Study of Transmutation in the Chemical Laboratory.

THE SIXTH LIVERSIDGE LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY ON DECEMBER 10TH, 1936.

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I. *Alchemy.*

I UNDERSTAND that it is laid down in the regulations that every Liversidge Lecture should deal " with the description of new knowledge." I hope that the subject I have chosen will give me the opportunity of complying with this request, although the study of transmutation in the chemical laboratory is by no means new; if we replace the title by the time-honoured word " alchemy," perhaps it becomes even more obvious that we are in fact speaking of one of the oldest branches of chemistry. An exhaustive treatment of the subject would therefore have to give at least an outline of the history of alchemy, for whatever interests, whether medical, philosophical, mystical, astrological, or even religious, were interwoven with alchemy, its original aim was the transmutation of base into precious metals.

If to-day I intend nevertheless almost completely to neglect past ages, my reason for doing so is by no means lack of interest in, or reverence for, the work of our chemical forefathers. Quite the contrary; the long history of alchemy is so colourful and fascinating—from the point of view not only of science but also of wider general human culture—that there is a real danger of devoting too much time to the historical part. For we chemists of to-day are more disposed to acknowledge the merits of the alchemists than were our confrères of the 19th century; their period was in fact the only interval of neglect during the whole 1700 years or so of European alchemy's ascendency. Then many chemists and historians considered alchemy as a more or less interesting form of mental aberration. They overlooked the fact that the growth of metals in the earth—a belief firmly held for centuries by miners and scientists alike—would *a priori* be no more mysterious than the growth of animals or plants; that there was no known reason why a minute quantity of powder—generally called the " philosopher's stone "—should not transform many times its weight of metal, even as the smallest amount of yeast can raise a large quantity of dough; and that nothing but the age-long accumulation of an enormous amount of negative experience could reveal the " law of conservation of the chemical elements," just as the failure of innumerable attempts at the construction of *perpetuum mobile* led to the discovery of the " law of conservation of energy."

Even Karl Christoph Schmieder (so far as I know, the only one of the 19th-century historians of alchemy who believed in the reality of some of the reported transmutations) was occasionally too ready to assume fraudulent intentions instead of an earnest desire to investigate. Let me quote just one example of some historical interest in this country. King Henry VI granted to several people a privilege to transmute base metals into gold and silver; and from the fact that a few years later the cautious Scots decreed by order of Parliament that no British gold should cross the Scottish border, Schmieder concludes that the King's privilege was tantamount to a permit to forge counterfeit coinage. Recently I was interested to find that the original text of the privileges reads quite differently. It states clearly that the King allowed the applicants to experiment on transmutation because he was anxious to find out whether their claims to obtain " perfect gold and silver which could stand all rigid tests " were justified. He expressed his regret that so far " the most learned men had been discouraged from the undertaking by the fear of incurring the penalties under a law made in the reign of our grandfather Henry IV against alchemists "; he therefore " selected men known to hate all deceitful metallic tinctures " and ordered all his officials to be " favourable and helpful in every way to the performance of this investigation." The documents appear to me to be not in the least discreditable but on the contrary an interesting example of the manner in which an enlightened government tried to promote scientific and industrial research in the 15th century.

The important result emerging from centuries of hard chemical endeavour was the knowledge that the transmutation of metals was not yet within the reach of men. It was not, however, in a spirit of disappointment that the 19th-century chemists faced this negative result. Most of them entirely abandoned the ideas of alchemy, but found ample compensation in the unexpected achievements of modern chemistry; Liebig probably expressed the general feeling when he declared that chemistry, with its marvellous powers of changing black coal into brilliant colours and efficacious remedies, had taken the place of the philosopher's stone. He and his colleagues were sufficiently far advanced as experimental chemists to see through the alchemists' errors and to be sure that the effects observed with the crude apparatus of previous generations were never due to real changes of one element into another; and to-day, with our knowledge of the extremely narrow limits within which transmutations may occur, we can only confirm their verdict. A glance at an alchemist's laboratory outfit—as shown in many carefully drawn pictures, especially of the Flemish School, in our galleries—is sufficient to convince one that with such primitive gear transmutation could neither be brought about nor detected.

The revival of the idea of alchemy belongs essentially to this century. Two dates are of special importance; in 1896 H. Becquerel detected the invisible rays of uranium, and in 1919 Rutherford and Chadwick observed the emission of a new type of rays when nitrogen was bombarded with α-rays. The former experiment led to the discovery of the spontaneous transmutation of the radioactive substances; the latter was the first example of an artificial transmutation. In the beginning, work on both lines was based on physical methods of detection, with photographic plate, fluorescent screen, electrometer, or Wilson chamber. In the study of the natural radioelements the assistance of chemists was of decisive importance from the very start; it was longer before they could offer any help in the investigation of artificial transmutation. In both cases they applied first radiochemical and later purely chemical methods to the study of the changing elements. It might be best to follow this sequence for to-day's brief record of the new phase in the development of alchemy.

II. *Spontaneous Transmutation.*

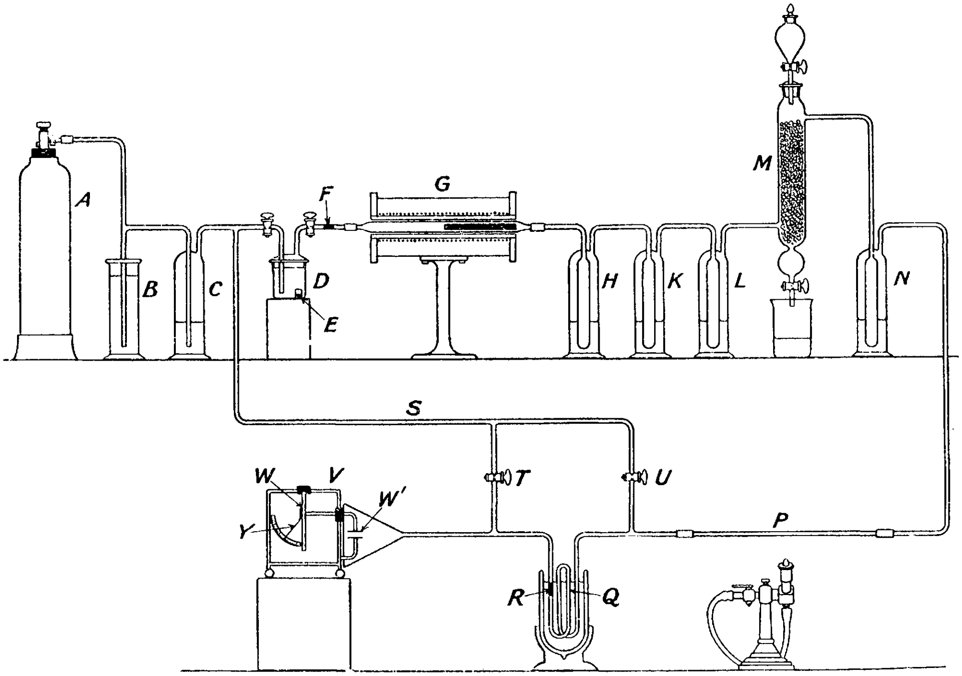
It is well known that the discovery of radium in 1898 was due to the new methods of "radiochemistry" introduced by Pierre and Marie Curie. By radiochemistry we understand the application of the methods of chemistry to invisible substances, the effect of the chemical operations being controlled by some sort of apparatus for the measurement of radioactive rays. For example, the barium chloride extracted from pitchblende proved to be active on the electroscope, and each step in the fractional crystallisation showed an increase of activity in the crystals, due to the higher ratio of radium to barium. Finally the new element radium was obtained in visible and weighable quantities.

