). These soft-radiation counters must be refilled after each experiment. For work with  $^{14}\text{C}$  or with noble gases it is advisable, and with  $^3\text{H}$  it is necessary, to admit the active material into the counter as a gas (Dodson and Fowler, 1940; Seelmann-Eggebert, 1940; Strassmann and Hahn, 1942; Black and Taylor, 1943; Brown and Miller, 1947; Miller, 1947; Miller and Price, 1947; Libby, 1947; Eidinoff, 1948; Kummer, 1948; Kamen, 1948; Melander, 1948). Gas-filled counters are distinguished by 100% efficiency, independently of specific activity, and also of the nature of the ( $\alpha$ - or  $\beta$ -) radiation. However, the filling must not destroy the counting quality, i.e. prevent the formation of a counting rate/voltage 'plateau'. Cell-type  $\gamma$ -ray counters give improved yields of photo-electrons

(Beyster and Wiedenbeck, 1948). For the measurement of the activity of exhaled air, otherwise than through use of an ionization chamber (Hess and McNiff, 1947), a counter has been designed to work at atmospheric pressure (Brown, Good and Evans, 1945). Specialized counters may fully utilize (solid angle  $4\pi$ ) the radiation from films (Simpson, 1944; Cohen, 1949), be resistant to solutions (Olson *et al.* 1936; Suess, 1939; Smith and Cowie, 1941; Wang, Mervin and Stenstrom, 1942; Solomon and Estes, 1948) or be introducible into small cavities (Strajman, 1946). Apparatus for high-speed counting has been described by Muehlhause and Friedmann (1946) and Curran and Rae (1947). For counting rate meters, see Bousquet (1949). Auxiliary devices include automatic sample changers for routine measurements (Peacock and Good, 1946; Labaw, 1948).

The efficiency of a counter may be determined by calibration with a standard source. For  $\beta$ -ray emitters of roughly comparable energies  $UX_2$  or RaE are suitable, as the strength of the standard can be measured by counting in an ionization chamber the  $\alpha$ -rays from (UI+UII) or polonium in equilibrium with the source (see Burt, 1949). A more elegant method, based on coincidence counting, has been given by Dunworth (1940).

### 10.5. Thickness corrections

In many applications, the reduction in the ionizing power and/or number of rays due to the interposition of absorbers, or to the finite thickness of the source, must be allowed for. For  $\alpha$ -rays, formulae describing the decrease in ionization due to absorbers have been developed by McCoy (1913), Schweidler (1913), Flamm (1913) and R. D. Evans (1934). Since the ranges of  $\alpha$ -rays are almost uniform, these formulae need consider only the influences of obliquity and of the variation of the ionization with residual range. The number of effective rays remains practically undiminished so long as the absorber thickness is much smaller than the range. The  $\alpha$ -emitting sample itself acts as an absorber unless it is very thin. However, the problem of the 'thick'  $\alpha$ -ray source seldom arises in radiochemistry.

$\beta$ -ray intensities are mostly determined with a counter rather than an ionization chamber. Therefore, the reduction in ioniza-

tion on penetration through absorbers is unimportant so long as the rays penetrate at all. However, with  $\beta$ -rays even thin absorbers reduce markedly the number of rays in a beam. This large spread in the effective range is due partly to the unequal initial energies, and partly to scattering, including back-scattering by the support (Yaffe and Justus, 1949). Calculation is hardly possible. However, it was found empirically at an early stage (Wilson, 1909) that to a good approximation the number  $I$  of  $\beta$ -rays decreases exponentially with absorber thickness

$$I = I_0 e^{-kl},$$

where  $I_0$  is the number without absorber,  $l$  the thickness (mostly measured in g./cm.<sup>2</sup>), and  $k$  a 'weakening coefficient'. Weakening is used as a neutral term to express the influence of absorption and scattering. The value of  $k$  (in cm.<sup>2</sup>/g.) depends but little on absorber material, but aluminium is a convenient standard material. In Table XVI, column 5, some weakening coefficients are listed. Clearly the 'weakening half-thickness' is given by  $(\ln 2/k)$ . It is approximately  $3 \cdot 10^{-3}$  g./cm.<sup>2</sup> for <sup>14</sup>C, and  $0 \cdot 17$  g./cm.<sup>2</sup> for <sup>56</sup>Mn.

