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CHEMISTRY WITHIN THE ATOM[1]

By Dr. S. C. LIND

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IN our present age we have become accustomed to a continual acceleration in the development of all phases of human activity. A "Blitzkrieg" in international affairs is but one of the many manifestations of this acceleration.

In the realm of science, particularly in that of chemistry and physics, the rate of development has been no less phenomenal. It is not my purpose to discuss whether there is a direct relation between the two, or to try to determine what effect the advances of science have on our economic, social and political life, but rather to invite your attention to a portion of science which is so far removed from the world surrounding it that it has almost, though not wholly, escaped the attention of those who make wars. Its only applications to human affairs have been beneficent ones. You may well wonder what branch of science has enjoyed such isolation that it could not be twisted or abused to render disservice to mankind instead of service. You may be surprised that this oasis is at the heart of chemistry far inside the atom.

Paradoxical as it may seem, a half century ago, the inside of the atom was more unknown to us than the distant stars. I suppose the antithesis of a vacuum would be absolute solidity of matter. Such the atom was supposed to be. We know now how wide of the truth this conception has been found to be, but it required several years after the first messages from the interior of the atom before its structure began to be revealed.

[1] Address of the president of the American Chemical Society, given at the centenary meeting, Detroit, Michigan, September 10, 1940.

It is not yet a half century since the first signals from far inside the atom were detected by Roentgen in the form of x-rays. Though the analogy is by no means perfect, one might say that they were the echo from the bombardment of inner electrons by electrons in electrical discharge in the form of cathode rays. The use of this terminology anticipates the actual discovery of the electron by J. J. Thomson which did not occur until two years later. And of course it was several more years before x-rays were identified as electro-magnetic pulses of short wave-length.

It was in 1896, the year between the discovery of x-rays and of the electron, that Becquerel discovered the first spontaneous messages from within the atom, spontaneous in the sense that they came without any external stimulation and had been coming undetected throughout the ages. Their emission is at the expense of the internal energy of the atom, which must be enormously great, both qualitatively and quantitatively. To this I shall refer again.

The spontaneous emission of energy from atoms takes three forms, the one like x-rays (γ-rays) another in the form of electrons (β-rays) and the third in the form of alpha rays (helium nuclei).

In 1898 Pierre and Mme. Curie discovered and separated radium. In 1902 Rutherford and Soddy announced spontaneous atomic disintegration to be the cause of radioactivity, the emission of rays or particles being the accompaniment of the disruption.

In the next few years there followed the discovery of about forty radioactive elements belonging to three different series or families, two of them having their origin in the previously known element uranium, in which Becquerel had just detected radioactivity, and the other from thorium, which Mme. Curie and Schmidt had independently discovered to be radioactive. These two elements are the primordial sources of natural radioactivity on the earth. Both have very long lives; otherwise they could not have persisted through geological ages. Neither of them is yet one fourth exhausted. Potassium should also be mentioned. Although but a feeble emitter of atomic energy, its great abundance in the earth's crust makes it an equally important geophysical source of energy.

The existence of the three radioactive series, each with a dozen or more successive genetically dependent members, is met only among the heavier atomic species. Although artificial radioactive species are now far more numerous throughout the entire range of atoms, heavy and light, the existence of genetic chains of any length is limited to the three natural series.

In 1912 Rutherford conceived the existence of the nucleus of the atom. It is quite impossible to overestimate the fundamental and far-reaching importance of this conception. It at once led to the Bohr hypothesis of electronic orbits and energy levels which afforded the key to spectroscopy. Only the neutron, found in 1932 by Chadwick, was needed to complete the picture of isotopes and the general ideas of atomic and nuclear structure.

But long before this in 1919 Rutherford had disrupted the nucleus artificially by alpha particle bombardment. This demonstrated that the nucleus could be attacked successfully from the outside as well as disrupted by its own internal forces.

But this artificial disruption still had to employ as its agent alpha particles from natural radioactive sources. It also lacked the most important characteristic of radioactivity. Its reactions were immediate. As soon as the bombarding agent penetrated the nucleus, disruption ensued without forming any intermediate product of definite life span. And this was found to be true although it was known that the alpha particle not only entered the nucleus but was permanently captured by it.