Here radiochemical methods had helped in the discovery of a new element, but not yet in proving the fact of transmutation, as radium was originally present in the material dealt with by Mme. Curie. Exactly the same methods, applied to substances of shorter life, led to the discovery of the fundamental fact that radioactive elements are formed and disappear in our laboratories.

Radiochemical Study of Spontaneous Transmutation.—It will be sufficient to recall here Rutherford and Soddy's experiments on thorium salts in 1902. They detected the possibility of chemically separating from thorium a short-living substance of different character, thorium-*X*; the study of its decay and regeneration gave the clue to the laws governing the radioactive changes. It was known by then that thorium-*X* produces another radioactive substance, of gaseous character; and by a combination of chemical and radioactive methods they were able to demonstrate that this substance, thoron, possesses the nature of a rare gas. This proof, carried out on a quantity of matter probably not exceeding 10^{-14} gram, will always remain one of the outstanding examples of a radiochemical investigation. It can be shown in a simple lecture experiment which illustrates well the general procedure of radiochemistry.

A convenient experimental arrangement is shown in Fig. 1 (taken from my book, "Radioelements as Indicators," New York, 1928, where a detailed description can be found). *E* is a sample of radiothorium. From the steel cylinder *A* a current of nitrogen gas is caused to pass over the radiothorium, thus carrying the emanating thoron through the cotton wool filter *F* and the different washing bottles, etc., to the electroscope *V*. The discharging effect of the thoron on the electroscope cannot be influenced by any chemical reagent, *e.g.*, hot metallic copper or copper oxide in *G*, oxidising, acid, or alkaline solutions in the washing bottles, or the temperature of a blow-pipe in the quartz tube *P*. From these facts it can be concluded that the gas under examination is of a degree of inertness comparable with that of nitrogen, and possibly even with that of the rare gases. If the nitrogen current is replaced by hydrogen, it is possible to demonstrate the inertness of the radioactive gas under investigation towards red-hot magnesium powder, and thus to prove that it cannot be nitrogen, but must be regarded as a member of the argon group. If the coil *Q* is cooled to the temperature of liquid air, the current of nitrogen immediately loses its power to discharge the electroscope, indicating that the radioactive gas has been removed by this treatment. The correctness of this deduction may be shown by allowing the U-tube containing the active material to warm to room temperature after the condensable product has accumulated for a few minutes. During the warming, the course of the stream of gas is altered, so that the nitrogen no longer passes through *D*, but through *S* and *U* to *V*. The discharge of the electroscope, again seen to take place, clearly demonstrates the fact that the radioactive gas has actually been condensed in *Q* and again vaporised. As the temperature of liquid air suffices for the complete condensation, without any more delicate experiment we can draw the further conclusion that thoron must be one of the heaviest of the group of rare gases.

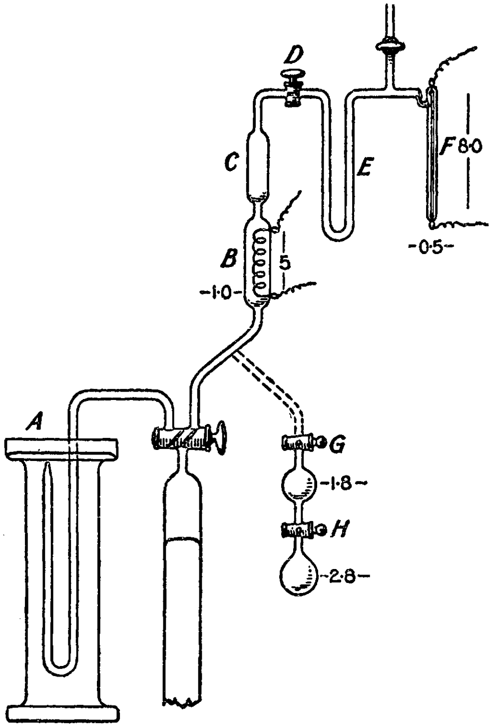
FIG. 1.



Radiochemical experiments were not only decisive in establishing the theory of radioactive disintegration; two other important discoveries were also a direct outcome, as Lord Rutherford pointed out a few months ago in his Faraday Lecture to this Society. The impossibility of separating by chemical means substances which in a radioactive sense were distinctly different led directly to the discovery of " isotopes " in the years 1910 to 1913, quite independently of J. J. Thomson's and Aston's studies on positive rays; and the combination of this fundamentally new conception with the genetic relations of the members of the radioactive series enabled Soddy, Russell, and Fajans to formulate the " displacement law." Although nowadays this law seems but a necessary consequence of the theory of atomic structure, and of the origin of α- and β-rays in the nuclei of the radioactive atoms, nevertheless radiochemistry deserves the credit of having discovered in a purely experimental manner this very important law governing natural transformation processes. While places in the periodic table could be assigned to most of the forty or so radioactive substances on the basis of a direct radiochemical study of their properties, the displacement law revealed without any possibility of doubt the positions of those with the shortest life.

