100 YEARS OF RADIUM:
THE COMPLEX HISTORY
OF AN ELEMENT

Maurice F. Dorikens

I. From philosophy to science

Introduction[1]

It has been generally accepted that the notion of "atom" was first used by Democritus (460 - 370 BC) around 420 BC. The original texts are lost, so we have to rely on citations. The ideas of Democritus can be summarised as follows. Everything that happens, consists of mechanical movement, necessary to nature, of small indivisible particles, called *atoms*, which are everlasting and differ from one another only in size, form and place. The worlds and the bodies arise from collisions. *"There exists an infinitely divisible space, in which there are immutable and invisibly small atoms. Space is emptiness, the atoms are fullness, definite"*.

The atomic model of the Greek philosophers was purely *theoretical*. They did not perform any experiments (if needed, these were done by slaves). It was not deemed necessary to confirm or reject any theory by doing an experiment.

Over the ages, the Greek atomic model was completely forgotten. In the Middle Ages "science" was reduced to the obscure doings of the alchemists who pursued the *transmutation* of matter. They believed that by changing some of the components of materials either quantitatively or qualitatively, one substance could be made to convert into another. For example: lead contains a lot of "earth", thus it is opaque and dark grey; gold on the other hand contains less "earth" and a small amount of "fire", which makes it bright yellow. Therefore, to make gold out of lead, it is sufficient to eliminate some of the "earth" and add some "fire".[2]

It is only through the publications of Descartes (1596-1650) and Newton (1642-1727) that new interest in serious scientific thought arises.

The atomic theory of Dalton

It would take up till the beginning of the 19th century before philosophy concerning the atom evolved to science. The contribution of Dalton (1766 - 1844) was important in that respect. On 21 October 1803 he made a speech in which he explained his atomic theory, before 9 members of the Literary and Philosophical Society of Manchester.

His atomic theory was based on the work of *Boyle* (1627 - 1691) (1661 - Chemista sceticus: an element is a material which is not divisible), *Lavoisier* (1743-1794) (chemical changes are due to the rearrangement of fundamental immutable building blocks) and *Proust* (1799: every chemical compound consists of fixed weight ratios - when a chemical compound decomposes the elements are always released in fixed ratios). The atomic theory of Dalton can be summarised as follows:

1. Matter consists of indivisible atoms.
2. All the atoms of the same element are identical (in weight and in all other properties).
3. Different elements consist of different atoms (and thus have different weights).
4. Atoms are indestructible; chemical reactions are rearrangements of atoms.
5. The formation of compounds arises from the formation of "compound atoms", which consist of small numbers of atoms of each of the elements concerned.

The importance of Dalton's theory was not its novelty, on the contrary. The fact that it stressed the *weight* of the atoms was a turning point in the history of science. He even determined some weight for different elements, many erroneous however. Only about 1860 some clarity would be achieved around the notion of *"atomic weight"*.

Mendeleev's table

It is obvious that elements can be classified by atomic weight. The big breakthrough comes when *Mendeleev (1834 - 1907) sees a periodic connection between the chemical properties of the elements and their atomic weight.* In 1869 his *Periodic System of the Elements* is published.

Periodic chart of the elements

	Ia	IIa	IIIb	IVb	Vb	VIb	VIIb	VIII			Ib	IIb	IIIa	IVa	Va	VIa	VIIa	0
1	1 H 1,0079																	2 He 4,0026
2	3 Li 6,941	4 Be 9,0122											5 B 10,81	6 C 12,011	7 N 14,007	8 O 15,999	9 F 18,998	10 Ne 20,179
3	11 Na 22,990	12 Mg 24,305											13 Al 26,98	14 Si 28,086	15 P 30,974	16 S 32,06	17 Cl 35,453	18 Ar 39,948
4	19 K 39,098	20 Ca 40,08	21 Sc 44,96	22 Ti 47,90	23 V 50,94	24 Cr 51,996	25 Mn 54,938	26 Fe 55,847	27 Co 58,93	28 Ni 58,70	29 Cu 63,546	30 Zn 65,38	31 Ga 69,72	32 Ge 72,59	33 As 74,92	34 Se 78,96	35 Br 79,904	36 Kr 83,80
5	37 Rb 85,47	38 Sr 87,62	39 Y 88,91	40 Zr 91,22	41 Nb 92,91	42 Mo 95,94	43 Tc 97±	44 Ru 101,07	45 Rh 102,91	46 Pd 106,4	47 Ag 107,87	48 Cd 112,41	49 In 114,82	50 Sn 118,69	51 Sb 121,75	52 Te 127,60	53 I 126,90	54 Xe 131,3
6	55 Cs 132,90	56 Ba 137,33	57 La 138,91	72 Hf 178,49	73 Ta 180,95	74 W 183,85	75 Re 186,21	76 Os 190,2	77 Ir 192,22	78 Pt 195,09	79 Au 196,97	80 Hg 200,59	81 Tl 204,37	82 Pb 207,19	83 Bi 208,98	84 Po 209±	85 At 210±	86 Rn 222±
7	87 Fr 223±	88 Ra 226,02	89 Ac 227,03															
			Lanthanides	58 Ce 140,12	59 Pr 140,91	60 Nd 144,24	61 Pm 145±	62 Sm 150,4	63 Eu 151,96	64 Gd 157,25	65 Tb 158,92	66 Dy 162,50	67 Ho 164,93	68 Er 167,26	69 Tm 168,93	70 Yb 173,04	71 Lu 174,97	
			Acti-nides	90 Th 232,04	91 Pa 231,04	92 U 238,03	93 Np 237,05	94 Pu 244±	95 Am 243±	96 Cm 247±	97 Bk 247±	98 Cf 251±	99 Es 254±	100 Fm 257±	101 Md 258±	102 No 259±	103 Lw 260±	

Table 1 : Mendeleev's Table

The place of the elements in this table is called the *atomic number*. Hydrogen has atomic number 1; the last element in the (normal) table is uranium, the heaviest element present in nature, which has atomic number 92.

To understand the rest of the story it is important to remember the following aspect "hidden" in the table. The elements in the columns of the table form "groups". The elements in such a group have comparable chemical properties. This is of primary importance in the discovery of new elements, among which radium. One can see that Ra and Ba are chemically related and react in a comparable way, which would prove to be the number one problem in the purification of radium.

II. The period 1894 - 1904

The end of the 19th century can be called one of the most important periods in physics. One discovery follows another. This period has been described in several modern review books [3] but let's see how it was perceived at the beginning of the century: *"The last decade, 1894 - 1904, will probably always be considered a remarkable one in the history of scientific progress on account of the advances made in connection with the phenomena of radiation".* [4]

The term "radiation" has to be understood as:

(1) The already well known group of ether-vibrations which permitted to explain everything up till 1895 (for example light propagates as a succession of waves in the "ether").

(2) A new group of "radiations" emitted by high-velocity particles: the discharge tubes of Crookes (1879) [5], [6] introduce the "cathodic rays". (During some 20 years the Crookes-tubes would be merely demonstration instruments).

Without going into too much detail we can cite the following dates:

* *1895: discovery of X-rays by Wilhelm Röntgen.*

It is Röntgen who establishes in 1895, by coincidence, that when cathode rays impinge upon the wall of the discharge tube, they produce an

invisible radiation that is very penetrating, and has the property of making some substances fluoresce (among which the glass wall of the tube).

These X- or Röntgen-rays also blacken photographic plates and ionise the air. They could be easily produced; everyone had the necessary instruments. One can surmise that if Röntgen hadn't stumbled on the "discovery", someone else would have done so within a few months at the most. In continuation of the research of Röntgen and Lenard, Poincaré suggests that the production of X-rays is a general effect *connected* to fluorescence.

* 1896: discovery of natural radioactivity by Henri Becquerel. [*]

Following the suggestion of Poincaré, Becquerel studies the fluorescence of uranium compounds. He sees that the exposure of the salts to sunlight has no influence on the imprint upon photographic plates, when the salts are put on the paper covering these plates. What is even more important is that he sees that the imprint on photographic plates is caused by *all uranium salts, not only by the fluorescent ones, and that the property is linked to uranium.* He had discovered a *new property of the element uranium.* A whole series of publications in the Comptes Rendus of 1896 [7] [†] describe the successive experiments and results. Recently these papers by Becquerel have been criticised; some of the results he published are being questioned, especially so since he never published any hard evidence for them [8] (at the Académie des Sciences, Becquerel did show some negatives, but he never published them). Becquerel has admitted that he made some mistakes (like the properties of reflection, refraction and polarisation of the uranium rays), but he always pretended that he himself had corrected his errors. Concerning the so-called "spontaneous emission" of the radiation, all is not clear either. Before 1898, Becquerel never mentions "spontaneous emission", but later, when it is obvious that this is the fundamental aspect, Becquerel manages to re-interpret his work, so that he can cover up for his

---

[*] For an overview of "radioactivity" before Becquerel and the Curies, see: L. Badash, *"Radioactivity before the Curies"*, Am. Journ. of Phys. **33**, (1965), 128.

[†] An overview of the publication meant here, can be found in K. Van Camp, "De ontdekking van de radioactiviteit", in "100 years of Radiology" R. Van Tiggelen and J. Pringot, Belgian Museum of Radiology, Brussels, 1965, p.65.

omission. This is not what can be called a sound scientific way of doing things, but it can be explained by the fact that Becquerel was a prominent figure in the Académie des Sciences. In spite of the criticism, it is a fact that it was Becquerel who discovered natural radioactivity. Without his research on uranium at the Muséum, Marie Curie would never have started her doctoral thesis on radioactivity.

