

## CLASSICS OF SCIENCE:

## Radio-active Substances

Chemistry

*Radio-active Substances*, by Mme. Sklodowski Curie; thesis presented to the Faculté des Sciences de Paris. Reprinted from the *Chemical News*, London, 1904.

M. Becquerel kept a piece of uranium for several years in the dark, and he has affirmed that at the end of this time the action upon a photographic plate had not sensibly altered. MM. Elster and Geitel made a similar experiment, and also found the action to remain constant.

Some researches were conducted to discover whether other substances were capable of acting similarly to the uranium compounds. M. Schmidt was the first to publish that thorium and its compounds possess exactly the same property. A similar research, made contemporaneously, gave me the same result. I published this not knowing at the time of Schmidt's publication.

We shall say that uranium, thorium, and their compounds emit *Becquerel rays*. I have called *radio-active* those substances which generate emissions of this nature. This name has since been adopted generally.

As I have said above, I made experiments to discover whether substances other than compounds of uranium and thorium were radio-active. I undertook this research with the idea that it was scarcely probable that radio-activity, considered as an atomic property, should belong to a certain kind of matter to the exclusion of all other. The determinations I made permit me to say that, for chemical elements actually considered as such, including the rarest and most hypothetical, the compounds I investigated were always at least 100 times less active in my apparatus than metallic uranium.

The following is a summary of the substances experimented upon, either as the element or in combination:

1. All the metals or non-metals easily procurable, and some, more rare, pure products obtained from the collection of M. Etard, at the Ecole de Physique et de Chimie Industrielles de la Ville de Paris.

2. The following rare bodies: Gallium, germanium, neodymium, praseodymium, niobium, scandium, gadolinium, erbium, samarium, and rubidium (specimens lent by M. Demarcay), yttrium, ytterbium (lent by M. Urbain).

3. A large number of rocks and



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minerals.

Within the limits of sensitiveness of any apparatus, I found no simple substance, other than uranium and thorium, possessing atomic radio-activity. It will be suitable to add a few words here concerning phosphorus. White moist phosphorus, placed between the plates of the condenser, causes the air between the plates to conduct. However, I do not consider this body radio-active in the same manner as thorium and uranium. For, under these conditions, phosphorus becomes oxidised and emits luminous rays, whilst uranium and thorium compounds are radio-active without showing any chemical change which can be detected by any known means. Further, phosphorus is not active in the red variety, nor in a state of combination.

In a recent work, M. Bloch has demonstrated that phosphorus, undergoing oxidation in air, gives rise to slightly motile ions, which make the air conduct, and cause condensation of aqueous vapour.

Uranium and thorium are elements which possess the highest atomic weights (240 and 232); they occur frequently in the same minerals.

I have examined many minerals in my apparatus; certain of them gave evidence of radio-activity, *e. g.*, pitchblende, thorite, orangite, fergusonite, cleveite, chalcocite, autunite, monazite, etc.

All the minerals which showed

radio-activity contained uranium or thorium: their activity is therefore not surprising, but the intensity of the action in certain cases is unexpected. Thus pitchblende (ores of uranium oxide) are found which are four times as active as metallic uranium. Chalcocite (double phosphate of copper and uranium) is twice as active as uranium. Autunite (phosphate of uranium and calcium) is as active as uranium. These facts do not accord with previous conclusions, according to which no mineral should be so active as thorium or uranium.

To throw light on this point, I prepared artificial chalcocite by the process of Debray, starting with the pure products. The process consists in mixing a solution of uranium nitrate with a solution of copper phosphate in phosphoric acid and warming to 50° or 60°. After some time, crystals of chalcocite appear in the liquid.

Chalcocite thus obtained possesses a perfectly normal activity, given by its composition; it is two and a half times less active than uranium.

It therefore appeared probable that if pitchblende, chalcocite, and autunite possess so great a degree of activity, these substances contain a small quantity of a strongly radio-active body, differing from uranium and thorium and the simple bodies actually known. I thought that if this were indeed the case, I might hope to extract this substance from the ore by the ordinary methods of chemical analysis.

## METHOD OF RESEARCH

The results of the investigation of radio-active minerals, announced in the preceding chapter, led M. Curie and myself to endeavor to extract a new radio-active body from pitchblende. Our method of procedure could only be based on radio-activity, as we know of no other property of the hypothetical substance. The following is the method pursued for a research based on radio-activity: The radio-activity of a compound is determined, and a chemical decomposition of this compound is effected; the radio-activity of all the products obtained is determined, having regard to the proportion in which the radio-active substance is distributed among them. In this way, an indication is obtained, which may to a certain extent be compared (*Turn to next page*)

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to that which spectrum analysis furnishes. In order to obtain comparable figures, the activity of the substances must be determined in the solid form well dried.