Chemical Study of Spontaneous Transmutation.—Although radiochemical methods came into use right at the beginning of the new science of radioactivity, it was not till 1903 that the fact of elementary transformation could be confirmed by classical chemical methods. Here the landmark is Ramsay and Soddy's spectroscopic detection of helium evolved from radium. Although Rutherford's recognition of the α-rays as charged helium atoms naturally led to the expectation that any radioelement which emitted α-rays would develop in the course of time a small amount of helium gas, the possibility of collecting helium in quantity from radium salts was valuable in convincing even the most sceptical that one element had actually been transformed into another. Ramsay and Soddy remarked: "This observation brings ordinary methods to bear on the changes occurring in radioactive bodies," and Rutherford referred to it as the "first definite evidence of the production of a known element during the transformation of radioactive matter."

FIG. 2.



The arrangement of the apparatus for this experiment was very simple—we could still further simplify it to-day—and is shown in Fig. 2, taken from Ramsay and Soddy's paper (*Proc. Roy. Soc.*, 1904, *A*, **73**, 348). The bulb under the stopcock *H* contained a solution of 32 mg. of radium bromide; the evolved electrolytic gas was burnt to water on a red hot spiral contained in *B*, the gases were then dried by phosphoric oxide in *C*, the mercury raised up to *D*, and finally carbon dioxide and radon condensed in *E*. In the spectral tube *F* a brilliant helium spectrum appeared.

Later the production of helium was proved in many of the other substances emitting α-rays. It is not very difficult, provided that radium salts of sufficient strength are available, to prepare also enough radon for a manometric measurement and a spectroscopic investigation. However, these two rare gases are singularly favourable cases, owing to the facility with which they can be separated and spectroscopically identified; besides them, few other products of radioactive disintegration will ever be detected by purely chemical methods. If the half-value period of the new element is long, the amount to be expected might be sufficient, but the radioactive equilibrium is reached too slowly; if, on the other hand, the half-value period is short, the maximum amount will be quickly attained, but then the quantity will not suffice for chemical detection. An example of the former case is the production of ionium from uranium; eventually its quantity will be not less than 1/50,000 of the uranium, but half of this equilibrium amount of ionium will be formed only after 80,000 years. Inversely, if we were to test the production of mesothorium from thorium, seven years would be sufficient to obtain half the maximum amount of mesothorium, but here less than a thousand millionth of the thorium quantity will ever be formed.

Besides helium and radon there is, however, one product of radioactive disintegration whose formation could be chemically detected, owing to its especially fortunate position in the disintegration series. Practically complete decay of radon takes place in one month; and since its immediate disintegration products, radium *A*, *B* and *C*, live only a few hours, after this time practically the whole of the radon is converted into the lead isotope, radium *D*, of a half-value period of 22 years. When in 1914 Dr. Hevesy and myself, working in the Vienna Radium Institute, had one curie of radon at our disposal, we allowed it to decay in a quartz vessel, from the walls of which the radium *D* was dissolved by nitric acid. An electrolysis on a micro-scale produced on a platinum wire anode a yellow coating of radium *D* peroxide; its chemical identity with lead peroxide could be proved by a determination of its electrochemical potential in lead solution.

III. *Artificial Transmutation.*

So far we have dealt only with the radiochemical and chemical detection of the products of spontaneous disintegration. We now proceed to the chemist's share in work on deliberate atomic transmutation.

It was only in the course of things that attempts at artificial transmutation should be made almost immediately after the spontaneous changes of elements had been established, for once it was proved that the atoms of elements were not indestructible it was obviously only a question of finding the right method for performing elementary transmutations at will. It is historically interesting, however, that even much earlier those scientists who believed in a primordial matter, of which all the elements are formed, never gave up the alchemistic conviction that elements can be at least theoretically changed; and I think it especially worth remembering that the very chemist who is usually quoted as the originator of the conception of the chemical element in the modern sense, Robert Boyle, expressed most clearly the doctrine that the stability of chemical elements can only be regarded as relative, since for general philosophical reasons their atoms must be complicated structures. According to him the atoms or, as he calls them, " corpuscles of gold and mercury " are composed of minute particles of the primordial matter, but are " able to concure plentifully to the composition of several very differing bodies, without losing their own nature or texture." Other founders of modern chemistry, *e.g.*, Lavoisier and Dalton, adopted Boyle's chemical views, but had not the deep theoretical insight which enabled him more than 250 years ago to bring the multiplicity of the chemical elements into accord with his belief in the existence of a simple fundamental substance. He had no means of experimentally demonstrating the composite nature of those substances which the strongest reagents of chemical analysis cannot decompose even to-day. But while stating that "corpuscles of a compounded nature may in all the wonted examples of chymists pass for elementary," he always had in mind the possibility that " there may be some agent found out so subtile and so powerfull, at least in respect of those particular compounded corpuscles, as to be able to resolve them into those more simple ones, whereof they consist."

I think there are few examples in the history of the atomistic doctrine which show so clearly the admirable guidance this theory has provided for speculations concerning the nature of matter. Although to-day we do not believe in the existence of a single primordial matter, but speak of four or five particles—neutrons, protons, positrons, electrons and neutrinos—all participating in the structure of the material world, yet Boyle's description of atoms built up of smaller particles, stable in all chemical tests and breaking down only under the influence of an especially potent force, sounds very modern.

The radioelements not only proved by their behaviour that the atoms of elements are changeable, but for the first time placed in our hands an agent of the requisite highly concentrated energy. The first worker who tried to use radioactive rays for artificial transmutations, and was convinced of his success, was William Ramsay. Unfortunately his chemical observations were not controlled by sufficient blank tests and are to be interpreted quite differently; we now know that any transmutations he may have achieved with the radioactive energy at his disposal were far too small to be detected by his analytical methods, and that all the effects he observed were spurious. As some of his claims were never withdrawn, it may be useful to give in one or two instances the explanation which to-day seems the true one.

Ramsay laid special stress on his experiment showing that in presence of water radon produced not only helium but also neon, a fact which in 1908 he declared to be " indisputably proved." His evidence was faint neon lines in the helium spectrum. Now it can be shown that, owing to the lower excitation potential of neon, a few thousandths of 1% of neon in helium is sufficient to render visible some of the neon lines in the helium spectrum. As Ramsay himself admits that there may have occurred in his experiments an air leakage, shown by the presence of argon, it is fairly obvious that the origin of the neon was that same air leakage. On another occasion, in an old *X*-ray tube, Ramsay discovered helium, which he considered to be a product of the transformation, under the impact of the *X*-rays, either of the elements in the glass walls, or else of the electrodes, or of the gas inside the tube. Suspecting that in this and in many similar cases the presence of helium was nothing but a consequence of the warming of the glass, which makes it pervious to the helium in the atmosphere outside, we made the following simple experiment. We attached a glass tube to an ordinary electric light bulb and let it burn for several days; it was then easy to pump off the gas content and to detect the presence of helium; when, however, the burning lamp was cooled by immersion in water, the amount of helium was too small to be ascertained.