Rarely do we consider to-day with which instruments these fundamental discoveries * where made. Becquerel used photographic plates, where the degree of blackness was a measure for the radioactivity. It was soon seen that the new radioactive radiation ionised the air (just like X-rays), an effect that could be observed by one of the oldest instruments of physics: the electroscope. Making a gold foil electroscope was easy, and every laboratory will have had one or more. *It was therefore not the lack of detectors which explains why "radioactivity" was not discovered any sooner*, as F.Soddy remarked in 1904. [9]

* 1897 - 1899: the discovery of the electron.

1897 is usually cited as the year when the electron was discovered. This is not entirely correct. [10] Indeed, on 7 august 1897 J.J. Thomson sends a paper to the *Philosophical Magazine,* in which he calculates the ratio e/m of the charge to the mass of the electron, determined with the help of cathode rays. In 1899 he applies the same technique to the photo-electric effect and thus proves that the emitted particles are *electrons*. He makes the particles describe a circular path in the magnetic field of a Wilson-chamber, and determines the elementary charge of the electron (using also droplet counting).

A. Pais puts that J.J. Thomson should be more cited for these last experiments than for the discovery of the electron in 1897. In 1899 the electron of the cathode rays is recognised as being identical to the beta-rays emitted by radium (experiments of Becquerel and Curie). This makes the electron the first known elementary particle.

In 1899 Michelson thinks that everything is solved: *"The main fundamental laws of physics have all been discovered now. They are so well established that the chance of them being replaced by new discoveries is very small. Our future discoveries have to be sought in the 6th digit after the decimal point...".* A very premature conclusion indeed.

This assertion also shows that the discoveries made in the period 1895 to 1899 are known only in a small circle and have not yet caused a revolution. The discovery of natural radioactivity in 1896 is the beginning of a new era, an era where experiment and theory will go hand in hand, push each other forward, broaden the limits of scientific knowledge, and this time not one small step at the time, but more often in huge bounds. After 1896 science will be quite different from what is was before. The whole thought process as well as the way of experimenting are completely changed. Many physicists and chemists have problems with that; in some laboratories the importance of what is happening is not recognised and they fail to join the new developments. They keep working in the old familiar research, which is interesting also anyway. In 1897 Pierre Curie suggests to Marie Curie that she take as subject for her doctoral thesis *"the new phenomenon of Monsieur Becquerel"*. Fascinated by these "new physics" she will deserve recognition world-wide in a few years time.

Pitchblende and St. Joachimsthal, the beginnings

St. Joachimsthal is situated in the *"Erzgebirge"* in Bohemia (now Czechia) close to the border with Germany. Even in the Middle Ages, iron was mined here. In 1516 silver was found in St. Joachimsthal, from which the "Joachimsthaler" was minted in 1519 (later to be called the "Thaler", a word which gave rise in 1600 to the English word "dollar"). The German self-made chemist Martin Heinrich Klaproth (1743 - 1817), in 1810 the first chemistry professor at the Berlin University, in 1789 manages to separate from the *pitchblende of St. Joachimsthal*, a greyish to black metallic substance. Looking for a name for it, he stumbles on the work of Sir William Herschel (1792 - 1871), who had just discovered a new planet, Uranus. To honour Herschel, Klaproth calls his new metal *uranium.*

The pitchblende from St. Joachimsthal, used by Pierre and Marie Curie for their first extractions, is an exceptionally "rich" ore, which contains more radium than most other ores that would later be found around the world.

In the beginning only small amounts of radium are produced, exclusively for use in science and medicine. The high price of radium then can be explained by the huge amounts of materials necessary in the radium ex-

traction. To obtain *one gram* of the element radium the following amounts were necessary:
8 tons of pitchblende (St. Joachimsthal) or 800 tons autunite
300 tons of chemicals
200 tons of coal
15.000 tons of liquids

III. Radioactivity becomes a subject of research

Uranium compounds and uranium minerals

Becquerel publishes his discovery of the natural radioactivity of uranium in 1896 - *les rayons invisibles, rayons uraniques* - in the Comptes Rendus de l'Académie des Sciences (C.R.). In 1897 it is Marie Curie who (as said above, as a start of her doctoral thesis [11]), starts a methodical research of the radioactivity of all uranium compounds and uranium minerals she can lay her hands on in the collections of the Muséum and the Ecole de Physique et de Chimie industrielles de la ville de Paris. She systematically compares their activity with that of pure uranium metal. [12]

Mineral	Intensity $(10^{-11} A)$	Found in
Uranium	2.3	-
Pitchblende Joachimsthal	7.0	Bohemia
Pitchblende Cornwall	1.6	England
Chalcolite	5.2	France, Portugal
Autunite	2.7	France, Portugal, Madagascar, United States, Australia
Monazite	0.5	Brazil, Madagascar
Carnotite	6.2	Colorado, Utah, Australia

Table 2: Some uranium minerals and their radioactivity as measured by Marie Curie

In 1896 Becquerel "measured" the activity of uranium by means of radiography, not a very precise method indeed. Marie Curie makes her measurements with an ionisation chamber (designed by Pierre Curie), a primitive version, yes, but an enormous step forward with regard to precision, and which permits to *compare the intensities with that of a standard of pure uranium*. She notes two very important facts:

* The absorption of the "uranium rays" by matter is very important.
* The radioactivity increases with the uranium content.
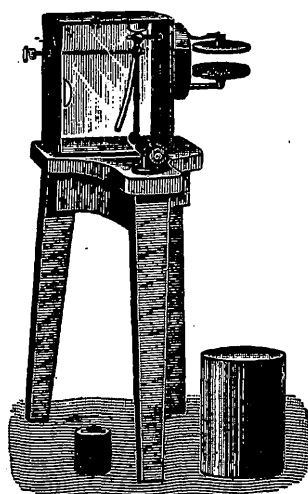
ÉLECTROSCOPE de M.ͬ CURIE
Sᵗᵉ CENTRALE de PRODUITS CHIMIQUES CONSTᵃ

Fig. 1: Ionisation chamber as designed by Pierre Curie

As early as 1899, Ernest Rutherford in studying uranium, uses the terms [13] α, β and γ-rays, but in 1910 Marie Curie in her Traité de Radioactivité continues to use the term "Becquerel-rays", when it comes to determining which substances can be called radioactive: *"Les substances qui ont été nommées radioactives sont celles qui émettent spontanément des rayons Becquerel, l'émission étant liée à une espèce d'atomes déterminée."* In the same book she also writes that one can *(...d'après les théories modernes de la radioactivité...)* assume that radioactivity is linked

to matter *(la matière qui en est douée)* and that when radioactivity disappears, matter also disappears and that atoms of a lower atomic weight are formed.

It is remarkable that in this text there is no real reference to the work and the publications of Rutherford who had already published a second edition of his book *"Radio-Activity"*[‡] in 1905. Of course the Traité de Radioactivité is meant for the students at the Université de Paris, a circumstance which can explain the omission, but the rivalry that existed between Marie Curie and Rutherford can also have played a role.

Searching for chemical elements by means of radioactivity

The measurements of the radioactivity of uranium minerals show Pierre and Marie Curie the way to the extraction of the radioactive components. Chemical analysis at that time is precise to about 1%, but in this case the amounts of material are much smaller, so the usual chemical techniques are of no use. This forces them to base their extraction methods on the measurement of the "radioactivity". The method works as follows: the radioactivity of a compound is measured, then a chemical separation is applied and one measures where the radioactivity goes to. It soon appears that by this method the "enriching" in active material can be followed. This gives rise to a whole new chemical technique. Rutherford also has seen this in 1904 as *"the first notable triumph of the study of radio-activity"*. [14]

In order to measure the radioactivity, all substances are carefully dried. A layer of sufficient thickness - *sufficient so that the measurement of the radioactivity would no longer depend on that thickness* - is formed and its radioactivity (α, β activity) is measured with an ionisation chamber. Usually a thickness of 1 mm is sufficient. By keeping identical all other parameters, like for example the surface of the product, measurements take place in the same conditions and can be compared. Problems arise when the activity becomes too intense. The surface of the product is then reduced by putting a plate with a slit on top of the layer. Another problem, this one less easily solved, comes from the steadily rising activity in the apparatus (i.e. background): there is not only contamination from the product itself,

---

[‡] Between 1903 and 1905 it was usual to write "radio-activity" with a hyphen.

but also - and that is something they did not know at the beginning - from the deposition of radium-emanation (radon Rn^{222}, half-life 3.8 d, first daughter-product of radium Ra^{226}, half-life 1600 y). The plates of the condenser of the ionisation chamber are *always more or less radioactive...* Later it would become clear that the whole laboratory, all apparatus and even the Curies themselves were highly radioactive.

Extraction of radium from pitchblende - the discovery of radium and polonium

The minerals that are radioactive contain either uranium or thorium. Some of these have unexpectedly high activities, such as the pitchblende from St. Joachimsthal. At that time there was no reason *why the activity would be higher than that of uranium or thorium itself.* Marie Curie therefore prepares one of the minerals, chalcolite, from its components. The activity of this product is - as could be expected - about 2,5 times lower than that of pure uranium. Therefore Pierre and Marie Curie conclude that *"...since pitchblende and other minerals are that radioactive, it is highly probable that these minerals contain in small quantities simple components ("des corps simples"), different from uranium and thorium, but highly radioactive".*

Thus it seemed that radioactivity was linked to the presence of uranium or thorium. It did not change, not with changes in the physical condition of the material, not with chemical transformations. It was logical for Marie Curie to ask herself *"s'il existe des substances radioactives autres que les composés d'uranium et de thorium".* That starts her on new and painstaking experiments, the type of research in which she excels. But all the substances from the collections of the Ecole de Physique et de Chimie industrielles de la ville de Paris prove to be at least 100 times less radioactive than the reference material uranium.

As can be expected from a good experimental physicist, she voices her findings in a very careful way (a style of writing that can be found in all the works of Pierre and Marie Curie): *"Dans les limites de sensibilité de mon appareil je n'ai pas trouvé de substance simple autre que l'uranium et le thorium, qui soit douée de radioactivité atomique".* [15]

The pitchblende from St. Joachimsthal which the Curies dispose of, has a composition that will not make chemical extraction any easier.