*Radium* is a substance which accompanies the barium obtained from pitchblende; it resembles barium in its reactions, and is separated from it by difference of solubility of the chlorides in water, in dilute alcohol, or in water acidified with hydrochloric acid. We effect the separation of the chlorides of barium and radium by subjecting the mixture to fractional crystallisation, radium chloride being less soluble than that of barium.

A third strongly radio-active body has been identified in pitchblende by M. Debierne, who gave it the name of *actinium*. Actinium accompanies certain members of the iron group contained in pitchblende; it appears in particular allied to thorium, from which it has not yet been found possible to separate it. The extraction of actinium from pitchblende is a very difficult operation, the separation being as a rule incomplete.

All three of the new radio-active bodies occur in quite infinitesimal amount in pitchblende. In order to obtain them in a more concentrated condition, we were obliged to treat several tons of residue of the ore of uranium. The rough treatment was carried out in the factory; and this was followed by processes of purification and concentration. We thus succeeded in extracting from thousands of kilograms of crude material a few decigrammes of products which were exceedingly active as compared with the ore from which they were obtained. It is obvious that this process is long, arduous, and costly.

Radium is, so far, the only member of the new radio-active substances that has been isolated as the pure salt.

It was of the first importance to check, by all possible means, the hypothesis, underlying this work, of new radio-active elements. In the case of radium, spectrum analysis was the means of confirming this hypothesis.

M. Demarcay undertook the examination of the new radio-active bodies by the searching methods which he employs in the study of photographic spark spectra.

The assistance of so competent a scientist was of the greatest value to us, and we are deeply grateful to him for having consented to take up this work. The results of the spectrum

analysis brought conviction to us when we were still in doubt as to the interpretation of the results of our research.

The first specimens of fairly active barium chloride containing radium, examined by M. Demarcay, exhibited together with the barium lines a new line of considerable intensity and of wave-length  $\lambda = 381.47 \text{ m}\mu$  in the ultra-violet. With the more active products prepared subsequently, Demarcay saw the line  $381.47 \text{ m}\mu$  more distinctly; at the same time other new lines appeared, and the intensity of the new lines was comparable with that of the barium lines. A further concentration furnished a product for which the new spectrum predominated, and the three strongest barium lines, alone visible, merely indicated the presence of this metal as an impurity. This product may be looked upon as nearly pure radium chloride. Finally, by further purification, I obtained an exceedingly pure chloride, in the spectrum of which the two chief barium lines were scarcely visible.

The general aspect of the spectrum is that of the metals of the alkaline earths; these metals are known to have well-marked line spectra with certain nebulous bands.

According to Demarcay, the position of radium may be among the bodies possessing the most sensitive spectrum reaction. I also have concluded from the work of concentration that in the first specimen examined, which showed clearly the line  $3814.7$ , the proportion of radium must have been very small (perhaps about 0.02 per cent). Nevertheless, an activity fifty times as great as that of metallic uranium is required in order to distinguish clearly the principal radium line in the spectra photographed. With a sensitive electrometer the radio-activity of a substance only  $1/100$  of that of metallic uranium can be detected. It is clear that, in order to detect the presence of radium, the property of radio-activity is several thousand times more sensitive than the spectrum reaction.

Bismuth containing polonium and thorium containing actinium, both very active, examined by Demarcay, have so far each only yielded bismuth and thorium lines.

In a recent publication, M. Giesel, who is occupied in preparing radium, states that radium bromide gives a carmine flame colouration. The flame

spectrum of radium contains two beautiful red bands, one line in the blue-green, and two faint lines in the violet.

### *Extraction of the New Radio-active Substance*

The first stage of the operation consists in extracting barium with radium from the ores of uranium, also bismuth with polonium and the rare earths containing actinium from the same. These three primary products having been obtained, the next step is in each case to endeavor to isolate the new radio-active body. This second part of the treatment consists of a process of fractionation. The difficulty of finding a very perfect means of separating closely allied elements is well known; methods of fractionation are therefore quite suitable. Besides this, when a mere trace of one element is mixed with another element, no method of complete separation could be applied to the mixture, even allowing that such a method was known; in fact, one would run the risk of losing the trace of the material to be separated.

The particular object of my work has been the isolation of radium and polonium. After working for several years, I have so far only succeeded in obtaining the former.

The atomic weight of radium is  $\text{Ra} = 225$ .

From its chemical properties, radium is an element of the group of alkaline earths, being the member next above barium.

From its atomic weight also, radium takes its place in Mendeleeff's table after barium with the alkaline earth metals, in the row which already contains uranium and thorium.

### *Characteristics of the Radium Salts.*

The salts of radium, chloride, nitrate, carbonate, and sulphate, resemble those of barium when freshly prepared, but they gradually become coloured.

All the radium salts are luminous in the dark.

In their chemical properties, the salts of radium are absolutely analogous to the corresponding salts of barium. However, radium chloride is less soluble than barium chloride; the solubility of the nitrates in water is approximately the same.

The salts of radium are the source of a spontaneous and continuous evolution of heat.