There can be no doubt that all the experiments by Ramsay and his co-workers in which they thought artificial transmutation had been effected are now disproved. However, in fairness to his premature claims, not only should it be emphasised that the radioactive rays which he used in many of his experiments finally led, on an infinitely smaller scale, to success, but one must also make allowance for the much greater difficulties against which he had to contend in his laboratory technique. The presence of air, one of the main sources of error in his experiments, can so easily be avoided by to-day's highly developed vacuum technique that it is well to remember how difficult, or at least tedious, it was to obtain a perfect vacuum in Ramsay's time. I never worked in his laboratory, but having studied micro-gas analysis in Soddy's laboratory in Glasgow in 1913 I am fairly well acquainted with the methods used in those days by Ramsay and his school. I still clearly remember how tiresome it was to evacuate a large glass apparatus by a Töpler pump. After raising the heavy mercury bulb for fifty times or so, one was only too inclined to believe that the vacuum must be absolutely perfect.

The first real success in transmuting elements was obtained by Rutherford and Chadwick in 1919. They also used radioactive rays as the agent " subtile and powerfull," but did not rely on chemical analysis for the detection of the new products, using instead the much more sensitive physical methods for observation of new rays. During the long period from 1919 to 1934 work on artificial transmutation had passed entirely into the hands of the physicists. Not only could chemistry be of no help in these researches, but even radiochemical methods could not be applied. For a capital difference between the natural radioactive substances and the artificially produced elements was that in the radioactive families long series of radioelements follow each other; and, as I stated at the beginning of this lecture, it is very easy radiochemically to control a disintegration process if the product influences an electroscope. But since in the first cases of artificial disintegration by α-rays the products were inactive, there was no possibility whatever of studying their nature by chemical means. In the famous example of the disruption of nitrogen by α-particles,

$$^{14}_{7}\mathrm{N} + ^{4}_{2}\mathrm{He} \longrightarrow ^{1}_{1}\mathrm{H} + ^{17}_{8}\mathrm{O}$$

the evidence of the Wilson chamber proved that only two products were formed; hydrogen was identified by its specific charge and mass, and the above equation was thus established beyond reasonable doubt; but no chemical or radiochemical proof could be adduced to identify the new product with an isotope of oxygen.

Radiochemical Study of Artificial Transmutation.—The whole situation changed when in 1923 the artificial radioelements were discovered. Let me mention only one of the first experiments by I. Curie and F. Joliot. Boron, bombarded with α-particles, yielded an element emitting positrons; its radioactivity decayed with a half-value period of 14 minutes, a time long enough to perform a simple chemical investigation. As a target, boron nitride was used, because boron itself is difficult to dissolve and the presence of nitrogen is of no account in the radioactive observations, since this element is not activated by α-ray bombardment; after irradiation the boron nitride was dissolved in caustic potash, whereby ammonia was produced. It was found that this ammonia carried with it the positron-emitting substance of 14 minutes period; this, of course, was to be anticipated if it were a nitrogen isotope, and so the following mechanism of reaction—which for other reasons was likely to occur—was chemically supported :

$$\begin{aligned} {}^{10}_{5}\mathrm{B} + {}^{4}_{2}\mathrm{He} &\longrightarrow {}^{1}_{0}n + {}^{13}_{7}\mathrm{N} \\ {}^{13}_{7}\mathrm{N} &\longrightarrow {}^{0}_{1}e + {}^{13}_{6}\mathrm{C} \quad (T = 14 \text{ mins.}) \end{aligned}$$

The complete analogy between this radiochemical proof and those applied since early days in the study of natural radioactivity is, I think, obvious. The only technical difference is that the electroscopes customary for radioactive measurements are rarely sufficiently sensitive for the detection of the weak activities of the artificial radioelements. The instrument mostly used in these investigations is the Geiger–Müller tube connected with some sort of amplifying system. It is not difficult, even in a chemical laboratory, to set up such a simple device—nearly all the apparatus can be bought in any wireless shop—and with its help the chemical nature of very many of the products of artificial transmutation has been studied.

This new field of research became of special interest to chemists when Fermi's discovery of the efficiency of neutrons in producing artificial radioelements showed the possibility of an enormous variety of transmutations. The following two tables give some selected examples to show that one and the same element—ordinary aluminium of mass number 27—can be transformed into various other elements, according to the manner in which it is treated; and that on the other hand one and the same artificial radioelement—radioaluminium of mass number 28 and half-value period 2·3 mins.—can be produced from very different sources. This recalls in a striking manner the variety of chemical changes effected in molecules by ordinary chemical methods, but this new branch of science deals with the decomposition and synthesis of atomic nuclei, not of molecules. It is alchemy, not chemistry.

TABLE I.

$$\begin{aligned} {}^{27}_{13}\mathrm{Al} + {}^{1}_{0}n &\longrightarrow {}^{28}_{13}\mathrm{Al} \\ {}^{28}_{13}\mathrm{Al} &\longrightarrow {}^{0}_{-1}e + {}^{28}_{14}\mathrm{Si} \quad (T = 2{\cdot}3 \text{ mins.}) \\[4pt] {}^{27}_{13}\mathrm{Al} + {}^{1}_{0}n &\longrightarrow {}^{1}_{1}\mathrm{H} + {}^{27}_{12}\mathrm{Mg} \\ {}^{27}_{12}\mathrm{Mg} &\longrightarrow {}^{0}_{-1}e + {}^{27}_{13}\mathrm{Al} \quad (T = 10 \text{ mins.}) \\[4pt] {}^{27}_{13}\mathrm{Al} + {}^{1}_{0}n &\longrightarrow {}^{4}_{2}\mathrm{He} + {}^{24}_{11}\mathrm{Na} \\ {}^{24}_{11}\mathrm{Na} &\longrightarrow {}^{0}_{-1}e + {}^{24}_{12}\mathrm{Mg} \quad (T = 15{\cdot}5 \text{ hrs.}) \\[4pt] {}^{27}_{13}\mathrm{Al} + {}^{1}_{1}\mathrm{H} &\longrightarrow {}^{4}_{2}\mathrm{He} + {}^{24}_{12}\mathrm{Mg} \end{aligned}$$