The bismuth and barium separated in the analysis show a radioactivity not usually found in these substances. Therefore Pierre and Marie Curie rightly conclude that in pitchblende *two* new radioactive elements have to be present. This is the start of their revolutionary research that would lead to the discovery of *polonium* (which follows the extraction of bismuth) and *radium* (which follows the extraction of barium). They surmise that the chemical properties of polonium have to be much like those of bismuth, the chemical properties of radium much like those of barium (see also the Table of Mendeleev). The discovery of polonium is published in 1898 in the Comptes Rendus under the names of Pierre and Marie Curie [16], the discovery of radium on 26 December 1989, under the names of the Curies and Bémont. [17]

Product	Content (%)
U_3O_8	75
PbS	5
SiO_2	3
CaO	5
FeO	3
MgO	2
Bi, Ba, Sb, Cu, Zn, Al, Ni, Co, V, Ag, Nb, Th, ...	7

Table 3: Composition of pitchblende from St. Joachimsthal

In her Traité de Radioactivité [18] Marie Curie summarises her research on pitchblende. In her text she always talks about "nous, nos recherches, P. Curie et moi", except in one place, there where she specifically describes the extraction of radium, where she writes: *"Je me suis spécialement occupée du travail ayant pour but l'isolement du radium et du polonium. Après un long travail j'ai réussi à obtenir le radium à l'état de sel pur, en quantité suffisante pour pouvoir déterminer son poids atomique et lui assigner ainsi une place définitive dans la série des corps simples".* [19] From this we may conclude that she *alone* performed the chemical separations. This is in stark contrast to the articles published shortly after the awarding of the Nobel Prize to Becquerel and the Curies in 1903, where

this titanic amount of work was completely suppressed. Some even pre-tended that Pierre Curie did the extractions. [20]

There is some confusion when it comes to the amount of minerals treated by Marie Curie herself. The myth around Marie Curie as a female researcher was sometimes instrumental in taking liberties with the truth, and producing stories that are questionable to say the least. The "tons of materials" that she is claimed to have treated herself, are vastly over-estimated; the truth lies more at about 100 kilos.

Marie Curie does her first experiments on a sample of pitchblende of merely 100 g (probably from the collections of the Ecole de Physique et de Chimie). Soon it is obvious that much larger quantities will be needed. Pierre Curie starts writing to his colleagues, in search of more ore. Thus they get 500 grams from the U.S. Geological Survey. [21] Via E. Suess of the University of Vienna they obtain 100 kilos of pitchblende-tailings from St. Joachimsthal from the Austrian government.

These (small) quantities are hand-ground by the Curies, treated with concentrated acids, in containers not suited to the purpose, without any suitable instruments, without any means to move the heavy vats and tubs, but most of all without any protection to themselves.

Between 1898 and 1902 they receive about 11 tons, also from St. Joachimsthal, having to pay only for the transport. For the first treatments of these large amounts of ore, they call upon the *Société centrale de produits chimiques*.

Marie, Pierre Curie and André Debierne are counsellors of the *Société centrale de produits chimiques*. The factory was established in 1904 by the French industrialist Emile Armet de Lisle in Nogent-sur-Marne. It would come to completely dominate French radium production. Over the years, the plant treated ore from Hungary, Sweden, Canada and Colorado; autunite (from Autun); chalcolite from Bohemia; carnotite from Portugal and Utah and thorianite from Ceylon (see below the industrial treatment). The final treatment, the most dangerous and most difficult one - the fractional crystallisation - is done by Marie Curie in her laboratory (that is: her hangar).

The atomic weight of radium and optical spectroscopy

A very important factor in the determination of new elements was optical spectroscopy. The Curies seek the help of an authority in the field, Demarçay. He studies the spectrum of radium in the range 5000 to 3500 Å [22] and finds a first new line at 3814.7 Å. After him, between 1900 and 1904, Runge, Precht, Exner, Haschek and Crookes also study the radium spectrum. The optical radium spectrum is thus perfectly well known, and could be considered proof of the existence of the *new element*. Alas, only in 1907, when Marie Curie manages to separate a large enough amount of radium to be able to directly determine its atomic weight, will radium be really accepted as a new element.

After the discovery of the element, determining the atomic weight of radium is without any doubt a major contribution by Marie Curie in this confusing early period of the development of radioactivity. It would give "the" proof that radium was an element and that radioactivity is an *"atomic property"* (*"la preuve définitive que le radium est un corps simple et que la radioactivité est une propriété atomique "* [23]).

Activity of radium chloride (Uranium = 1)	Atomic weight of Ra	Intensity of the radium and barium lines in the spectrum (Ra: 4554.2 Å Ba: 4533.3 Å)
3500	140	very weak Ra spectrum
4700	141	idem
7500	145.8	stronger ·spectrum, but Ba domi-nates too much
10^6	173.8	Ba and Ra are about equal in inten-sity
idem	223	the three strongest Ba lines are still visible
idem	225.3	the three strongest Ba lines are present but weak (0.1 g chloride material)
idem	226.45	the strongest Ba line is very weak (0.4 g chloride material)

Table 4: Evolution of the determination of the atomic weight of Ra (Marie Curie -1907)

Between 1899 and 1907 Marie Curie publishes several figures. [24] Each time the enrichment of the material in radium and the available quantity of radium grow larger, optical spectra are recorded and the atomic weight is determined. Marie Curie handles amounts of 0.5 to 1 gram of radium...

In order to check the accuracy of the method, the atomic weight of barium is also determined in each run; it is always between 137 and 138. A first determination of the atomic weight of radium at 140, points towards an atomic weight *larger* than that of barium. As the enrichment of the available samples grows, so does the atomic weight.

In the last stages, the radium chloride used in 1907 contains maximum 0.06% of barium chloride. The atomic weight of radium is therefore exact to 0.1.

In Great Britain in 1908 [25], Thorpe also determines the atomic weight of radium (using Marie Curie's method). He obtains the value 226.7. This leads Marie Curie to remark: *"Cette concordance entre les résultats obtenus par des expérimentateurs différents, sur un sel préparé indépendamment en France et en Angleterre, est très remarquable et constitue une garantie sérieuse de l'exactitude du nombre obtenu pour le poids atomique du radium."* But she feels it is necessary to "protect" her own results, as she often does: *"...Il semble, d'ailleurs, naturel d'adopter pour ce dernier la valeur 226.45 donné par M. Curie, dont les expériences ont porté sur une quantité de sel pur cinq fois plus grande que celle dont disposait M. Thorpe ..."*

Runge and Precht, who published very precise optical spectroscopy data for radium, in 1903 [26] publish an atomic weight for radium of 258, markedly different from the 226 measured by Marie Curie on chemical bases. Rutherford takes a stand (albeit carefully) and supports the results obtained by Marie Curie: *"Considering that the number found by Mme Curie agrees with that required by the periodic system, it is advisable (!) in the present state of our knowledge to accept the experimental number rather than the one deduced by Runge and Precht from spectroscopic evidence."* [27]
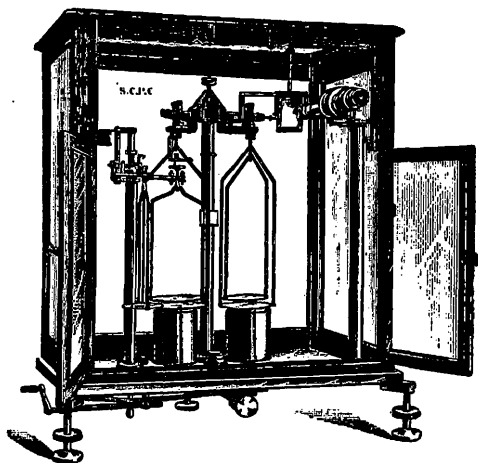
Fig 2.: Pierre Curie's aperiodic balance

It is evident that in order to determine the atomic weight very precise weighing is required. Marie Curie does that with the aperiodic balance [28] § designed by Pierre Curie. Weights below 100 mg can be read directly with a microscope, and this, says Marie Curie to a precision of 0.1 to 0.05 mg (Pierre Curie pretends he can read as precisely as 0.01 mg). The weighing works very fast. Equilibrium is obtained after only 10 seconds, thanks to the special air-buffers. This is very important because radium chloride is hygroscopic. Even with drying-agents present in the balance, the weighing has to succeed from the very first attempt, otherwise the salts have to be returned to the oven. An experienced manipulator can follow the oscillations on the micrometer scale through the microscope and read the exact weight even before the oscillations stop.

## Luminescence and other spectacular effects of radium salts

Many of the *"properties"* of radium, mentioned in the early papers

---

§ The Museum for the History of Sciences of the University of Gent has an aperiodic balance by Pierre Curie on display (inventory number MW 95/1018)

are linked to the very high intensities of radiation which the scientists handled. Some properties can now be easily explained and may even seem commonplace nowadays, but in 1905-1910 the Bohr model of the atom was still unknown, the scientists knew little or nothing about radiation damage, radiochemistry was a long way off. The very origin of radioactivity is a problem to them: *"Le radium est doué de radioactivité permanente".* [29]

Three examples to illustrate this:

1. In 1903 Marie Curie presents her doctoral thesis in Paris. In the evening there is a garden party at which Rutherford is present (he was in Paris by coincidence). In the twilight, Pierre Curie shows to his guests the blue light emitted by a tube of radium salts, carried in his vest pocket.

2. Giesel does an "experiment" on himself in which he puts highly radioactive barium-radium salts on his eyelid, eyes closed, and sees a light effect.