At large absorber thicknesses the exponential relation breaks down. No rays penetrate beyond a certain maximum range  $R$  (Table XVI, column 4).  $R$  may serve to characterize radioelements as an alternative to  $k$ . The numerical value of  $R$  is usually determined by means of a 'Feather plot' (see Glendenin, 1948). For  $\beta$ -rays of  $> 0 \cdot 7$  MeV.  $R$  is connected with the maximum energy  $E$  (in MeV.; Table XVI, column 3) through the relation (Feather, 1930, 1938; Widdowson and Champion, 1938; Sargent, 1939; Glendenin and Coryell, 1946)

$$R = 0 \cdot 543 E - 0 \cdot 160.$$

Glendenin (1948) gives for  $0 \cdot 15 < E < 0 \cdot 8$  MeV. the equation

$$R = 0 \cdot 407 E^{1 \cdot 38}.$$

For  $E < 0 \cdot 2$  MeV. Libby (1947) proposes

$$R = 0 \cdot 67 E^{\frac{1}{2}}.$$

Flammersfeld (1947) has, for  $0 \cdot 05 < E < 3$  MeV.,

$$E^2 = 3 \cdot 7(R^2 + 0 \cdot 22 R).$$



Table XVI. Data on the weakening of  $\beta$ -rays

Active species	Half-life	Maximum energy (MeV.) $E$	Range in Al (g./cm. <sup>2</sup> ) $R$	Weakening coefficient (cm. <sup>2</sup> /g.) $k$	Self-weakening coefficient (cm. <sup>2</sup> /g.) $k'$	References
<sup>3</sup> H	12 years	0.018	0.00023	~ 23,000	~ 9000	Libby (1947) (§ 8.7)
<sup>11</sup> C	20.35 min.	0.98	0.39	13	—	Townsend (1941); Libby (1947)
<sup>14</sup> C	5700 years	0.15	> 0.020	~ 250	~ 120*	Yankwich, Norris and Huston (1947); Reid, Weil and Dunning (1947); Libby (1947) (§ 8.8)
<sup>24</sup> Na	14.8 hr.	1.44	0.62	8.1	—	Feather (1938); Libby (1947)
<sup>32</sup> P	14.3 days	1.69	0.82	6.3	—	Feather (1938); Libby (1947)
<sup>35</sup> S	87.1 days	0.17	> 0.020	220	100 †	Hendricks <i>et al.</i> (1943) (§ 10.3)
<sup>56</sup> Mn	2.59 hr.	2.87	1.40	4.0	1.4 †	Guéron <i>et al.</i> (1948)
<sup>128</sup> I	25 min.	2.02	0.93	5.4	2.6 §	Guéron <i>et al.</i> (1948)
<sup>210</sup> Bi(RaE)	5 days	1.07	0.475	14	—	Feather (1930, 1938); Curie (1946)
<sup>232</sup> Pa(UX <sub>2</sub> )	1.14 min.	2.32	1.105	5.1	2.9	Feather (1938); Guéron <i>et al.</i> (1948)

\* In BaCO<sub>3</sub>.† In BaSO<sub>4</sub>.‡ In Mn<sub>2</sub>O<sub>3</sub>.§ In PbI<sub>2</sub>.|| In Na-UO<sub>2</sub> acetate.

The question of a connexion between  $R$  (or  $E$ ) and  $k$  presents some interest. According to Perey (1944, 1945) for  $0.6 < E < 5$  MeV.

$$E = 14.7/k + 0.17.$$

Evans (1947) gives for a not very clearly defined interval

$$E = (22/k)^2.$$

On combination of Perey's and Feather's rules, and substitution of the weakening half-thickness  $l_{\frac{1}{2}}$  for  $k$ , the useful relationship

$$R = 11.5 l_{\frac{1}{2}} - 0.32$$

is obtained. For  $E < 0.2$  MeV., Libby assumes a hyperbolic relationship

$$Rk = \text{const.}$$

Generally speaking, agreement between the various formulae supposed to cover identical intervals, and also with the experimental data, is rather poor.

The monoenergetic rays from internal conversion are absorbed, over most of their ranges, not according to an exponential, but according to a linear law (see Glendenin, 1948).

The investigation of weakening is important for the identification of  $\beta$ -ray emitters and in making allowance for absorption in counter walls, etc. Naturally, absorption in the sample itself also cuts down the observed intensity. Unless one can work with sources of constant thicknesses, or of very large thicknesses (at the expense of the total count) one must normalize with the help of data referring to the 'self-absorption' of 'semi-thick' films. The necessary self-weakening corrections are derived from calibration curves taken with equal quantities of the radioelements embedded in films of different thicknesses (see Guéron *et al.* 1948). Calibration curves should be considered as valid only for the particular arrangement used. It is generally found that the 'apparent specific activity'  $I$  (measured intensity per unit weight of film), issuing from a semi-thick film, can also be expressed, over a wide range, by an exponential equation

$$I = I_0 e^{-k'l},$$

with  $I_0$  as the specific activity of the same material when spread out as a very thin film, and  $l$  as the mass-thickness (g./cm.<sup>2</sup>) of the film. The 'self-weakening coefficient'  $k'$  (Table XVI, column 6)

is often about half the weakening coefficient; again its value does not greatly depend on the nature of the material.

