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Physical Science

APPLICATIONS OF ARTIFICIAL RADIOACTIVITY TO PROBLEMS IN CHEMISTRY

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The tremendous activity in nuclear physics during the past five years and the consequent production of hundreds of new forms of the elements are of great theoretical interest because the knowledge accumulated leads us to a more intimate picture of the nature of matter than we have previously commanded. The results of the physicist's work are also of great practical interest to men in other fields of natural science, because the new elements produced by nuclear disintegrations become available for use as indicators for their better-known stable isotopes in a wide variety of investigations. It is our purpose in this paper to point out some of the types of problems of particular interest to chemists in which the method of radioactive indicators has proved to be a unique and powerful tool. It will not be possible in the limited time to attempt to make a comprehensive review of all the papers which have appeared in this field, but rather an effort will be made to give illustrations of the kinds of things that can be done by this method:

The simplest type of problem is that of determining whether or not an exchange of the atoms of a given element will take place between two different compounds of that element under stated conditions. This question really has no meaning within the ordinary methods of chemistry, because the state of all bodies in the system after the hypothetical exchange is identically the same as before the exchange, and no instrument incapable of following the course of an individual atom would be able to detect the interchange. However, if we can mark some of the atoms with a property not characteristic of all the atoms, such as radioactivity or abnormal atomic weight, then the question takes on a real significance and can be answered by a properly planned experiment. Thus, we prepare a sample of the first compound in which a small quantity of a radioactive isotope has been mixed with the ordinary form of the element. A sample of the second compound is made entirely of the ordinary stable form of the element. Now the two compounds are mixed together under the desired conditions, and later separated and tested separately for radioactivity. If only the first compound is found to be active, we can conclude that no exchange has taken place. If, however, the second compound is found to be also active, then we know that exchange has occurred. By comparing the activities with each other, quantitative information as to the extent of the interchange can be obtained. The evidence furnished by the

radioactive atoms is very closely valid for the bulk of stable atoms, because the radioactive atoms are so similar in their chemical properties to the ordinary atoms that when they have once been mixed together in the same state of chemical combination, only very slight separations can be produced in subsequent reactions.

Many experiments of this type have been reported already (by Grosse and Agruss¹; Roginsky and Gopstein²; Hull, Schiffett, and Lind³; McKay⁴; Voge and Libby⁵; and others to be mentioned). To give a few examples of the results: Liquid bromine in contact with an aqueous solution of sodium radiobromide is found to exchange readily. Chlorine and chloride ion also interchange freely. Likewise, radioactive iodine dissolved in sodium iodide solution shares its activity readily. In this later case, the dissolved iodine is in the form of the tri-iodide complex, and the result obtained leads to the interesting conclusion that in this complex the iodine atoms must all be equivalent, regardless of which one carries the extra electron when the compound is formed. Iodine and iodate ion undergo exchange at a measurable rate in hot, concentrated sulfuric acid, but not in cold, dilute acid. No rapid exchange takes place between sodium iodide and ethyl iodide in alcohol solution if the mixture is at room temperature, but above 30° the exchange takes place within a few minutes. There is evidence that only half the bromine in cupric bromide can be easily replaced when it is heated with gaseous bromine, indicating that there is a difference in the binding of the two bromine atoms in this compound; although the analogous compounds of aluminum and mercury undergo complete exchange under the same conditions.

Sulfur atoms are not exchanged between sulfide and sulfate or between sulfite and sulfate. However, an exchange does take place slowly between sulfide and thiosulfate when they are mixed in a hot alkaline solution. There is also an exchange between sulfur and sulfide when radioactive sulfur is dissolved in ammonium sulfide to form the polysulfide. This exchange seems to be quite rapid and points to the equivalence of the sulfur atoms in the complex ion. There is no exchange between sulfur dioxide and sulfur trioxide at 100° and one atmosphere in the presence of the catalysts ordinarily used in the manufacture of sulfuric acid.

The chlorine-chloride exchange has been done (by Long and Olson⁶) under conditions which give an indication of the speed of the process. It is known that when chlorine is passed into a solution of acetanilide the chlorination takes place at an immeasurably rapid rate. Now, suppose that the solution also contains some sodium radiochloride, and that chlorine is passed in. The resulting chlor-

¹ Grosse and Agruss, *Journ. Am. Chem. Soc.* 57, 591 (1935).

² Roginsky and Gopstein, *Zeits. Phys. Sov.* 7, 672 (1935).