$$\begin{aligned} {}^{27}_{13}\mathrm{Al} + {}^{2}_{1}\mathrm{H} &\longrightarrow {}^{1}_{0}n + {}^{28}_{14}\mathrm{Si} \\[4pt] {}^{27}_{13}\mathrm{Al} + {}^{2}_{1}\mathrm{H} &\longrightarrow {}^{1}_{1}\mathrm{H} + {}^{28}_{13}\mathrm{Al} \\ {}^{28}_{13}\mathrm{Al} &\longrightarrow {}^{0}_{-1}e + {}^{28}_{14}\mathrm{Si} \quad (T = 2{\cdot}3 \text{ mins.}) \\[4pt] {}^{27}_{13}\mathrm{Al} + {}^{2}_{1}\mathrm{H} &\longrightarrow {}^{4}_{2}\mathrm{He} + {}^{25}_{12}\mathrm{Mg} \\[4pt] {}^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} &\longrightarrow {}^{1}_{0}n + {}^{30}_{15}\mathrm{P} \\ {}^{30}_{15}\mathrm{P} &\longrightarrow {}^{0}_{1}e + {}^{30}_{14}\mathrm{Si} \quad (T = 3{\cdot}25 \text{ mins.}) \\[4pt] {}^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} &\longrightarrow {}^{1}_{1}\mathrm{H} + {}^{30}_{14}\mathrm{Si} \end{aligned}$$

TABLE II.

$$\left.\begin{aligned} {}^{25}_{12}\mathrm{Mg} + {}^{4}_{2}\mathrm{He} &\longrightarrow {}^{1}_{1}\mathrm{H} + {}^{28}_{13}\mathrm{Al} \\ {}^{27}_{13}\mathrm{Al} + {}^{2}_{1}\mathrm{H} &\longrightarrow {}^{1}_{1}\mathrm{H} + {}^{28}_{13}\mathrm{Al} \\ {}^{27}_{13}\mathrm{Al} + {}^{1}_{0}n &\longrightarrow {}^{28}_{13}\mathrm{Al} \\ {}^{28}_{14}\mathrm{Si} + {}^{1}_{0}n &\longrightarrow {}^{1}_{1}\mathrm{H} + {}^{28}_{13}\mathrm{Al} \\ {}^{31}_{15}\mathrm{P} + {}^{1}_{0}n &\longrightarrow {}^{4}_{2}\mathrm{He} + {}^{28}_{13}\mathrm{Al} \end{aligned}\right\} \; {}^{28}_{13}\mathrm{Al} \longrightarrow {}^{0}_{-1}e + {}^{28}_{14}\mathrm{Si} \quad (T = 2{\cdot}3 \text{ mins.})$$

As seen from the tables, some of the transformations are effected by bombardment, not with α-rays or neutrons, but with accelerated particles of hydrogen or deuterium. For these experiments, of course, the high voltage apparatus, or the " cyclotron," of the physicist is necessary, but many of the products have been studied and identified by radiochemical methods. The help of the chemist is, of course, especially welcome in cases where several atomic species are simultaneously formed; for example, he can easily separate, and so distinguish, radioactive sodium from magnesium, if both are produced from aluminium by neutron bombardment.

Chemical Study of Artificial Transmutation.—We have seen that the field of artificial radioelements offers a great number of examples where the success of the transmutation can be checked by radiochemical methods. The last question we have to discuss is whether we are to-day able to study artificial transmutation also by purely chemical means.

It is at once evident that the chemical detection of artificially produced elements will be much more difficult than those of natural transformations. If we have at our disposal a quantity of 100 mc. of radon, then 2×10^{-4} c.c. of helium is formed by its complete decay, and it is quite a simple matter, with our present-day laboratory technique, to identify and measure this amount. If, however, the same quantity of radon is used for the disintegration of nitrogen, in the classical experiment on artificial disintegration mentioned above, the amount of hydrogen produced is only of the order 10^{-9} c.c., as only about 1 in 100,000 α-particles liberates a proton from a nitrogen nucleus. Small as this amount is, it did not seem entirely impossible to detect it chemically; but prolonged attempts in this direction by myself and my co-worker Günther in Königsberg have failed.

It may be useful to compare here the sensitivity of radiophysical, radiochemical, and purely chemical methods in the detection of transmutation. The founder and doyen of the Austrian school of microchemistry, F. Emich, introduced the distinction between " theoretical " and " practical " sensitivity, the former being the smallest amount of a substance which gives an observable effect, the latter the smallest quantity of matter with which an identification can actually be obtained. Here we are concerned only with the practical sensitivity. It is well known that a track in the Wilson chamber, or a kick in the Geiger–Müller counter, is caused by the flight of a single atom, and it may be said, therefore, that the theoretical sensitivity is here one atom. As, however, disintegration follows the laws of probability, a much greater number of atoms of the disintegrating substance must be present if we want to study its rays. The practical sensitivity of the detection in a Wilson chamber or Geiger counter depends in the first place on the half-value period: the shorter this is, the smaller is the quantity of the substance that emits sufficient rays for an identification during the time of observation. On the other hand, too short a period renders the handling of the substance impossible. No systematic investigation has been carried out in order to determine the smallest amount of matter detectable by the above-mentioned physical methods, but we may assume it to be of the order of 10^3 atoms. If the substance has a half-value period comparable with that of radium *C* (20 minutes), at the beginning about one ray would be emitted every 2 seconds and it might be possible to send a sufficient fraction of them into the measuring instrument to enable the substance to be identified. If such a half-value period is long enough for the carrying out of some simple chemical operation, the practical sensitivity of the radiochemical identification can be said to be of the same order of 10^3 atoms.