3. In his book "Radio-Activity", F. Soddy publishes a picture in which the text "Ra" is written on a photographic plate *with a tube containing a few mg pure radium bromide.* [30]
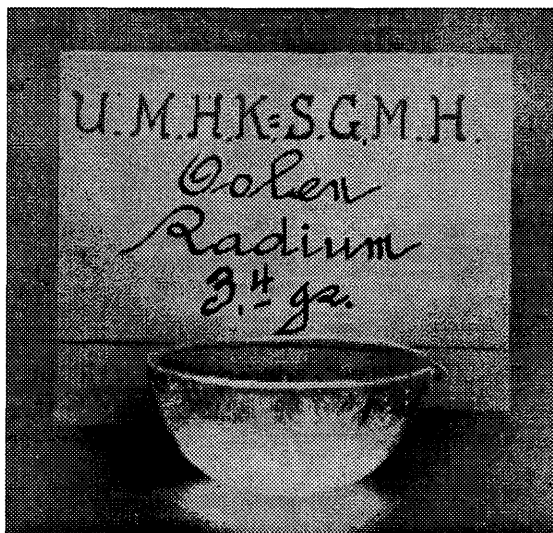
Fig.3: 3.4 grams of radium -
Union Minière - Oolen, Belgium

IV. The origins of radioactivity (1900 - 1905)

Giving names...

In the (small) world of research in radioactivity, the confusion is enormous. Everyone thinks he has discovered some new radioactive substance. The names given to these follow no logical pattern.

Each time a new radioactive substance is discovered, people think it is a new element. Thus Giesel in Germany discovers *"emaninium"* in pitchblende, which is identical to *"actinium"* discovered as early as 1899 by Debierne. [31] Marckwald finds *"radiotellurium"* also in pitchblende, which is identical to *"polonium"* discovered by the Curies.

About the *nomenclature* (a term coined by Rutherford) there also is a lot of confusion. In 1905 [32] Rutherford insists on coming to some unity, in what we now call the radioactive families: *"... since there are at least seven distinct substances produced from radium, and probably five from thorium and actinium, it is neither advisable nor convenient to give each a special name such as is applied to the parent elements. At the same time, it is becoming more and more necessary that each product should be labelled in such a way as to indicate its place in the succession of changes* (see also the footnote "transformation").

Rutherford's nomenclature was in principle quite clearly structured. An example:

Radium $\rightarrow$ Radium emanation $\rightarrow$ Radium A $\rightarrow$ Radium B $\rightarrow$ Radium C $\rightarrow$ Radium D $\rightarrow$ etc.

If we write this down in to-day's terminology, we can see that what *seemed* simple according to the nomenclature, was not. This partly explains the big confusion about the determination of radioactive substances:

$U^{238} \rightarrow Th^{234} \rightarrow Pa^{234} (UX_2) \rightarrow U^{234} (UII) \rightarrow Th^{230} (Io) \rightarrow Ra^{226} (Ra)$
$\rightarrow Rn^{222} (Rn) \rightarrow Po^{218} (RaA) \rightarrow Pb^{214} (RaB) \rightarrow Bi^{214} (RaC) \rightarrow$
$Tl^{210} (RaC") \rightarrow Pb^{210} (RaD) \rightarrow Bi^{210} (RaE) \rightarrow Po^{210} (RaF) \rightarrow Pb^{206}$

Explanation of radioactivity in the first decade of the 20th century

Between 1900 and 1904 several papers by P. Curie, A. Debierne and J. Danne formulate hypotheses about induced radioactivity: an object placed in the proximity of a radioactive salt becomes radioactive itself. In

1902 [33] Rutherford finds the explanation for this and introduces the term *transformation**. In Paris however, other ideas prevail, and the old notions in which the nature of the material on which the activity is deposited, the surrounding air, the temperature, etc. play a role. But even in Paris Rutherford is cited. [34] *Emanation: "Pour expliquer ces phénomènes M. Rutherford admet que le radium ou le thorium dégagent constamment un gaz matériel radioactif qu'il nomme émanation." Nature de l'émanation: "... l'on a pu observer jusqu'ici aucune pression due à l'émanation, et l'on n'a pas davantage constaté par une pesée la présence d'un gaz matériel... on n'a pas encore constaté avec certitude la production d'un spectre caractéristique dû à l'émanation..."*

Here Pierre Curie invokes the classical vision of chemistry, uses the arguments with which the existence of radium was proven by the Curies, to tone down Rutherford's idea as much as possible. Up till then, and with one exception, the French school considers radioactivity something permanent; radioactive decay and half-life were new concepts.

Marie Curie is occupied with the purification of radium and the determination of its atomic weight; Pierre Curie is more interested in finding the explanation for radioactivity, but he cannot accept Rutherford's theory, and tries out all possible issues.

In March 1904 Curie and Danne [35] write in a paper in which they measure a compound decay: *"On peut interpréter théoriquement ces résultats en adoptant la manière de voir de M. Rutherford et en imaginant*

---

* Transformation: Why was not the term transmutation used here? The story (about a conversation between Rutherford and Soddy) goes as follows: Soddy: Rutherford, this is transmutation: the thorium is disintegrating and transmuting itself into an argon gas. Rutherford: For Mike's sake, Soddy, don't call it transmutation. They'll have our heads off as alchemists" Ref.: A. Pais, Inward Bound, Oxford University Press, 1994, p.112; L. Badash, How the "Newer Alchemy" Was Received, Sci. Am. 215, (1966), 154.

In his book "Radio-Activity" in 1905 Rutherford is very careful: Chapter X bears the title: "Transformation products of uranium, thorium and actinium"; when he describes the daughter products of radium, again: "... It is possible that further investigation will show that transformation does not end with radium F".(RaF = Po^{210}). Even in 1930 in the publication by Rutherford, Chadwick en Ellis, "Radiations from Radiactive Substances" there is still talk of radioactive transformations. Soddy on his own does not have these scruples and in his 1904 book "Radio-Activity" boldly mentions "transmutation" in the summary table.

que l'émanation agit sur les parois solides de façon à créer une substance radioactive qui disparaît spontanément suivant une loi exponentielle ..."

In the same year 1904 a paper by Pierre Curie [36] appears, written in collaboration with James Dewar at the Royal Institution, in which the heat generated by radium bromide is measured at liquid hydrogen temperatures. A quartz tube with radium bromide is evacuated, then it is heated till it is red hot and the radium bromide melts. The gasses that are produced are caught in a U-tube which is cooled with liquid air and thus absorbs the emanation. The tubes are luminescent and the spectrum is recorded. After a recording that takes three days, the tube has become violet in colour, but the spectrum does not show anything spectacular, only the nitrogen bands. Now the vacuum is made a lot better by condensing the nitrogen with liquid hydrogen. Immediately after sealing off the tube, the spark-spectrum only contains the hydrogen lines. Pierre Curie takes the quartz tube with the specimen with him to Paris. *Twenty days* after the sealing of the tube, Deslandres sees the spectrum of *helium* in the tube. (After twenty days of alpha-emission of the sample, a sufficient amount of helium had accumulated in the tube to be observed spectroscopically). In a footnote Pierre Curie writes: *"Ce résultat est en accord avec ceux obtenus par M. Ramsay sur la production de l'hélium par des sels de radium dissous dans l'eau".* After 1904, Pierre Curie completely accepts Rutherford's theory.

These experiments are clearly a turning point in Pierre Curie's way of thinking. Before that time, all references he made were to the French research (mainly by Becquerel and the colleagues of the Curies) or to the Germans (Giesel), but now suddenly he turns his attention to the English school. Another point is that from 1903 onward, the Physical Review becomes very important in the scientific world (the first volume of the Physical Review dates from 1893). Under the influence of its publications, the

---

* To perform these experiments in 1903, Ramsay disposed of 30 mg pure radiumbromide. Later he would obtain 350 mg from the Viennese Academy of Sciences for University College in London. These he had to share with Rutherford, something that didn't work out all that well, in view of the prevalent climate of rivalry. Rutherford then obtained another 350 mg from Vienna, for his laboratory, just before WW.II. After WW.II the British government wanted to impound this radium as "ennemy property". Rutherford then managed to have the British government purchase this radium officially. With this money the Austrian physicists could start their research again (ref. 62, p.102).

style in which Pierre Curie's papers are written becomes more concise, more "modern"; especially the presentation of the graphs is more clear. [37] Unfortunately 1906 would see the end of Pierre Curie's life and work. Had he lived, his work would certainly have continued on a very high level; in 1905 no one in France had a more clear insight in the origin of radioactivity than Pierre Curie.

Among all the hypotheses propounded to explain radioactivity, two schools can be seen: one accepts that the energy emitted in radioactivity comes from a form of energy present in the *interior* of the atom, the other thinks that the energy emitted comes from some *external* source, but that radioactive elements have some sort of mechanism to convert this energy into radioactivity.

Rutherford, who has a very clear insight in the "atomic structure", writes, as early as 1905 [38] : *"Of these two sets of hypotheses the first appears to be more probable, and to be best supported by the experimental evidence. Up to the present not the slightest experimental evidence has been adduced to show that the energy of radium is derived from external sources."* This is a very clear reference to the opinions of the Curies (mainly Pierre Curie) who suggested in 1904 that space was pervaded with a sort of Röntgen-type radiation, and that radio-elements had the property of absorbing this.

In 1903 Mc Lennan [39] finds a very penetrating radiation in some buildings, not due to radioactive sources (no radioactive source had ever been present in the building). A lead shield of 5 cm thickness around the electrometer decreases the ionisation current by 30%. More lead has no effect at all. The radiation comes from all directions. There is no difference between day and night. The radiation therefore has to be present at the surface of the earth. At that time no explanation can be given.*

Rutherford analyses the different hypotheses and comes to the conclusion that even if the radio-elements possess the power to absorb energy from some unknown type of radiation, this radiation being one that can penetrate any other matter with only a slight absorption, the fundamental problems in trying to explain the properties of radio-elements remain.