³ Hull, Schiffett and Lind, *Journ. Am. Chem. Soc.* 58, 535, 1822 (1936).

⁴ McKay, *Nat.* 139, 283 (1937).

⁵ Voge and Libbey, *Journ. Am. Chem. Soc.* 59, 2474 (1937).

⁶ Long & Olson, *Journ. Am. Chem. Soc.* 58, 2214 (1936).

acetanilide will contain radiochlorine if, and only if, the exchange between chlorine and chloride ion is even faster than the substitution reaction. In the experiment it was found that the resulting compound was indeed radioactive, and the activity was in the correct proportion to that of the sodium chloride to show that complete equilibrium was attained in the chlorine-chloride interchange before the substitution took place.

Another interesting experiment has been reported (by Juliusberger, Topley, and Weiss⁷) on the stability of diphenyl-iodonium iodide toward interchange with sodium radio-iodide in alcohol solution. It was shown that half of the iodine in this compound is subject to exchange with radioactive ions in the solution, but the other half could under no conditions, even up to decomposition of the compound, be made to change places with the ions in solution. This experiment gives strong corroborative proof of the accepted theory of the structure of this compound, in which one of the iodine atoms is tied between two benzene rings, the whole acting as a positive radical from which the other iodine atom may break away as a negative ion.

The use of radioactive isotopes of the common elements will be of decided value in studies of the surface area and the aging of precipitates which are now being conducted, notably by Kolthoff and his associates. The number of atoms in the surface of a precipitate is readily determined by shaking the solid with a solution of known concentration containing a measured quantity of radioactive atoms, and noting the decrease of activity in the solution. With fresh precipitates, the rate at which the radioactive ions disappear from the solution is a measure of the speed of the recrystallization process. The use of radiochlorine to determine the surface of a silver chloride precipitate in this way has been reported by Kolthoff and Yutzy.⁸ More extensive work on silver bromide has been done by Kolthoff and O'Brien.^{8a}

The use of radioactive indicators promises to become an invaluable tool in the study of the mechanism of reactions. Suppose we wish to test a theory in which a certain intermediate has been postulated to account for the kinetics of a given reaction. With a little ingenuity it may be possible to prepare a radioactive compound which would exchange readily with the hypothetical intermediate but not with the initial or final compounds. With this active compound at our disposal, we carry out the reaction in a solution containing some of the "marked" atoms. Then by testing the final product for radioactivity, we can easily determine whether any of the marked atoms have found their way into the compound. The presence of such an activity would favor the existence of the assumed intermediate, while its absence would indicate a different

⁷ Juliusberger, Topley, & Weiss, *Journ. Chem. Soc.* 1925 (1935).

⁸ Kolthoff & Yutzy, *Journ. Am. Chem. Soc.* 59, 1634 (1937).

^{8a} Kolthoff and O'Brien, *Journ. Chem. Phys.* 7, 401 (1939).

process. This procedure would hardly serve as a general method, but it does at least indicate the possibilities. A few examples of what has actually been done in this field will prove more illuminating.

The mechanism of the Walden inversion has long been a subject for speculation, but only recently has direct experimental evidence been brought to bear on the problem. The attractive mechanism proposed by Polanyi and by Olson is that in which the entering halogen atom approaches the tetrahedral carbon atom on the side opposite to the attached halogen, and at the moment of reaction the tetrahedron snaps inside out, the new halogen atom becoming attached by the bond now directed through what was formerly the base of the tetrahedron. Evidence for the correctness of this view was first offered by Olson and Long⁹ in a complicated series of rate measurements. A simpler and more direct experimental test of the hypothesis has been made by the use of radio-iodine in a study of the inversion of secondary octyl iodide (in experiments reported by Hughes, Juliusberger, Mastermann, Topley and Weiss¹⁰). This octyl iodide is, of course, optically active. The active form is racemized in the presence of sodium iodide in acetone solution. It was found that when optically active octyl iodide is dissolved in acetone with sodium radio-iodide, the speed of interchange of iodine atoms between the ions and the organic compound is the same as the speed of the racemization of the compound. This shows that the same mechanism is involved in the substitution as in the inversion, in accordance with the model proposed. A similar experiment involving the racemization of α -phenyl ethyl bromide in the presence of lithium radio-bromide, and the accompanying exchange of radiobromine atoms, has been performed by these authors with the same result.¹¹