Precise values of the absorption coefficients of  $\gamma$ -rays of various energies in the interval interesting for the radiochemist have been measured by Cowan (1948). The analysis of complex  $\gamma$ -ray spectra, the evaluation of  $\gamma$ -ray absorption coefficients, etc., have been outlined, for use in radiochemistry, by Glendenin (1948).

### 10.6. The photographic plate in radiochemistry

References to older nuclear work with plates are given by Shapiro (1941). A new impetus has been given to such work by the recent invention of 'concentrated' emulsions (Zhdanov, 1935; Demers, 1947; Ilford 'Nuclear Research Plates'—see Powell *et al.* 1946; Webb, 1948; Yagoda, 1949), i.e. of emulsions with a silver bromide content up to 90% by weight. Because of the high silver content the concentrated emulsions are characterized by small grain spacing, and therefore the tracks stand out very clearly. At the same time the background consisting of scattered isolated developed grains is small. Hence the lengths of the individual tracks and consequently the energies of the particles are better defined than with previous plates. The stopping power of these emulsions for  $\alpha$ -rays is about 1600–1850 times that of air. The thickness of emulsion used in radiochemistry is usually 20–100  $\mu$ . The tracks are viewed with a microscope. If precise determinations of track lengths and orientations are needed (see Powell, 1943; Champion and Powell, 1944) high power is used. If the tracks merely have to be counted, as is mostly true in the radiochemical applications, lower power and a larger field of view may be preferable.

Particles, including neutrons which produce recoil proton tracks from the hydrogen in the gelatine, can be shot into the emulsion from outside. The radiochemist, however, will mostly impregnate (load) the emulsion with a material which is active or can be activated. The photographic plate is loaded by bathing in a solution of the radioelement, or by letting a drop of the solution dry on top of the emulsion. After loading, the plate is kept dry (exposed) for the desired time, developed and fixed. The uptake of radioelement by the emulsion is measured in calibration experiments (Broda, 1946, 1947*a, b*). If too much foreign material is

introduced into the emulsion, the tracks become distorted and the sensitivity of the emulsion is reduced. Discrimination between tracks due to different types of particles may be based on grain spacing (see Blau and Wambacher, 1934, 1936; Demers, 1947; Wollan, Moak and Sawyer, 1947). Alternatively, the emulsion can be desensitized chemically by oxidizing agents against the action of rays of inferior ionizing power (see Perfilov, 1944; Powell *et al.* 1946). For instance, treatment with 1% chromic acid (Wambacher, 1931) will make the plate insensitive to fogging by  $\beta$ - and  $\gamma$ -rays, and also to protons;  $\alpha$ -ray tracks will be weakened, but fission tracks will remain solid. Plates are also manufactured which are sensitive only to the more heavily ionizing particles. During the storage of the exposed plates the latent picture fades (Blau, 1931; see also Lauda, 1936; Albouy and Faraggi, 1949). The rate of fading depends on oxygen pressure, moisture and temperature. Emulsions sufficiently sensitive to show the tracks of individual electrons have been produced recently (Berriman, 1948; Spence, Castle and Webb, 1948).

Radiochemical applications include the following: (1) Nuclear reactions involving the emission of charged heavy particles may be identified (Taylor and Goldhaber, 1935). (2) Decay constants are derived from the absolute numbers of tracks per unit time and unit concentration (Cuer and Lattes, 1946; Jenkner and Broda, 1949). (3) When the decay constant is known, but the concentration unknown, this can be calculated from an absolute track count. Since in any case only small areas of plate can be inspected, not only small concentrations, but also small absolute quantities can be assayed in this fashion. This constitutes probably the most sensitive method of analytical chemistry. (4) Track counts serve to determine nuclear reaction cross-sections when the reactions involve emission of heavy charged particles. The loaded plate is exposed to a known dose of radiation, and the tracks are counted (Broda, 1946; Green and Livesey, 1946). (5) Conversely, radiation doses can be measured with the help of nuclear reactions of known cross-section. E.g.  $^{10}\text{B}(n, \alpha)^7\text{Li}$  will serve for slow, and fission of thorium for fast neutrons (see Cuer *et al.* 1949). The general advantages of track count methods are: (A) simplicity and cheapness; (B) high sensitivity, every single disintegration being recorded;

(C) absence of background, since spurious and genuine effects can as a rule be distinguished after the event. Against the advantages must be set the tediousness of the inspection of large areas of plate.