---

* McLennan sees cosmic rays of course. These are studied experimentally for the first time in 1911. Their properties are studied in detail by Millikan in 1925.

Anyway the possibly absorbed energy would be much too small to explain the energy emitted by the radioactive substances.

In 1903 [40] Pierre Curie measures, together with Laborde, the heat emitted by 1 gram radium, using a Bunsen ice-calorimeter: 1 gram radium produces enough energy to bring 1.3 grams of water in 1 hour from 0° to 100°C. *"Le dégagement d'une telle quantité de chaleur ne peut s'expliquer par une transformation chimique ordinaire... cette transformation doit être due à une modification de l'atome de radium lui-même... l'énergie mise en jeu dans la transformation des atomes serait extraordinairement grande.."*, a very astute observation, were it not that the paper ends with these words: *"Ce dégagement de chaleur peut encore s'expliquer en supposant que le radium utilise une énergie extérieure de nature inconnue."* Kelvin[41] also was a great defender of the "external energy" theory, and since Kelvin greatly esteemed Pierre Curie's work (especially his very important contributions to the theory of magnetism), Kelvin's opinion was influential in Pierre Curie's thinking. Of course both Kelvin and Pierre Curie in the end have to admit that Rutherford was right.

V. The industrial preparation of radium

The initial treatment

The industrial extraction of radium is a complicated process, that can be subdivided into two stages: in the first stage chemical separations are performed with ordinary chemicals. In the second stage comes the fractional crystallisation of the different salts. In these extractions first the radium-containing barium salts, polonium-rich bismuth and rare earth metals with actinium are deposited. Afterwards an adapted fractional crystallisation will allow to separate the radioactive substances from these three mixtures. Because of the many different ores from which the process can start, all the extraction procedures differ in one way or another, sometimes only in details, sometimes fundamentally, sometimes also because the process was improved over the years. The separation is easiest when starting from carnotite, the most difficult when starting from autunite. A lot also depends on the quantities to be treated (from milligrams to tons). About the separation technique developed by Marie Curie, she says: *"Le traitement*

de ce minerai à l'usine a été organisé par M. Debierne, après étude pré-
liminaire de la question". [42]

For historical reasons we describe in what follows the procedures developed by Marie Curie [43] :
* Grinding of the ore: Because large amounts have to be treated it is important to have an efficient system which needs little manpower. Per working day, about 1.5 tons of ore can be ground to grains of about 2 mm.
* Treatment of the ore with hydrochloric acid, in the presence of barium chloride. The process takes place in wooden barrels of about 1 m³ (300 kilos of ore) which revolve around a horizontal axis (50 turns/s).
* Then the radium-containing barium sulphate is deposited by adding sulfuric acid. In this, process the 300 kilos of ore is converted to about 700 liters of solution. The treatment with acid, the rinsing and the subsequent pressing and filtering takes place in stages, and takes a day and a night.
* The first radium-containing sulphates have about 100 mg of the element radium per ton of ore from which the process started. Now the sulphates are converted to carbonates by heating to high temperatures, in the presence of sodium carbonate.
* Then the radium-containing carbonates are treated with hydrochloric acid, in wooden vats which are heated by steam (in lead pipes and under pressure). The process ends with filtering and pressing. This gives fairly pure barium chlorides containing radium, which then go to the "fractional crystallisation workshop", i.e. the laboratory in Marie Curie's hangar.
* The fractional crystallisation: The fractional purification is based on the property that radium salts (bromides and chlorides) are less soluble than the barium salts (bromides and chlorides) and therefore they first crystallise when evaporation takes place. The crystallisation first separates out the radium-containing chlorides, then the radium-containing bromides. The separation of radium seems to work better via bromides than via chlorides. In 1902 Giesel starts working with bromides, in 1907 Armet de Lisle and the Société des Produits Chimiques too.

The fractional crystallisation

At the start of the fractional crystallisation the chlorides contain about 0.2 mg of radium element per kilo. Marie Curie does the first steps of the crystallisation from a watery solution of chlorides. She boils them and

lets them cool down in closed capsules. On the bottom nice crystals form. Then the solution is drained away with rubber tubes. In this way there are two parts "1" and "2" with which she starts over again. Each of these parts gives two new parts. After crystallisation the least radioactive part of "1" is added to the most radioactive part of "2", since these two are about equally radioactive. This gives three parts, "1", "2" and "3". The process continues in the same way. When 6 parts are reached, the 6th solution is too weak in activity to be used any further. It is discarded. At the same time, solution "1" is so far enriched in radium that it is also taken out of the process.
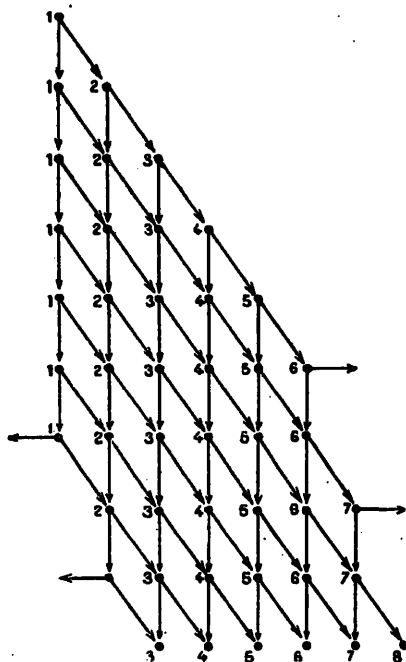

Fig 4: Fractional crystallisation as developed by Marie Curie

The crystals are long needles, which unfortunately look the same for barium chloride as for radium chloride. When one considers how radio-

active these crystals were, one shudders at the following description of the experiments Marie Curie does with them: *"Les uns et les autres sont biréfringents"*. [44] Or elsewhere: *"Les cristaux de chlorure de baryum radifère se déposent incolores, mais, quand la proportion de radium devient suffisante, ils prennent au bout de quelques heures une colloration jaune allant à l'orange, quelques fois un belle coloration rose. Cette coloration disparaît par la dissolution. Les cristaux de chlorure de radium pur ne se colorent pas, ou tout au moins pas aussi rapidement, de sorte que la coloration paraît due à la présence simultanée de baryum et du radium."* This coloration is even used as a means of controlling the process. As long as there is coloration, a sizeable amount of barium is present; when all the crystals are colourless it is pure radium chloride.

From 1907 onward all chlorides are converted to bromides.

The last fractional crystallisation of the bromides takes place in open porcelain crucibles, heated with a flame. To reach an enrichment of about 50% some 20 fractional crystallisations are needed. The crucibles get smaller and smaller. The enrichment is followed by the coloration in a flame. For medical purposes, radium bromide, which is soluble in water, it is converted to insoluble radium sulphate by treatment with sulphuric acid, evaporation and heating.

The final fractional crystallisations are critical, and the distilled water must be absolutely pure. Glassware always gives some impurities, thus contaminating the distilled water. Therefore Marie Curie uses a distilling apparatus and bottles in platinum. [45]

VI. Belgium and radium production

Union Minière controls the uranium-ore from the Belgian Congo

In 1902-1903 the Austrian government puts an embargo on the export of pitchblende, so other sources have to be found. In early 1913 rich deposits of uranium ore are found in the copper mines of Katanga (the Belgian Congo) and in 1915, during World War I, a rich deposit of pitchblende is found there in Shinkolobwe.

At the end of 1921 the *Union Minière du Haut Katanga* starts to mine these ores. Shinkolobwe is 125 kilometres from Elisabethville

(Lubumbashi). Pitchblende is mined in open mines. Also present, among other minerals, is chalcolite. The minerals are put in bags in Shinkolobwe and then transported by lorry over 20 kilometres to the railroad, which takes it to Rhodesia and from there to the seaport of Beira in Mozambique, from where it is shipped to Antwerp.

The *Société générale métallurgique de Hoboken* (in which the Union Minière has interests) starts up a uranium-ore treating plant in Olen near Antwerp (then spelled Oolen), under the direction of P. Leemans. It is a large factory, very modern for its time. On 5 December 1921 for the first time 12 tons of minerals arrive in Antwerp. On 13 November 1922 the existence of "Belgian radium" is made public in a ceremony in the Colonial Museum of Tervueren, in the presence of King Albert I. From then on Belgium and the Belgian Congo are an established part of the world of radium. On 15 December 1922 the first batch of a few grams of radium leaves the plant. The first 4 grams produced in Olen, are granted to four Belgian Universities for (medical?) research.

The process used by the Société Métallurgique Hoboken - Union Minière

The process used in Olen for the ore coming from the Belgian Congo is derived from Marie Curie's process, used by Debierne (and improved by E. Armet de Lisle). Armet de Lisle is not involved in the Olen factory. [46] On the other hand, the American companies Standard Chemical Company and Radium Company of Colorado give advice in the building of the plant. Later on, they will also act as agents for the sale of Belgian radium in the USA. The National Radium Institute in the USA describes the new factory as *"more like a fine kitchen than an actual metallurgical plant".* [47]

Union Minière (in 1931) [48] and Maurice Curie (in 1925) [49] give slightly different descriptions of the three last phases of the process applied by the Métallurgique Hoboken. In the main however it is the same as what Marie Curie already published in 1910. [50] We will not describe the whole process here but just cite some details, which can give an idea about the volume and quantity of highly radioactive material treated at the plant.

The fractional crystallisation scheme takes one month. During that time several grams of radium are treated. The concentration in radium

bromide reached is about 97 to 98% of the marketable product. Before the radium bromide is sealed into glass tubes it is carefully dried, then the tubes are closed with a gas-flame. The substance in the tubes is then a whitish powder that emits a bluish light.

Around 1925 several factories in the world produce radium: the principal ones are in the USA (6), in France (4), in Belgium (1) and smaller ones in Portugal, Czechoslovakia, Germany and Great Britain. Some research institutes possess large quantities of radium for the treatment of cancer, but the bulk of the product is at the hands of private medicine, in all possible countries. In that period about 100 grams of radium must have been around.