Some years ago a controversy was raised as to the mechanism of the rearrangement of N-chloracetanilide (an example of the Hoffman rearrangement). One group contended that the reaction is intramolecular, involving a direct exchange of the chlorine and hydrogen atoms between their respective carbon atoms, while the other maintained that the rearrangement proceeds through hydrolysis of the chloramine group, followed by the production of chlorine and the direct chlorination of the acetanilide. With the use of radio-chlorine to test the presence of the proposed intermediate, it has become possible for the first time to settle the dispute. The work of Olson, Porter, Long, and Halford,¹² and later, of Olson, Halford and Hornell¹³ showed that when the rearrangement is carried out in the presence of radioactive hydrochloric acid, radiochlorine is present in the resulting compound, and in just the proportion to be

⁹ Olson & Long, *Journ. Am. Chem. Soc.* 56, 1294 (1934).

¹⁰ Hughes, Juliusberger, Mastermann, Topley, & Weiss, *Journ. Chem. Soc.* 1525 (1935).

¹¹ Hughes, Juliusberger, Scott, Topley, & Weiss, *Journ. Chem. Soc.* 1173 (1936).

¹² Olson, Porter, Long & Halford, *Journ. Am. Chem. Soc.* 58, 2467 (1936).

¹³ Olson, Halford, & Hornell, *Journ. Am. Chem. Soc.* 59, 1613 (1937).

expected if the rearrangement proceeds wholly by the chlorine intermediate mechanism.

Using radioactive manganese, Polissar¹⁴ has shown that complete exchange is effected within a few seconds between the manganic oxalate complex and manganous ion, but that no rapid interchange takes place between these and the higher (4 and 7) valence states. These results forced into discard a theory of the mechanism of the reduction of permanganate in which a rapid equilibrium between the higher and lower valence states had been assumed.

In the kinetic theory it is always assumed that when a reversible reaction is allowed to come to equilibrium, the condition attained is not a static one, but one in which both the forward and reverse reactions are proceeding at the same speed, thus making the resultant change nil. With radioactive indicators, the correctness of this assumption has been experimentally demonstrated for the first time (by Wilson and Dickinson¹⁵). They used the reaction between arsenious acid and iodine, for which the kinetics and specific rate are well known. Using radioactive arsenic to prepare the arsenious acid they first established that no exchange takes place between the trivalent and the pentavalent arsenic, either in acid or in alkaline solution. However, when potassium iodide was introduced, the exchange was observed to take place, as would be expected from the equation. They made up equilibrium mixtures of the substances included in the reaction, using radio-arsenious acid and inactive arsenic acid, and then measured the rate at which the pentavalent arsenic became radioactive. The observed rate was in satisfactory agreement with the rate determined by other methods when the system is far from equilibrium. So, at least in this case, the forward and reverse reactions continue at equilibrium, and at the same specific rate as when the reaction is proceeding visibly in either direction. This experiment is an important one because it places the kinetic theory of equilibrium on a sounder experimental foundation.

The method of radioactive indicators has recently been applied to another interesting type of experiment not feasible by other means. It has been impossible to determine directly the speed of diffusion of a substance in a field of uniform concentration, because it has been only by the change in concentration at a certain point in a field having an initial gradient of concentration that the diffusion could be experimentally observed. A direct method of observing this interesting experiment is obtained when a solution of a radioactive substance is allowed to diffuse into a solution of its stable isotope having the same concentration. Furthermore, the observation of the diffusion rates of individual ions has hitherto been beyond our reach, since the existence of electrostatic forces between ions requires that the positive and negative ions of a salt shall diffuse toward a less concentrated region at the same rate, even though the two ions might

¹⁴ Polissar, *Journ. Am. Chem. Soc.* 58, 1372 (1936).

¹⁵ Wilson & Dickinson, *Journ. Am. Chem. Soc.* 59, 1358 (1937).

differ quite markedly in mobility. In these recent experiments, by making only one ion of the salt radioactive, it has been possible to measure the rate of diffusion of this single ion.

Such diffusion experiments were carried out by Jehle.¹⁶ They were performed with sodium chloride over a range of concentrations from 2 M to 0.00005 M, with both radiosodium and radiochlorine in separate samples. The experiments were done by placing a long tube of radioactive salt mouth to mouth with a similar long tube of ordinary salt of the same concentration, and measuring the activity with a counter placed so as to receive the radiations from a limited section of the tube near the junction. He found that at all concentrations the chloride ion diffuses more rapidly than the sodium. Previously determined values for the speed of diffusion of sodium chloride lie between the curves for the individual ions.