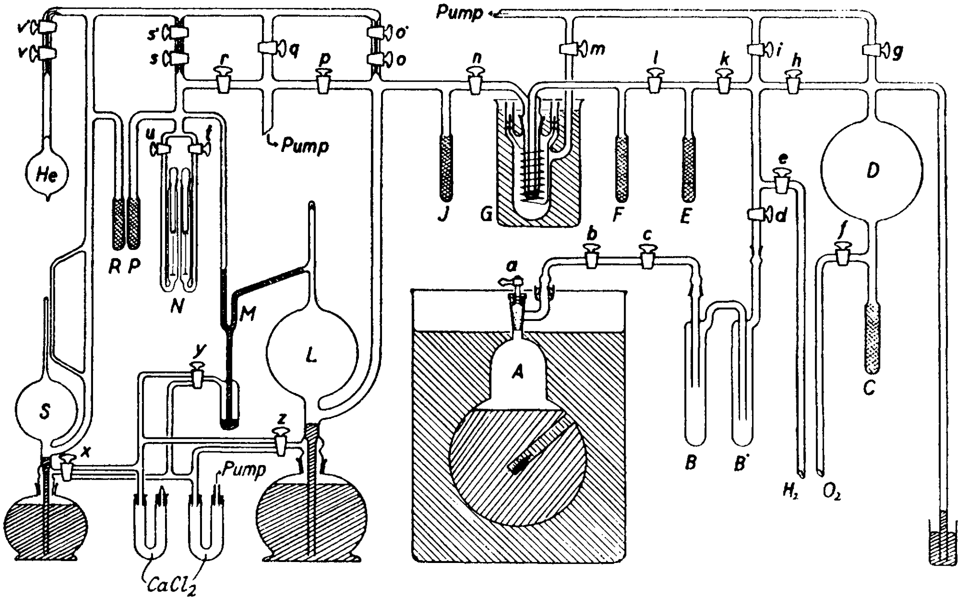
If the substance is not radioactive, nothing approaching this limit can be obtained. The most sensitive test for an inactive element is, in general, spectroscopic observation; in the case of neon and helium the advantage of a characteristic spectrum is coupled with qualities which make the analytical separation easy. This explains why we could identify pure helium and neon when only some 10^{-10} c.c., or 10^9 to 10^{10} atoms, were present. As already mentioned above, it is possible to detect very small traces of neon in helium; we found that 0·002% of neon can be seen, even if not more than 10^{-7} c.c. of the mixture is available. This means that as little as 2×10^{-12} c.c., or 5×10^7 atoms, of neon can be recognised. Although these are outstanding examples, the practical sensitivity is still 10^4—10^6 times higher than in the radiophysical and radiochemical cases just discussed.

Since the identification limit of helium is especially low, and because several processes of artificial transmutation, all producing helium, are now known, two years ago we renewed our attempts to prove by purely chemical methods the fact of artificial transmutation. For various reasons we chose the following reaction,

$$^{10}_{5}\mathrm{B} + ^{1}_{0}n \longrightarrow ^{4}_{2}\mathrm{He} + ^{7}_{3}\mathrm{Li}$$

which was discovered by Chadwick and Goldhaber by employing the usual physical methods for the detection of the rays. Our endeavour was to separate the helium from the boron in which it was produced by the neutron bombardment, to purify and to measure it. The last seemed especially interesting, as it is difficult to derive quantitative figures from the physical observations.

FIG. 3.



In Fig. 3 the general arrangement is shown. The copper flask *A* is filled with boron methoxide; it contains a pocket in which the neutron source, a mixture of beryllium powder and radium (or radon), is placed. As only slow neutrons are captured by boron according to the above equation, the flask *A* is surrounded by a water tank. We carried out the experiment four times with varying strengths of the neutron source. In the final experiment neutrons produced by the decay of a little more than 2000 mc. of radon, mixed with beryllium, were used for the bombardment of 4 litres of boron methoxide. Less than 10^{-10} gram of boron was disintegrated and the corresponding 10^{-7} c.c. of helium could be separated from the methoxide by boiling the latter. After removal of all the other gases by adsorption on charcoal in the tubes *E* and *F*, and the burning of the hydrogen with oxygen in the furnace *G*, nothing but the small quantity of helium remained. Its purity was tested spectroscopically in the capillary tube on the top of *L*, and its quantity finally measured by a special manometer *N*. (Fig. 3 is taken from *Proc. Roy. Soc.*, 1936, *A*, **157**, 417.)

So, by slightly changing Ramsay and Soddy's statement about the first detection of helium in a natural transmutation, we may say that this observation brings ordinary methods to bear on the changes occurring in artificial transmutations. In both cases the qualitative result could be predicted; but the way to quantitative measurements has thereby been opened. And it is evidently a step nearer to the old alchemistic aim, for the whole transmutation can be brought about in the chemist's laboratory without any help whatever from a physicist's apparatus. All we have to do is to prepare radium salt and beryllium metal, mix the two, and bring the mixture near to a boron compound. Then we are sure partly to convert the boron into helium.

If we describe the experiment in such terms, it becomes obvious that some essential features of the procedure of the old alchemists are retained in this process of modern alchemy. However much their descriptions differed in detail they all agreed that the philosopher's stone had first to be prepared; then, directly this miraculous substance was available, by " projecting " it on other substances, these would be transmuted. In our experiment we see the same two steps : first the preparation of the philosopher's stone, the radium-beryllium tube with its marvellous property of emitting neutrons; and secondly, by the projection of the neutrons on other elements, the transformation of almost any of them. But there is, unfortunately, one serious discrepancy between the alchemists' promises and our achievement. Most of them expected that a small quantity of the philosopher's stone would transmute many times its weight of matter; Louis Figuier in his history of alchemy (1854) has amusingly compared the different claims. Kunckel thought the stone would transmute only twice its own weight, Arnold of Villanova promised 100 times, Roger Bacon 100,000, Isaac of Holland 1,000,000; Raymond Lully thought that each ounce of the transmuted metal would possess the power of transmuting a thousand other ounces, and Salmon even assumed an increase of transmuting power in each such operation. Compared with these claims the modern philosopher's stone is disappointingly feeble. In the radon-beryllium tube about 10,000 α-particles are necessary to produce one neutron, which at its best can transmute only one boron atom into one atom of helium. Hence a big discrepancy between the philosopher's stone and the transmuted matter does exist, and unfortunately on the debit side.

IV. *Future Research on Transmutation by Radiochemical and Chemical Methods.*

As the regulations of the Liversidge lectureship demand that the lecturer should " point out the directions in which further research work is desirable," I will try to indicate the lines on which chemical research on transmutation would seem at present to be most promising.

Let us first consider the *radiochemical methods.* I do not think that in the field of natural radioactivity many more radiochemical researches are necessary. There are no doubt still a few places in the disintegration series where the actual happenings are not well known, for instance, the beginning of the uranium and the actinium series, and it may further be that there are a few branch products and one or two—very feebly active—radioelements yet to be discovered; however, for chemists interested in radioactivity there are so many far more urgent problems that the elucidation of these minor points may well be postponed.