The price of radium.

The quantity of radium that can be obtained from different ores varies greatly (see Table 5), and this has has a big influence on the price.

In Utah and in Colorado, in the USA, the uranium-containing mineral carnotite is found. In 1910 the Standard Chemical Company starts the production of radium. Together with the Radium Company of Colorado, founded during the first World War, they produce 80% of the world production of radium in 1922. The price of radium then is about 100.000 $ per gram. Portugal and Madagascar supply the French plants with weakly radioactive minerals.

Ore	Ra-element content per ton
autunite	2 mg
carnotite	5 mg
pitchblende Joachimsthal	25 mg
pitchblende Belgian Congo	50 to 100 mg

Table 5: radium content of different ores

From the moment the industrial production of radium is a fact in Olen, the world-wide price of radium decreases in a sensational manner and soon falls to half of what was charged when the USA had the monopoly. In a very short time Belgium becomes the main supplier of radium. The only producer competitive with Olen, is Port Hope (Ontario), near

Great Bear Lake in Canada. In 1931 pitchblende is found there, which contains about 30 to 60% uranium oxide. In 1932 Port Hope produces about 2 grams of radium a month, in 1938 double that quantity. In 1938 an agreement is reached with Union Minière, fixing the price of radium at 40.000 $ a gram. After 1940 the price would fall a bit more. After World War II attention would go much more to uranium, and the radium production is stopped in 1954 in Canada and in 1960 in Belgium.

Marie Curie and Union Minière - Métallurgique Hoboken

Marie Curie is in regular contact with the "Métallurgique". It is all a bit secretive and little has been published about these contacts. On Sunday 18 March 1923, Marie Curie and Dr. Regaud (the director of the medical section of the Institut du Radium), visit the plant in Olen, together with Emile Francqui. The previous day they had attended a meeting of the *Commission du Radium,* founded by the *Fondation universitaire,* and a dinner offered by Francqui. It is not clear what was discussed on this occasion. At present, plans exist to publish the whole correspondence of Marie Curie as it is kept in the Bibliothèque Nationale in Paris, completed with what is dispersed throughout the world. Maybe this will clarify things.

In 1926, at the 4th Solvay Congress, Marie Curie insists that the Métallurgique produce more intense alpha-ray emitters like actinium and polonium, which in her opinion, are needed for research. The Belgian ores are quite suited to such a production. She also proposes a collaboration and promises to make all her findings available. It will take until 1930 however, before Irène Curie will have regular contacts with the Métallurgique regarding intense polonium sources (see below).

VII. The International Radium Standard

The Congrès de Radiologie et d'Electricité - Brussels 1910

In the radium-related research of the early 20th century some fundamentally important results are obtained by scientists, but they cannot be

compared because the figures depend on the purity of the radium. Some examples:
* the intensity of the emission of alpha-particles
* the production of He
* the heat generation
* the total ionisation

In order to compare the results they have to be expressed as a function of one and the same Ra-standard. In September 1910 the *Congrès de Radiologie en d'Electricité* [51] takes place in Brussels. Marie Curie is commissioned to make the International Radium Standard. In August 1911 this is ready: 21.99 mg of pure $RaCl_2$ sealed in a glass tube. In March 1912 the "Commission du Radium" meets in Paris and decides to compare this standard with the ones produced by Hönigschmidt who used material from the Viennese Academy of Sciences. These consist of three tubes containing respectively 10.11, 31.17 and 40.43 mg of $RaCl_2$, all prepared from uraninite from St. Joachimsthal (about which it is known that it contains only a very small amount of Th, a possible source of contamination). The standards agree very well indeed, the deviations being less than 0.3%. The standard prepared by Marie Curie is adopted as International Standard and deposited at the Bureau international des Poids et Mesures in Sèvres. The 31.17 mg standard from Vienna becomes the secondary standard. The committee also takes measures to make duplicate-standards. These are calibrated at the Institut für Radiumforschung in Vienna, using the gamma-activity.

In principle Marie Curie is not willing to yield the first standard, which she considers to be *her radium*. She has to concede however, and keep a secondary standard at the Institut du Radium. Using this standard, certificates can be supplied, which give, just as the Viennese standard did, intensity calibrations of radium sources, based on the gamma-radiation. Of course Union Minière is very interested in a comparison of the first radium products from Olen with this standard. This brings about many contacts between Marie Curie and the Métallurgique (director P.Leemans). These contacts are not direct, but go through an intermediary, E. Sengier. It is clear from the correspondence that Marie Curie becomes aware that Union Minière and the Métallurgique are interested *solely* in the *commercial* aspects of relations with research.

Purity of the radioactive products

In preparing pure radium sources, one has to make a distinction between "chemically pure" and "radioactively pure". Indeed radioactively pure preparations will not remain so because of the decay products which are formed over a period of time. In the case of radium, a radon contamination (and its decay products) will build up. "Radioactively pure" therefore is something that is not permanent; thus each source is delivered with a dated certificate. For the same reasons, old radon tubes will contain concentrated polonium preparations.

VIII. Applications of radium, radon and polonium as alpha-sources for experiments

The Cavendish research under E. Rutherford

1. The Marsden-Rutherford scattering and disintegration experiments (1914 - 1919).
In 1914 Marsden [52] makes the first experiments concerning scattering of alphas. As a source he uses *radon* in a thin-walled tube. The radon tube is placed in a copper vessel, filled with hydrogen. The scattering is measured by visually observing and counting the scintillations on a ZnS screen. The range of the alpha's is determined by placing metallic foils before the ZnS screen until the scintillations stop. The range of the less heavy *hydrogen atoms* is measured to be about 4 times that of the alpha's.
Unexpectedly Marsden observes that when the vessel is vacuum (not filled with hydrogen) the radon tube itself *"gives rise to a number of scintillations like those from hydrogen".* [53] Rutherford can't believe that the source is producing *yet another* type of radiation, i.e. hydrogen atoms. Marsden then returns to Australia, and Rutherford continues the experiment by himself. It is by then halfway through the war, and Rutherford is more occupied with military research (tracking down submarines), but he still manages to sneak in some scattering experiments. In 1917 he writes to Bohr [54]:
"I occasionally find an odd half day to try a few of my own experiments and have got I think results that will ultimately prove of great importance. I wish you were here to talk matters over with. I am detecting and counting

the lighter atoms set in motion by alpha particles... I am also trying to break up the atom by this method.".
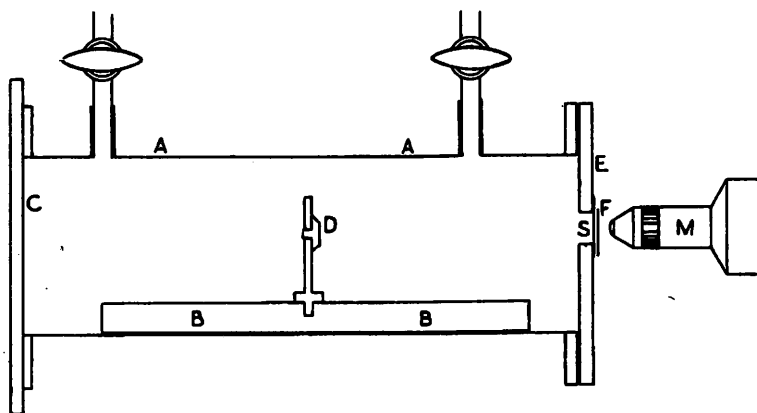

Fig.5: The experiments of Marsden and Rutherford

As an alpha-source he uses a copper disk on which radium is deposited. The "detector" still remains the well-known ZnS screen, coupled to a measuring microscope and the very well trained eye of Rutherford. It is said that Rutherford (and Chadwick, also at the Cavendish laboratory) are extremely skilled in observing scintillations.

The apparatus used by Marsden and Rutherford is typical for the Cavendish design: simple, but where the skill of the experimenter plays an all-important role. The apparatus is described twice in the standard-publication *"Radiations from Radioactive[**] Substances"* [55] from 1930. It is used by Marsden for scattering experiments and by Rutherford for disintegration experiments. For these last the radium-source (*"radium deposit"*) is at D, the distance source-detector S is adjustable. F is where the absorbers are placed. M is the measuring microscope to observe and count the scintillations. The chamber can be filled with gas through A. The whole apparatus is so small that it fits into the palm of a hand. (A photograph exists of Rutherford holding the apparatus).

[**] Unlike the years 1900, in 1930 the word *radioactive* is spelled as one word.

The observations by Marsden could have been due to a hydrogen contamination of the source; this was not the case, as was proved. Later the vessel is filled with dry air. In stead of diminishing, the number of scintillations increases, even *doubles* in number. After another series of tests (to exclude all contaminations), he has to come to the conclusion that this increase is due to hydrogen atoms, coming from the nitrogen in the air (not oxygen, that had been tested before) and not from the radioactive source. Rutherford presents his findings in a typically British manner: [56] *"From the results so far obtained it is difficult to avoid the conclusion that the long-range atoms arising from collision of (alpha) particles* (of the Ra-source) *with nitrogen are not nitrogen atoms but probably atoms of hydrogen... If this be the case, we must conclude that the nitrogen atom is disintegrated."* The newspapers of 1919 are less reticent and boldly claim *"Rutherford had split the atom".*

In June 1919 Rutherford [57] publishes a four part paper in which he says: *"... the hydrogen atom which is liberated formed a constituent part of the nitrogen nucleus...The result as a whole suggests that if alpha particles - or similar projectiles - of still greater energy were available for experiment, we might expect to break down the nucleus structure of many of the lighter atoms."*

In a modern notation, he has produced the following reaction (note that He^4 is in fact an α-particle, H^1 a proton):

$$_7N^{14} + _2He^4 \rightarrow _8O^{17} + _1H^1$$
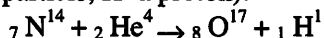
Split an atom is not really what Rutherford has done, but anyway the dream of the alchemists had finally come true (although it was not lead that had been changed into gold....). Thanks to the judicious use of strong radium and radon sources, physics suddenly evolved from *atomic physics* to something very close to *nuclear physics*.