In 1933 Cockcroft and Walton, working in Rutherford's laboratory in Cambridge, made the atomic disruption completely artificial by employing, instead of the alpha particle from a natural radioactive source, the nucleus of the hydrogen atom or the proton, accelerated in a high voltage field obtained by the use of electrical transformers. This was soon followed by the invention of much more powerful and more convenient means of obtaining high fields—the cyclotron of Lawrence and the electrostatic generator of Van de Graaff. Also new projectiles were available in Urey's deuteron and the artificial alpha particles or helium nuclei. And as a by-product of certain bombardments or of some of the artificial radioactive reactions Chadwick's neutron was found by Fermi to be capable of entering any nucleus no matter how large or how great the nuclear charge. This possibility of course comes from the fact that the neutron having no electrical charge is not repelled on approaching a nucleus with positive charge proportional to its atomic number or the number of protons contained.

In 1934 artificial radioactivity was discovered by P. Curie and F. Joliot. In the bombardment of certain light nuclei by alpha particles they discovered intermediate products which continued to emit particles after removal from the source of bombardment. This was true artificial radioactivity for the first time.

The application of other bombarding agents—the proton, the deuteron, the slow neutron, the helium nucleus—soon followed with astonishingly fruitful results. More than seven hundred nuclear transformations have been brought about in practically all the atomic species. Nearly half of these nuclear reactions have produced new radioactive isotopes. About 20 classes of reactions have been established, based on the character of the projectile used and the type of the subsequent emission of particles and energy.

The new artificial radioactive atoms, like the older ones, undergo transmutation, accompanied by the emission of some kind of particle with or without a simultaneous emission of gamma radiation, into a stable isotope of a neighboring element. The lack of chain or series activity has already been mentioned. A greater variety of particle emissions is observed than in natural radioactivity: protons, positrons, deuterons and neutrons in addition to the alpha, beta and gamma emissions from the natural radioactive elements. In addition, the gamma radiation exhibits a much wider range of energy.

It is not too much to say that these reactions within the atoms, in the nucleus, present a wholly new field of chemistry. In the short space of five years ten times more artificial radioactive species have been produced and identified than we previously had of the natural kind, and this in spite of the fact that we have not had good means of detecting either the very short-lived or the very long-lived species like those which exist in nature. Of course the absence of other long-lived radioactive atoms in nature itself indicates that there are no others in any abundance with lives longer than the age of the earth, else they would, if existent, have survived and been discovered.

In this connection it is interesting to observe that nearly all the new artificial isotopes have sources that fit into the missing mass numbers among the known stable isotopes of any given atom. This is assuming that only one isotope of the same mass can have any existence in time. Or in other words, there can be only one stable nuclear structure made up of a given number of protons and of neutrons. While this rule that there can be no nuclear isomers is quite general, there are some definite exceptions which are becoming more numerous.

When one speaks of the atomic mass of any isotopic species of an artificial radioactive element, it is not implied that enough of any such element has been produced to measure the atomic mass by any means—not even by means of the mass spectrograph. The atomic mass of these new rare species is therefore a matter of deduction from a number of applicable principles, one of the most useful of which is the Einstein equation for the conversion of mass to energy or *vice versa.*

The relative atomic weights that are determined by the mass energy balance of Einstein represent by far the most refined atomic measurements that we possess. Their continued extension from the fourth to the fifth and sixth decimal places is no longer a matter of surprise.

When such a large quantity of energy is equivalent to so small an amount of mass as represented in the Einstein equation the determination of the energy even crudely suffices to give relative masses with extraordinary accuracy.

In all the nuclear reactions of atomic disruptions that we have discussed so far or that were known up to the beginning of 1939, the change in the nucleus was accompanied by the emission of particles of small mass, as electrons, a positron, a proton or a neutron; and only one of these for each atom disrupted. The alpha particle was the heaviest particle known to be emitted from the nucleus. In fact the amount of energy necessary for the ejection of a heavy particle from the nucleus would have been regarded as impossibly high.

Apparently no one had seriously considered the possibility that the nucleus might be split into two more or less equal parts; but that is exactly the interpretation of the reactions which certain uranium or thorium atoms undergo when the nucleus is entered by a neutron of slow speed.

In his studies of the action of neutrons on atoms of high atomic weight, Fermi had discovered that uranium atoms, as well as those of thorium, show exceptional behavior after their nuclei are pierced by slow neutrons, in that they exhibit radioactive properties accompanied by or consisting of a multiple emission of neutrons with extremely high velocity—three of the high-speed ones for one initial slow one. This represents a great gain or multiplication of energy at the expense of the intra-atomic energy. In addition there was a successive emission of electrons or beta particles.