The intense activation possible with the ion-beams now available has made possible a new method for the detection of minute traces of chemical substances. A radioactive element can be identified by its half-life if the initial intensity is only a few times the background or natural drift of the measuring instrument. Many elements can be activated to an intensity a million times as great as the background of a good ionization chamber (or even 10 million in some cases) by deuteron bombardments of the order of 100 micro-ampere-hours at 6 to 8 million volts. Thus, if such an element is present as an impurity to an extent of only one part in a million, it can be readily identified by subjecting the whole sample to deuteron bombardment, and noting the decay curve characteristic of the impurity. Furthermore, if the cross-section of the process which produces the activity is known, a fairly good estimate of the quantity of the impurity can be made. Of course, the procedure will generally include the chemical separation of the activity characteristic of the impurity, since otherwise the weak activity sought would be masked by the much more intense activity characteristic of the bulk of the sample. However, for the detection of greater amounts of impurities, of the order of 0.01% to 0.1%, the chemical separation can often be omitted and the identification made by an analysis of the composite decay curve.

Experiments of this kind have been reported by Seaborg and Livingood.¹⁷ They found, after bombarding a sample of iron with deuterons, two activities which are characteristic of gallium. By comparing the intensities of these radiations with that of the radioactive iron formed at the same time, and making corrections on all three to an infinite bombarding time, they were able to calculate the ratio of gallium to iron in the original sample, under the assumption that the cross-sections for all three processes are equal. The result was 6 parts per million of gallium in the iron. The authors state that one-tenth of this amount could have been detected

¹⁶ Jehle, Thesis, Univ. of California (1938).

¹⁷ Seaborg & Livingood, *Journ. Am. Chem. Soc.* 60, 1784 (1938).

readily. In other experiments not involving the chemical separation of the activities, they demonstrated the presence of copper in a sample of nickel, of iron in a sample of cobalt oxide, and a trace of sulfur in a sheet of paper. This is a new method of chemical analysis. It is not expected that it will supplant the chemist's methods in the near future, for the obvious reason that test tubes are more plentiful than cyclotrons; yet it is an interesting application of the new tools of the physicist to the problems of the chemist.

Another application of the use of these new radioelements to the chemist's problems, which is a rather simple one, is in checking the completeness of separation in analytical procedures. The method is obvious — merely add a convenient quantity of the radioactive isotope of the element being studied, and then measure the relative activities of the two portions after the precipitation or extraction or distillation. No further analysis of the separate portions need be made, and since the radioactive measurement can be carried with accuracy down to very small quantities, it seems likely that this method will prove to be a convenient one.

The general field of study of the properties of chemical elements in quantities far smaller than those detectable even with the spectroscope is an interesting one which is opened up by the recent work in nuclear physics. Since, in many cases, a radioelement can be prepared by transmutation from a different element, it is possible to prepare such an element in an almost isotopically pure state. The total quantity of such a preparation would be far less than could be detected by any chemical or spectroscopic test, and yet, because of its radioactivity, it would still be possible to measure with accuracy the relative quantities of this element in a chemical experiment. The approximate range of quantities which can be thus used at the present time is from 10^{-11} g. to 10^{-17} g. These circumstances will make it possible for us to study the properties of matter in extremely small concentrations. It is known from work previously done with naturally occurring radioelements that in solid-liquid systems marked differences are found between the behavior of minute amounts and tangible amounts of an element. The phenomena of adsorption and coprecipitation are responsible for this difference in behavior. Such studies may now be extended to a much larger number of elements. Experiments of this kind in a two-phase liquid system have been reported by Grahame and Seaborg.¹⁸ Their results indicate that in the separation of two liquid phases the distribution of extremely small quantities of substances follows the same law as does that of tangible quantities. Their work on the distribution of gallium chloride between ether and aqueous hydrochloric acid serves to illustrate this type of measurement. The radiogallium was prepared by deuteron bombardment of zinc. In order to obtain a sample of radiogallium free from the ordinary isotopes, the zinc used for the bombardment was first specially treated to

¹⁸ Grahame and Seaborg, *Journ. Am. Chem. Soc.* 60, 2524 (1936).

remove any possible traces of gallium. The sample of radiogallium thus obtained was estimated to be about 10^{-12} g. The distribution of this quantity of gallium between the ether and the hydrochloric acid was found to be in the same ratio as the distribution of 7 milligrams in another experiment.