The polonium sources derived from the radium and radon sources, as used by Rutherford and the other European scientists, give alphas that have an energy too low (a few MeV) to break through the Coulomb barrier in heavy nuclei, and make nuclear reactions possible. Thus as early as 1920 Chadwick and others in the Cavendish laboratory were trying to accelerate the particles, so that higher energies could be reached. Rutherford, who had made his greatest discoveries using the most simple apparatus, fundamentally distrusted complicated experiments and opposed the attempts. Without this opposition *nuclear* physics might have evolved even faster.

2. Rutherford and the Bakerian Lecture [58]: the road to the neutron.

In May 1904 Rutherford gives his (first) *Bakerian*[‡‡] *Lecture: "The Succession of Changes in Radio-Active Bodies"*. It mainly treats radium, thorium, uranium and actinium. Rutherford's reasoning goes as follows: if radium has a half-life of about 1000 years, then all radium older than 100.000 years should have disappeared. Therefore the radium quantities *had to be replenished* by longer-living radioactive matter. Rutherford considers uranium as responsible for this, but first wants to see experimental proof. He reasons that if this were true, the ratio radium/uranium should be the same in all minerals, a supposition that is later confirmed. Rutherford had an unbelievably clear *insight* into the radioactive phenomena; only Bohr would equal and even surpass him eventually.

On 3 June 1920 Rutherford gives a second *Bakerian Lecture* before the Royal Society in London: *"Nuclear Constitution of Atoms"*. As an innovative thinker, he speculates about the existence of a third building block in the nucleus. Most physicists were satisfied with the symmetrical image of the elementary components in the atom, as it was accepted up till then: a negatively charged electron and a positively charged proton. (In the lecture the word *proton*, to describe the positive particle in the nucleus is not used. Rutherford keeps referring to the hydrogen nucleus, or charged hydrogen atoms). He keeps hammering on the question: if the building blocks of the nucleus are protons and electrons, how is it possible to build up a heavy positively charged nucleus. The only answer to that seems to be a *neutral* particle: *"an atom of mass 1 which has zero nuclear charge"*. He does not see it as a new *elementary* particle, but more like a bond between proton and electron. According to Rutherford such an "atom" should have extraordinary properties: because of the almost total absence of an electric field it should be able to move freely through matter, be difficult to detect, and practically impossible to contain in a vessel. As it can easily penetrate the structure of the atom, it can bind to a nucleus or disintegrate it, due to the very strong fields existing there.

The *neutron*, as he calls this particle one year after the Bakerian Lecture, *"might be the most effective of all tools to probe the atomic nucleus"*. The speculations of Rutherford voiced in this Lecture have impor-

---

[‡‡] Named after Henry Baker who supplied the funds for such lectures in 1775.

tant consequences. Radium alpha-sources remain for many years to come the essential tool for the research in physics.

3. Polonium, decay product of Radium, becomes important for research - Specialisation in scintillation-counting - Introduction of the Geiger counter.

James Chadwick, *Assistant Director of Research* and Rutherford's right hand, is present at the *Bakerian Lecture* of course. In his opinion Rutherford's hypothesis is based on too weak arguments and he has serious reservations. From 1920 onward the problem keeps nagging. Together with Rutherford he sets up reaction experiments on heavier elements. In the winter of 1920 Chadwick develops a better version of the scintillation counter, by improving the microscope used. Before starting the actual counting, an experimenter would sit for at least half an hour in complete darkness, to allow the eye to observe the very weak light flashes. Meanwhile Rutherford's technician would bring the radium source (Rn derived from a 400-mg Ra solution [59]) from the radium-room to the cellar where the experiments took place, and install the apparatus. During this time of course discussions about the *Bakerian Lecture* went on. Later Chadwick would say that it was there that he understood that the image Rutherford had of the neutron was not exact, and that the *neutron* had to be something else, not an electron bound to a proton. On a theoretical level also (among others by the developments in quantum theory about 1920) a number of conclusive reasons were formulated, to explain why the image of electrons present in the nucleus had to be false, but that is another story.

Detecting radioactive radiation by the scintillation method has reached its highest possible level of sensitivity in those days. It was not possible to observe more than 150 counts/min in a reproducible and dependable way, or to process less than 3 per minute by one single observer.

Then a vehement discussion arises between the Cavendish Laboratory and the Radium Institute in Vienna, where they are unable to reproduce Chadwick's experiments and pretend the apparatus used is of inferior quality. Chadwick once more repeats the experiments (improving the experimental set-up in the process, by putting the ZnS screen directly onto the objective of the microscope) and can only confirm earlier results. He goes to Vienna and sees that the counting is done by three young ladies, as the people there are convinced that they have better eyes than men, and are less

distracted from the counting than men. Chadwick closely observes the young ladies, and notes that since they know what is expected from the experiments, they produce the expected results, and count non-existing scintillations. He asks them to do another experiment, one they don't know anything about. Then their results perfectly match his. [60]

It is high time then for counting-techniques to change, something Rutherford is well aware of. Hans Geiger, also working at the Cavendish, reverts to an old counter developed by Rutherford in 1908, and builds a much better version, which was to become the famous *Geiger-Müller counter,* still in use to day. Electronics had made giant steps forward, so that an amplifier can be built, and each impact of radiation is heard as a distinct "click" in the loudspeaker. This counter is an *objective observer* and expands the counting limits over a few orders of magnitude.

The introduction of the Geiger-counter has a big problem however: the visual scintillation counting with ZnS screens was practically impervious to gamma rays, the Geiger counter detects them! Radium sources emit a strong gamma component and the Geiger-counters go crazy. From the introduction of the Geiger counter onward, it is mostly polonium that is used as a source (little used since it was discovered by Marie Curie in 1898). Polonium (Po^{210}, RaF) is an almost pure alpha-emitter, thus reducing the background in the Geiger-counter over a factor of almost 100.000 as compared to a radium source of the same alpha-intensity.

Unfortunately polonium is not readily available, in fact only as a decay-product of radium. Here the Cavendish Laboratory is at a disadvantage as compared to the Paris laboratories of Marie Curie: the medical radon capsules, which were returned (for free) to Marie Curie after use, gave her plenty of polonium. We will see that, even as late as 1930, this will be of capital importance for the Joliot-Curies.

The discovery of the neutron made possible thanks to strong polonium sources, derived from radium

In 1928 Bothe starts on a research about the gamma-radiation following alpha-irradiation of light nuclei. It is of course very important that the background due to gammas be as low as possible and therefore polonium sources are used. Chadwick has a polonium source from Lise Meitner, but it is far too weak to even try to reproduce Bothe's experiments. At

the end of 1930 Bothe and Becker publish a remarkable result: *irradiation of beryllium with the alphas from the polonium source gives rise to radiation that is more energetic than the radiation coming from the alpha-source.* This is a conflict situation with regard to the conservation of energy. Therefore it is concluded that disintegration of the nucleus has occurred, even though no protons are seen. These are extremely fascinating experiments for those who have the necessary source... very frustrating for those who have not.

Chadwick keeps very busy. On his suggestion, his student Webster directs the radiation coming from a polonium-beryllium combination into a Wilson chamber. Chadwick reasons that if the neutron is really an electron-proton combination, it might still have a very weak electrical charge and give a faint ionisation track in the Wilson chamber. Evidently, nothing is found, and Chadwick is disappointed. Webster leaves for the University of Bristol and in the years 1929-1930 Chadwick continues the research on his own. His first aim is to obtain a much stronger polonium source. At the Kelly Hospital in Baltimore (USA) he finds hundreds of radium needles, no longer used. Together they contain almost as much polonium as the Curies (Marie and Irène) have amassed in Paris. The hospital gives them to the Cavendish laboratory, and Chadwick does the very dangerous chemical purification himself.

The experiments of Irène Curie and Frédérick Joliot - a missed opportunity

Starting in 1929 the Joliot-Curies work on developing a new technique to make polonium sources. In 1931 they have purified so much polonium that they have a source 10 times more intense than any other existing one: 100 mCi (1.5×10^9 α/s in 2π). With this source they start a research on beryllium ("glucinium" as it was then called). Now many things happen in rapid succession:

* *December 1931*: Irène Joliot-Curie finds that the "beryllium radiation" of their extra-strong Po-Be source is even more penetrating than Bothe and Becker had found. The Joliot-Curies wonder whether this radiation could liberate protons from the nucleus, as alpha-particles do. They surmise that the radiation coming from the Po-Be source is *gamma-*

radiation. Different materials are placed in front of the window of their ionisation chamber. They find nothing, except when using thin layers of paraffin-wax, or other hydrogen-rich substances: then the current in the ionisation chamber increases. They make Wilson-chamber photos (see fig.6) and prove that protons are emitted from the material. [61]

    * *18 January 1932*: the Joliot-Curies present a communication at the Académie des Sciences and publish a paper in the Comptes Rendus, where they claim that the protons are due to Compton-effect of the gammas from the Po-Be source. By building on this Compton-effect theory, the Joliot-Curies make very improbable suppositions: a very high energy for the gammas and an inordinately large reaction cross-section. Gammas can indeed easily librerate electrons, but for them to liberate protons, with their 1836 time larger mass, was a bit too optimistic (the reaction cross-section to liberate protons should have been 3.10^6 times larger than for electrons). The possibility of the presence of a neutral particle is not even considered, since Rutherford's Bakerian Lecture has not been read...
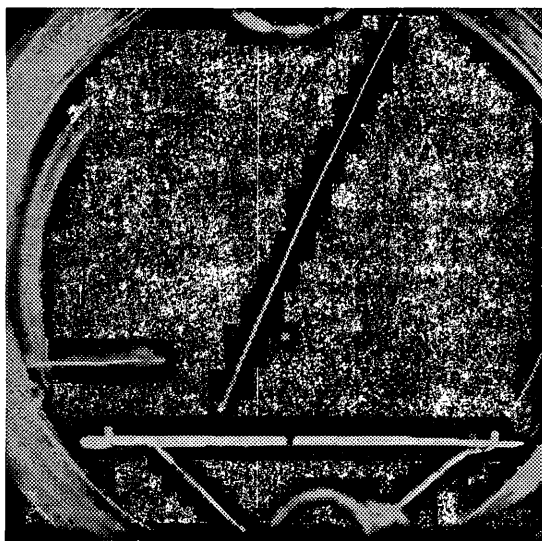

Fig. 6: Wilson-chamber photograph by Joliot and Curie of a scattered proton.