The really startling problems are those connected with the production of artificial radioelements. As new radioactive types of atoms can be created in almost every place of the periodic system, it needs a constant co-operation of chemists with physicists to identify the nature of these new atomic species. I have mentioned several cases where this collaboration has already resulted in the ascertainment of the equation of transmutation. But there are many processes where even now we are ignorant of the actual mechanism, and others which need further confirmation. Let me mention in this connexion only the very interesting discoveries of a radioactive isotope of helium, of a new radioactive series produced from thorium, and of elements with atomic numbers higher than that of uranium. The chemical nature of the radiohelium seems to be beyond doubt and only the atomic weight of this new helium isotope yet remains debatable, but the number and mode of production of four new radioelements from thorium, and of the five or so trans-uranium elements are still much in need of further radiochemical work. It may be emphasised that our conviction that elements with atomic numbers 93 to, probably, 97 have been formed is entirely based on radiochemical studies; simply because some of their analytical reactions are not to be found in the elements with atomic numbers up to 92 we are confident that the higher atomic numbers have been reached.

The reward for the by no means simple investigation on the trans-uranium elements will be not only the satisfaction of knowing the effect of neutron bombardment on the peculiarly unstable uranium nucleus but eventually knowledge of the chemical properties of elements so far not represented on our earth. Further, the more new radioactive isotopes of the ordinary elements are chemically identified, the richer becomes our store of " radioactive indicators " applicable to the solution of chemical and biological problems.

If we try to plan ahead what contribution purely *chemical methods* can make to questions of transmutation, we find that here the field of naturally occurring transmutations seems at least equally promising.

It is unlikely that amongst artificially produced elements the one example of a chemical detection mentioned above will remain unique. It might be useful to repeat some day the same experiment with greater quantities of boron methoxide, thereby catching practically all the neutrons produced, and so obtaining a larger and better-defined amount of helium. Further, there will probably be no difficulty in proving by the same method the production of helium from lithium under neutron bombardment. Chemistry should be able to decide even questions inaccessible to physical methods; for instance, whether $^{8}_{4}$Be is stable or disintegrates into two $^{4}_{2}$He as soon as it is formed by the irradiation of $^{9}_{4}$Be with γ-rays—a problem in the study of which we are engaged at present. But if we remember what has been said about the limits of practical detection of elements, we can at present hardly hope chemically to deal with other products of artificial transmutation besides the elements helium and neon. Of course, if we do not use neutron sources but collaborate with physical laboratories, the amount of artificially produced elements can be greatly increased; however, the bigger and more complicated the apparatus for producing the new elements, the harder it will be for the chemist to avoid contamination. If the product of disintegration should be an atomic species not represented in Nature, only then might its isolation be effected in spite of the difficulties of excluding impurities. If, for example, a helium isotope of atomic weight 3 or 5 could be artificially produced to an amount of 10^{-7} c.c. or so, it should be possible to separate it from all other gases besides the ordinary helium 4, and to detect its presence therein by the methods of interferometric spectroscopy; especially by using E. O. Lawrence's cyclotron—which produces a beam of accelerated particles outside the apparatus—should a sufficiently rigorous exclusion of ordinary helium be possible.

While, as we see, the application of chemical methods to artificial transmutations is not too easy, it seems quite likely that several modern microchemical methods are sensitive enough for use in the study of natural transmutations which constantly occur on our earth but so far have remained obscure. It has frequently been supposed that the property of spontaneous transmutation is not confined to the three radioactive series and the three isolated radioelements potassium, rubidium and samarium, but that other elements also may undergo a change, only too slowly to emit ionising rays. Here, of course, no radiophysical or radiochemical methods can be of any use; but a study of the quantities of elements associated in minerals can lead to the discovery of such hidden processes.

Let us imagine that the discovery of radioactivity had not taken place in 1896. It is well known that it was due not to any systematic development but to a piece of good luck. Because H. Poincaré had supposed that the origin of *X*-rays is connected with the fluorescent spot on the glass walls of the Roentgen tube, H. Becquerel investigated the effect of a fluorescent uranium salt on a photographic plate and discovered the invisible rays emitted from uranium. To-day we know that in the case of neither the *X*-rays nor the uranium rays has the fluorescence—which was the connecting link in the discovery—anything to do with the invisible rays; and it is, therefore, not without interest to speculate if, and when, radioactivity would have been discovered without this happy accident.

I think that only a few years later a systematic development of the chemical analysis of rocks would unavoidably have led to the discovery of transmutation processes going on in the earth's crust. As early as 1888 F. W. Hillebrand had described the surprising presence of an inert gas in certain minerals; it was supposed to be nitrogen, but after the discovery of argon (January, 1895) a re-examination of its nature seemed advisable. Simultaneously (April, 1895) this work was carried out in Ramsay's laboratory in London and in Cleve's laboratory in Upsala and the inert gas was identified as helium. A further study of the peculiar occurrence of a gas without chemical activity in certain minerals ought to have led in a perfectly logical way to the recognition that this inert gas could only have been formed after the solidification of the minerals; and the constant presence in these minerals of the heavy elements uranium or thorium or both would have suggested a genetic relation. (Hillebrand had already noticed the parallelism between gas- and uranium-content!) Probably even the dependence of the amount of helium on the age of the minerals would have been recognised after more extended researches, and by the next systematic step, namely, the laboratory study of the production of helium from uranium and thorium salts, even the order of the velocity of the helium formation from both these elements could have been discovered—without any knowledge of the rays emitted by radioactive substances!

I have sketched this imaginary line of development to make it clear that purely chemical researches may perhaps be able to detect transmutation processes which are actually going on without the emission of detectable rays. It seems very likely at present that one such process is already known in its outlines. In 1908 Lord Rayleigh discovered that the mineral beryl contains helium, although neither thorium nor uranium is present in sufficient quantity to account for it. Many rather far-fetched hypotheses have been formulated in explanation, for instance, the presence in beryl of channels in the crystal lattice, just large enough to permit the entrance of helium from the air, and the like. In 1926, after developing methods for the detection of very small quantities of helium, we tested another possibility, namely, the rayless formation of helium in beryllium salts, but by reason of difficulties of procedure our experiments were not conclusive. They have twice been started again, in Berlin and in Königsberg, but in both cases I had to leave the laboratory before a sufficient time for the accumulation of the helium had elapsed, and the delicate glass apparatus could not be transported. In 1933 a paper by Lord Rayleigh, attacking the problem in a more indirect way, made it very probable that the formation of helium in beryl must be due to some sort of atomic disintegration, as he proved that the younger minerals usually contain small, but the oldest formations relatively large, amounts of helium. While, however, the mean helium values of the beryls, grouped according to geological periods, show a decrease from Archæan to Tertiary, there is a very strong overlap, due perhaps to the fact that only a fraction of the helium has been retained in the minerals. In spite of the indirect evidence already available it is therefore by no means superfluous to examine directly the spontaneous production of helium from beryllium. About two years ago, with the help of Mr. J. W. J. Fay, I began these experiments for the fourth time, on a broader basis, and on this occasion I hope to reach definite results.