The method of 'contact prints' or 'autoradiographs' is radically different from the track-count methods above described. A structured specimen, e.g. a section of biological material or a polished mineral, is pressed against the emulsion, and in this way a picture is obtained of the distribution of radioelements ( $\alpha$ - or  $\beta$ -emitting) in the specimen (Lacassagne and Lattes, 1924). Generally, only the combined effect of many individual rays is observed, but with  $\alpha$ -rays some counting has also been done. This elegant method of applied radiochemistry is now very widely applied in many branches of science (see Yagoda, 1949).

### 10.7. The mass spectrograph in radiochemistry

Apart from its preparative possibilities, the main importance of the mass spectrograph in nuclear and radiochemistry (see Thode, 1948) is analytical. It is employed in the clear assignment and assay of activities. The active fraction on the collector is traced either with a Geiger counter or through the blackening of a photographic ('transfer') plate in a contact print (Rall, 1946; Inghram and Hayden, 1947*a*). High yields of ions from the source, and high efficiency of collection are clearly essential in this type of work (Hayden and Lewis, 1946).

The natural activities of potassium and samarium have been assigned to the isotopes 40 and 152, and the fissility of uranium by slow neutrons to isotope 235, following separation in the mass spectrograph. Among artificial isotopes, the assignment of the 46 hr. activity of samarium to mass 153, and of the 9.2 hr. activity of europium to 152 are examples of the use of the method (Hayden and Inghram, 1946; Inghram and Hayden, 1947*a, b*). Many chains of fission products have also been identified and their yields determined in this manner (Siegel, 1946; Thode, 1948).

When the capture of neutrons leads to the formation of inactive isotopes the effect can in some cases be assigned to individual isotopes; the ordinary mixed element is exposed in a chain reactor, and the alteration of the relative abundances of the isotopes is

observed in the mass spectrograph. The major part of the slow neutron capture in samarium has thus been attributed to isotope 149, in gadolinium to 157 and 155 (Lapp, van Horn and Dempster, 1947), and in cadmium to 113 (Dempster, 1947; § 6.9).

### 10.8. Ultra-microchemistry of radioelements

Radiochemistry has been defined in the Introduction as the chemistry of substances which are detected through their radiations. On the other hand, microchemistry and its extension, ultra-microchemistry (Kirk, 1940; Benedetti-Pichler, 1942; Kirk and Benedetti-Pichler, 1946; Cunningham and Werner, 1949; Cunningham, 1949), use ordinary chemistry in adaptation. Therefore, strictly speaking, radiochemistry ends where ultra-microchemistry begins. Yet at least a short reference to the border region may be useful. Ramsay and Soddy (1904) measured non-radiochemically the development of helium by natural radioelements. Paneth and his associates (Paneth and Loleit, 1935; Paneth, Glückauf and Loleit, 1936) were the first to synthesize an element in quantity sufficient for non-radioactive (spectroscopic) detection (§ 6.11). Later, Wiens and Alvarez (1940; see Wiens, 1946; Meggers, 1948) made spectroscopically pure  $^{198}\text{Hg}$  by bombardment of gold with slow neutrons from a cyclotron, the production of  $^{198}\text{Hg}$  following the spontaneous decay of the  $^{198}\text{Au}$  first formed by neutron capture. Finally, enough plutonium for the application of ultra-microchemical techniques was made using cyclotron sources (§ 8.2) before large-scale production was achieved in chain reactors.

The ultra-microchemical investigation of the transuranic elements has been described in outline by Seaborg (1946*a, b*). For individual tests between 0.1 and 100  $\mu\text{g}$ . were used. Since it was essential to perform the reactions at concentrations comparable with those envisaged for the technical applications, the tests were carried out in minute volumes of solution ( $10^{-1}$ – $10^{-5}$  c.c.). These were handled in capillary containers, pipettes and burettes. Liquid volumes were measured in calibrated capillary tubing, in which the movement of the liquid was governed by air pressure under sensitive control. The smaller pipettes were built to fill automatically by capillary attraction. The test-tubes and beakers were

made of capillary tubing with an inside diameter of 0.1–1 mm. Levels were observed under the microscope, a precision of 0.5% being attained. Pipettes, etc., were worked with micro-manipulators. Liquids were usually separated from solids by centrifuging rather than by filtration. For weighings quartz balances of various types (see Neher, 1946) were employed. A specially developed quartz torsion balance (Kirk *et al.* 1947) carries a load of 100 mg., and is capable of weighing a sample as large as 300  $\mu\text{g}$ . with a sensitivity of better than 0.005  $\mu\text{g}$ . Dry reactions on a microgram scale were also performed (Kirk and Baumbach, 1946).

The results of the ultra-microchemical tests on plutonium, etc., have generally been in full agreement with the results of tracer work. This finding again strikingly confirms Soddy's view, expressed as long ago as 1911: 'Conclusions as to the chemical nature of the radioelements drawn from the investigation of minute quantities proved seldom wrong when the behaviour of larger quantities of the material could be examined.'

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