In this connection, we should mention that the discovery of radioactive isotopes of masurium, produced by the deuteron bombardment of molybdenum, is of unusual interest, because of the great scarcity of this element in nature. Through the use of these isotopes, work has been begun by Perrier and Segre, and by Seaborg and Grahame on the chemistry of masurium.¹⁹ The preliminary results indicate that masurium will follow the chemistry of rhenium much more closely than that of manganese.

These examples indicate the very significant possibilities of solving chemical problems of the most diversified character by the method of radioactive indicators. The question naturally arises as to just how generally it will be possible to carry on experiments of this nature. How many of the elements have been favored by nature in the possession of radioactive isotopes, and particularly, which of these have decay periods which are convenient to the experimenter?

We can now state that every one of the elements in the periodic table, from hydrogen to uranium inclusive, are known to have radioactive isotopes, the number for each element lying between one and nine. Of these perhaps one or two are somewhat in doubt, and await confirmation. Even elements 85 and 87, as well as the disputed illinium and masurium, are definitely known in the radioactive form. An examination of the half-lives of these elements discloses that among the elements having atomic numbers 14 and greater, there is only an occasional one which does not have at least one period of the order of an hour or greater. Unfortunately, some of the most interesting elements are among the lightest, where shorter periods are more common. The longer period in oxygen, for example, is only 2 minutes; in nitrogen it is 11 minutes. Hydrogen and carbon are rather exceptional in having long-lived radioactive isotopes (about 230 days and several years, respectively), but the radiations from these elements are so soft that special technique is required to detect them. The disadvantage of a short period can be overcome to some extent by starting an experiment with a sample of very high activity, such that even after ten or more half-lives an easily measurable quantity remains. Thus, in spite of the brief existence of some of these elements, the large quantities produced in the cyclotron makes their use surprisingly feasible. As a matter of fact, some studies in photosynthesis have actually been made with 20-minute carbon as an indicator.²⁰

Consideration of these facts leads one irresistibly to the conclusion that the experiments with radioactive indicators described in

¹⁹ Perrier and Segre, *Journ. Chem. Phys.* 5, 715 (1937).

²⁰ Ruben, Hassid and Kamen, *Journ. Am. Chem. Soc.* 61, 661 (1939).

this brief review are but the opening wedges into an important field of research, which may be expected to grow rapidly in the near future, and which will make a lasting contribution to our knowledge of chemistry.

1 1 1

THE BIOLOGICAL USE OF THE STABLE MASS ISOTOPES

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The purpose of this article is to discuss briefly the uses, advantages, disadvantages, difficulties and limitations of the stable isotopes in biological research. The discovery of methods of concentrating the stable isotopes, for which major credit must be given to Prof. Harold Urey of Columbia University, has provided biologists with a new and important tool for investigating the course of chemical reactions in tissues. There are two types of isotopes which are used to trace chemical reactions of tissues, namely (1) the radioactive isotopes and (2) the stable mass isotopes. The radioactive isotopes are produced by bombardment of various elements with high speed particles with the result that an unstable element is produced which then disintegrates at a definite rate. On disintegration it emits radiation or electrons which can be measured electrically. The artificial radioactive elements are produced by high speed ionic bombardment in a Van de Graaf apparatus or a cyclotron. The radiation emitted on disintegration is measured with a Geiger-Muller counter which is activated by the ionization produced. Very minute quantities of radioactive materials can be detected with this apparatus, and the method has proved valuable in tracing the metabolic course of such elements as sodium, potassium, phosphorus, iron, and iodine. The radioactive method suffers from the disadvantages that the radioactive elements have a limited life with the result that there is a time limitation on the experimental work. Also, practically all substances contain slight traces of radioactive impurities, and cosmic radiation produces ionization in the measuring chamber, resulting in a "background" which invalidates measurement of weak radiation. The elements of importance to the organic and biological chemist, namely carbon, nitrogen and hydrogen, do not have suitable radioactive isotopes. However, carbon, nitrogen, and hydrogen do have stable mass isotopes which can be concentrated and accurately measured. The stable mass isotopes fill in the deficiency caused by the non-existence of suitable radioactive isotopes and in addition have certain advantages.

The stable mass isotopes are naturally occurring elements. In nature, carbon, nitrogen and hydrogen exist as mixtures of light and heavy elements. The natural abundance of deuterium, H^2 or D , the