It might here be mentioned that a precision measurement of the development of helium from uranium and thorium salts is at present probably the best method of determining the disintegration constants of these long-living radioelements, which so far have been deduced from more indirect observations. Work on these lines is also in progress in my laboratory.

Not only beryllium but also potassium minerals frequently contain helium, but no uranium or thorium in sufficient quantity to account for its presence. Here O. Hahn has suggested that during the crystallisation of the mineral a fairly short-living helium-producing radioactive substance, radium *D*, was included, which has in the meantime decayed. This is one possible explanation of the presence of helium; but it is certainly desirable to confirm or exclude the alternative contingency of a helium-decay of potassium itself. Attempts in my laboratory in 1928 to discover a helium production in potassium salts were entirely negative and so already gave a maximum value of the velocity of such a hypothetic process; the amount of helium produced per year from 1 gram of potassium is less than 5×10^{-12} c.c. (uranium produces $1{\cdot}4 \times 10^{-8}$ c.c.).

There is also a special reason why it is desirable to have a complete knowledge of all transmutation processes going on in minerals by which helium might be produced. For geological age determinations the " helium method " is at present the most valuable of all. As this is an instance of a chemical study of transmutation processes useful also to other sciences, a reference to it is certainly not out of place in this lecture. Here is the principle : We know the velocity of disintegration of uranium and thorium, and also that the stable end products of both these radioelements are lead and helium; by measuring the quantities of uranium and thorium in a mineral, and of one of the end products, lead or helium, it is possible to determine the time which has elapsed since the mineral's solidification. As we now know how to determine very small quantities of helium, the " helium method " has the great advantage over the " lead method " of being applicable not only to radioactive minerals in the strict sense but to practically every rock of every geological period (which always contain traces of uranium and thorium). A former co-worker of mine, Dr. Urry, now at the Massachusetts Institute of Technology, has for years devoted his energy to geological age determinations by the helium method; and from the latest report of the Committee on the Measurement of Geological Time, edited by leading American geologists, chemists and physicists, it is obvious that Urry's work has been the most valuable contribution to geological time determination during the last year. The same method applied to meteorites has already yielded results of interest to astronomers, and we may expect that in future many more workers will make use of it. Now it is obvious that a helium development from elements outside the uranium and thorium series would, as soon as established, necessitate special precautions and perhaps slight corrections. But at present there is no reason to doubt the reliability of the results obtained.

It would take too long to discuss here other cases where a careful chemical analysis of the elementary composition of minerals, or of the generation of new elements in salts, will be able to throw light on rayless transmutation processes continuing for geological periods. In many cases the analytical methods are not yet sufficiently developed and the limits of identification of the suspected elements remain behind the necessary sensitivity by several orders of magnitude. But it will certainly be worth while to pay attention to all cases where an especially careful micro-analysis might be able to discover processes of disintegration.

By all these researches we can hope to contribute in a small measure to the solution of a problem which has interested mankind for ages : the question of the evolution of our chemical elements. In the past century " evolution " was one of the leading ideas of the biological sciences, but few were inclined to apply this conception to inorganic matter. In earlier centuries no such dividing line was drawn, and to-day science has returned to a discussion of the genesis problem of the chemical elements. Even before the days of radioactivity the periodic system indicated some sort of relation between the elements, and many of you will remember the rather fanciful hypotheses which were suggested. In this country the best known is probably Crookes' idea of a building-up of all the elements from a very light primordial matter, " prothyl," by some sort of condensation process. However, the first experimental fact about the genesis of elements seemed flatly to contradict this, as the natural radioactivity revealed only disintegration, the breaking up of heavy elements into lighter ones. But since the discovery of the changes following atomic bombardment, especially since the production of artificial radioelements under the impact of neutrons, we know that all sorts of processes are actually occurring; the product of a transmutation may equally well be lighter or heavier than the original element (see Table I).

It seems certain that similar processes, of much greater intensity and variety, occur in stars. What we are accustomed to call " artificial radioactivity " is no more than a poor copy of some of Nature's performances, *e.g.*, in the interior of the sun, where under a pressure of a thousand million atmospheres and a temperature of about twenty million degrees the atoms of the elements are crushed. Under these extreme conditions the "law of conservation of the chemical elements" breaks down completely; all matter is changed into a sort of gas consisting of reactive nuclei and electrons. Out of the almost infinite variety of nuclei formed, only those can be found on our earth which, owing to their stability or long half-value period, have survived since the time when the earth separated from the sun; *i.e.*, the permanent atomic species and uranium, actino-uranium, thorium, potassium, rubidium and samarium. The others have decayed, and can only be " artificially " revived in our laboratories to their ephemeral life. There is, however, no intrinsic difference between them and the others, and it is even certain that occasionally in our cold earth transmutation processes occur outside the above-mentioned six radioelements and their families. For example, Dr. Hevesy has recently pointed out that the mineral gadolinite contains amongst other elements uranium, thorium, beryllium and gadolinium; as the mixture of uranium, thorium and beryllium must produce neutrons, and as the gadolinium nucleus is the strongest absorbent for slow neutrons we know, the heavier isotopes of gadolinium must have increased since the solidification of gadolinite, thereby slowly changing the combining weight of this rare earth. In other cases, as a consequence of neutron bombardment, new elementary species must be formed right in the minerals; also it is possible that the cosmic rays exercise some small influence on the stability of elements in our earth's crust.

So we see that even the old alchemistic idea of the growth of metals in mines is after all not so very far from the truth. Although it is not likely that these changes can at present be experimentally investigated, we may well hope that future refinements in the micro-analytical methods will open new possibilities for chemists to contribute to the study of transmutation.