It was at first thought that these phenomena could be interpreted as the production of a series of transuranian elements with atomic numbers 93, 94, 95, 96 and 97. Subsequently Hahn and Strassmann found that the new elements were not transuranian but were new radioactive isotopes of atomic number a little more and correspondingly a little less than half the original atomic number of uranium.

In these reactions the multiple emission of neutrons and the successive emissions of electrons both are understood if one recalls the ratio of neutrons to protons in normal atoms as a function of their atomic number or mass. In the light atoms the ratio is unity, one neutron for each proton as evidenced by the atomic mass being just twice the atomic number for the light atoms. With increasing atomic mass the ratio of neutrons to protons increases steadily and reaches the value 1.6 for heavy atoms like uranium. If then a heavy atom could be split into two nearly equal parts, each part would have a large excess of neutrons over protons and hence a tendency to get rid of neutrons. This can be done in two ways: either by their ejection from the nucleus, hence their multiple emission; or by their conversion into protons with liberation of electrons, hence the successive beta ray emissions. The result of the bombardment of uranium by slow-speed neutrons is the splitting of the atom, termed *fission,* with the production of some new radioactive elements about midway in the periodic system, and the liberation of an astonishingly high amount of energy.

It is the latter which has recently attracted attention as a possible source of intra-atomic energy that might be utilized as a practical source of power.

The multiplication of neutrons was found to be in the ratio of three emitted for one absorbed. Evidently if this should be continued into a chain process of any length the multiplication of energy liberated would lead to explosive reaction. It was even feared, under the supposition that ordinary atoms of U^{238} were responsible for the reaction, that it would be dangerous to have a large amount of pure uranium collected at one time and one place. This supposition could be set aside, however, in the light of the experience of the U. S. Bureau of Mines which at one time had and kept in Colorado for some years several tons of 100 per cent. uranium oxide without any unusual consequences.

The question then became whether one of the rarer isotopes of uranium might not be responsible for the behavior just discussed. Besides U^{238}, the common isotope of uranium, there are two others, U^{235}, long known as the head of actinium series which occurs in the proportion 1 U^{235} to 139 U^{238}; and U^{234} known in the uranium family as U_{II}, the immediate parent of ionium, with an abundance of 1 U^{234} to about 450 U^{238} or about 3 per cent. of the number of U^{235} atoms.

By a very skilful mass spectrographic separation of the gaseous ions of uranium tetrabromide, Nier obtained enough material to show in collaboration with Booth, Dunning and Grosse that it is the isotope U^{235} that is responsible for the remarkable multiplication of neutron emissions and of energy.

This discovery has led to much speculation as to the possibility of utilizing this material as a large source of power. Two questions arise. Is there enough of it and can it be obtained in a state of purity suitable for the proposed uses?

The first question can be answered readily in the affirmative. A very modest estimate of the radium production per year would be 10 grams of the element. Associated with this in nature is about 80,000 pounds of uranium. Of this, 1/139 part of 570 pounds would represent U^{235}. Since it is estimated that only five pounds would suffice for a very considerable power production, it is evident that the natural source is large enough to be very important.

The second question is: Can the isotope be separated from U^{238}? This is a problem to which the answer may not be so soon found. It seems agreed that the mass spectroscopic method used for separation in minimal quantities will not be applicable for such amounts as would be useful in power production. Only experimentation can show whether some other method may not be efficacious. It would be hazardous to predict that at some time in the future one or another method may not succeed.

One other question still might be pertinent: Admitting that it may be possible to obtain isotope U^{235} in quantities and at costs that make it available for practical power production, is it certain that the calculated amount of energy will be delivered and that it can be suitably controlled? The answer to this is necessarily highly speculative. The entire field is new. The methods of measurement, however, appear to be reliable and there seems to be no doubt of the energy emission when U^{235} is bombarded by slow-speed neutrons. This very fact, that it is the slow-speed ones which are effective in setting off the reaction but that high-speed neutrons are ejected, simplifies the control, at least theoretically. The presence of water slows down the high-speed neutrons so that the reaction becomes continuous and the excess energy absorbed by water is rendered available through its mediation. By withdrawal of the water the reaction is retarded or stopped. This seems simple enough for adequate control, but what practical difficulties may intervene in large-scale operation if and when we have pounds of pure U^{235} remains to be seen.

But whether or not the nucleus of the atom ever becomes an available source of intra-atomic energy, it has already furnished us one of the most interesting chapters of chemical science. A finer illustration of man's persistence and perspicacity can scarcely be found. The challenge of the atom has been met, the impenetrability of the nucleus has been conquered.

That these triumphs extend far beyond the bounds of chemistry and physics is well known to you all. The new elements are used as tracer elements in the fields of biology, botany, medicine and genetics. Even the age and energy of both the earth and sun are no longer mysteries.

But of greatest importance to the chemist is the new knowledge of atoms of different elements and their relation to each other. Prout's hypothesis has been more than justified. The Periodic System has been elucidated and extended. The nature of isotopes is no longer a mystery; even progress in their separation is being made.

It is well to keep in mind, however, that reactions resulting from bombardment occur in infinitesimally small amounts. A very small target is being shot at. Most of the projectiles fly wide of the mark. The neutron, however, has new and astounding properties of great promise. It must, however, be obtained through some nuclear reaction of bombardment with all the attendant inefficiency.

These difficulties, however, challenge but do not discourage the scientist. When he has once found the way to the nucleus, the heart of the atom, he will never give up until this new field of chemistry is in complete surrender to the scientific "Blitzkrieg."

OBITUARY

RAYMOND SMITH DUGAN

THE death of Raymond Smith Dugan on August 31 deprives American astronomy of one of its best observers.

Born at Montague, Mass., on May 30, 1878, he was of Irish descent through his paternal grandfather, and from his mother received a Puritan inheritance going back to Myles Standish. His early training was characteristic of the New England village in which he lived, and led naturally to Amherst College, where he received his A.B. in 1899. Three years followed as instructor in mathematics and astronomy at the Syrian Protestant College at Beirut, and three more at Heidelberg with Max Wolf—where he discovered a considerable number of asteroids, including (508) *Princetonia,* (516) *Amherstia* and (535) *Montague,* and received his Ph.D. in 1905. Returning to America, he was appointed instructor in astronomy at Princeton, beginning an association of thirty-five years with that university, and with the writer.

The 23-inch equatorial and polarizing photometer of the observatory offered a field of research then new to him, in which he soon became a recognized authority, and continued active for his whole career. Realizing that precise observations are most valuable in cases which are capable of detailed discussion, he specialized on eclipsing variables, seeking to secure highly accurate light-curves for a few stars rather than provisional results for many. This involved great labor—for Z Draconis 1149 sets of 16 readings each—but the soundness of his judgment has been shown by the wealth of information regarding the dimensions, densities, forms, and even the internal constitution, of the stars which can thus be obtained.

Observations of such stars are a lifelong task, for many of them show slow changes in period, most of which are as yet unexplained, and unpredictable, and have to be followed year by year.

The discussion of his observations was made with equal thoroughness, making his monographs excellent reading for the student.

He was the first to detect the brightening of the faint companion on the side heated by the radiation of the primary—generally known as the "reflection effect."

His work was recognized by his advancement to the professorship at Princeton which he held for twenty years, by election to the American Philosophical Society, and as chairman of the Commission on Variable Stars of the International Astronomical Union. He was an active member of the American Astronomical Society and served as its secretary from 1927 till 1936 and vice-president from 1936 till 1938, to the great satisfaction of its members. In this position, and on the many occasions when he was acting director of the observatory at Princeton during the writer's absence, he showed excellent judgment, executive capacity and diplomatic skill.

He was a good teacher, especially of graduate students. A long series of these inspired by him shared in the photometric observations. In 1937, when he took account of the record, these had made more than 200,000 photometric settings and he himself 300,000.

He bore an important part in the preparation and revision of the text-book on astronomy, in which J. Q. Stewart and the writer shared.

No account of him would be complete without reference to his humor—a combination of Irish wit and dry Yankee shrewdness of expression—which crops out again and again in his reports as secretary and in his whimsical account of work in the old dome at Princeton,[1] which will rouse sympathetic chuckles from those who have never worked with what a student on examination once called a "refractory telescope" and deep memories in those who know the old place.

Shortly after the modern and convenient equipment of the new observatory became available he began to suffer from arthritis, which soon put an end to night work. He bore the physical suffering which followed with unbroken courage and the dry humor characteristic of him. Till within a few months, he continued active research, reducing his accumulated observations and working upon variations in period of eclipsing stars, with the aid of photographic data generously supplied from Harvard. The continued strain of his illness proved too much for his constitution, and the end came.

His widow, a sister and two adopted children survive him.

The writer can not close without an expression of his personal regret at the loss of a colleague with whom in the course of these many years there has never been any occasion of serious difference.

HENRY NORRIS RUSSELL

[1] *Popular Astronomy,* 43: 146, 1935.