When Chadwick sees the paper he is flabbergasted. He shows it to Rutherford who exclaims *"I don't believe it"*. Such a spontaneous reaction is very unlike Rutherford. Of course he does believe the experiment, but not its explanation in terms of Compton effect. On reading this paper in the Comptes Rendus in Rome, Majorana, still very young then, says: "What fools. They have discovered the neutral proton and they do not recognise it."[62]

The Joliot-Curies had difficulty admitting that they had missed the neutron. In a leter paper they write: *"Les rayons H produits dans un écran mince de paraffine placé à l'intérieur de la chambre. Certains rayons ont plus de 14 cm et traversent tout l'appareil.... L'interprétation du phénomène est facilitéé si l'on suppose, comme l'a fait J. Chadwick et plus récemment, Webster, que le rayonnment émis par Po + Be se compose de neutrons... L'hypothèse du neutron avait déjà été émise, dans des cas différents, par plusieurs savants (Bragg, Rutherford, Meitner, Rosenblum, Fournier, Pauli, etc. L'existence de ce nouveau rayonnement avait été envisagée à la suite de considérations générales et n'avait aucun fondement expérimental. ... "*

The Chadwick experiment - the discovery of the neutron

* 7 February 1932 (Sunday) [63] With his strong Po-Be source, Chadwick repeats the experiments. He is convinced that the Joliot-Curie experiments cannot be explained in terms of Compton-effect, but that something a lot more fundamental and new is going on!

The ionisation chamber (air at 1 atm.) has an Al-foil window. By adjusting the amplifier Chadwick sees pulses on the oscilloscope, proportional to the ionisation in the chamber, and can deduce from that the energy of the incoming particle. Thus he disposes of a lot more information than the Joliot-Curies who used an electrometer.
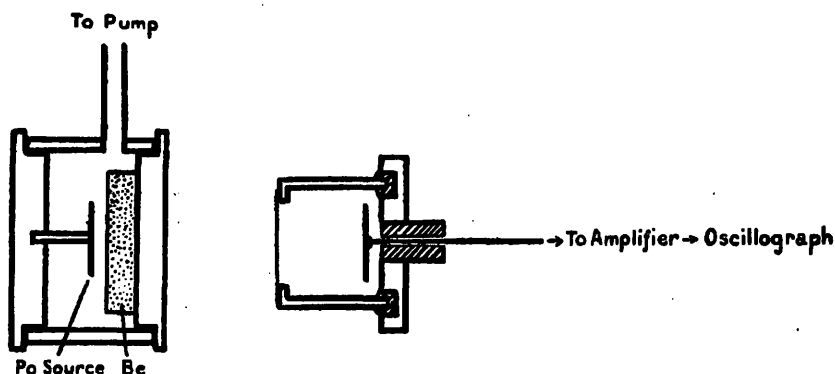
Fig.7: Chadwick's set-up with the Po-Be source and the ionisation chamber linked to an oscilloscope.(The Po-Be source in mounted on a silver plate of 1 cm diameter; the Be has a diameter of 2 cm)

The ionisation chamber (air at 1 atm.) has an Al-foil window. By adjusting the amplifier Chadwick sees pulses on the oscilloscope, proportional to the ionisation in the chamber, and can deduce from that the energy of the incoming particle. Thus he disposes of a lot more information than the Joliot-Curies who used an electrometer.

Chadwick soon notices that *the energetic radiation generated by the alpha's in the Be, penetrates 2 cm of lead without any absorption* (gamma radiation would certainly decrease in intensity). 2 mm of paraffin placed in front of the ionisation chamber makes the counting rate increase noticeably. This means that particles get *into the chamber from the paraffin.* Placing absorbers in the path of the particles shows that their range is 40 cm of air-equivalent, therefore they must be *protons.* This far the experiment is just a repeat of the Joliot-Curie one. But now Chadwick goes his own way! He takes away the paraffin and replaces it with materials like Li, Be, B. Gasses are introduced directly into the ionisation chamber: H, He, N, O, Ar. Each time he sees an increase in the counting rate, which means that protons are liberated from each of these elements. In his paper about the discovery of the neutron, Chadwick writes [63] : *"The experimental results show that if the recoil atoms are to be explained by collision with a gamma-ray (photon) we must assume a larger and larger energy for the*

(photon) as the mass of the struck atom increases. It is evident that we must either relinquish the application of conservation of energy and momentum in these collisions or adopt another hypothesis about the nature of the radiation. If we suppose that the radiation is not a gamma radiation, but consists of particles of mass nearly equal to that of the proton, all the difficulties connected with the collision disappear, both with regard to their frequency and to the energy transfer to different masses. In order to explain the great penetrating power of the radiation we must further assume that the particle has no net charge. We may suppose it (to be) the "neutron" discussed by Rutherford in his Bakerian Lecture of 1920."

17 February 1932: Chadwick works on this research for 10 days, with barely 3 hours of sleep per night. On Wednesday 17 February 1932 he sends his first short report to "Nature" [64] in order to claim the discovery of the neutron. The Joliot-Curies had missed the big discovery (and in the process set at defiance the fundamental rules of conservation of energy and momentum).

On Tuesday 23 February Chadwick gives a talk about the neutron in the so-called *"Kapitza club"* (an informal discussion group within the Cavendish laboratory). It must have been the shortest communication ever on such an important discovery. At the end Chadwick says: *"Now I want to be chloroformed and put to bed for a fortnight."* A very understandable wish of the exhausted discoverer of the third elementary particle! Rutherford insists that Chadwick get the Nobel prize. To someone who remarks that the Joliot-Curies have some merit too, Rutherford replies: *"For the neutron, to Chadwick alone; the Joliots are so clever that they soon will deserve it for something else."*

Chadwick's discovery now opens the way to the real research into the nucleus. As a consequence alpha particles become less important to experiments. The existing alpha-sources (mainly polonium) are converted to neutron sources, but these are in fact too weak to do any serious experiments. They emergence of accelerators would soon change the whole world of physics research. Hans Bethe remarks that everything that happened before 1932 belongs to the prehistory of nuclear physics; real nuclear physics started in 1932. The discovery of the neutron is the big turning point.

1932: Fermi in Rome: Rn production for the first neutron reactions

Enrico Fermi, professor of theoretical physics, knows of the existence in the cellars of the Physics Institute in Rome, of a container containing 1 gram of radium. He gets the permission to extract the radon from it. Each time 50 mCi are taken out (at that time they called that "small quantities"!). Each week the radon source has to be renewed [65], not an easy task. The glass tube in which the radon is caught breaks repeatedly, thus spreading the activity all over the place. The aim of the experiments is to systematically irradiate all the elements in Mendeleev's table with the neutrons from the Rn-Be.

On 24 March 1934 Fermi publishes [66] his first results about artificial radioactivity caused by neutron irradiation. The glass tube with the beryllium powder and 50 mCi radon produces a flux of some 10^5 neutrons, a lot for the time.

The first results are obtained with fluor and aluminium:
$$F^{18} + n^1 \rightarrow N^{16} + He^4 \qquad Al^{27} + n^1 \rightarrow Na^{24} + He^4$$

On 15 January 1934, only two months prior, the Joliot-Curies had published their results with alpha-irradiations in the Comptes Rendus [67], thus proving correct Rutherford's prediction that they also would get a Nobel prize. With an alpha-source of 100 mCi of polonium they got the following reaction:
$$He^4 + Al^{27} \rightarrow P^{30} + n^1 \qquad P^{30} \rightarrow Si^{30} + e^+ + \nu$$
After the Po source was removed, the active P^{30} remained ($T_{1/2} = 2.5$ min.)

These α- and n-reactions open up the whole world of artificial radioactivity, and a new chapter in nuclear physics. Marie Curie, then already very ill, writes to her daughter: *"Nous voici revenus aux beaux temps du vieux laboratoire."*

IX. 1939: the research moves to the USA

Starting from 1933 the political developments in Nazi-Germany have a big influence on science. Many physicists leave Germany and even continental Europe to go to Great Britain or the USA. For the experimental physicists the fact whether or not Ra-Be sources are present in a laboratory

is an important argument in the choice of their destination. Many also wander about from one laboratory to another university.

Ra-Be in the search for secondary neutrons in fission studies of uranium - the role of Union Minière

January 1939: Leo Szilard, emigrated to the USA, by way Great Britain, learns that Fermi has held a talk at the 5th Conference for Theoretical Physics in Washington, about the possibility of a chain reaction in uranium. Shortly afterwards they meet and Fermi confirms *"... there is the remote possibility that neutrons may be emitted in the fission of uranium and then of course perhaps a chain reaction can be made"*. Upon that Fermi is asked to specify what he means by "remote possibility". The reply is *"Ten percent"*. Upon that Rabi remarks: *"Ten percent is not a remote possibility if it means I may die of it. If I have pneumonia and the doctor tells me that there is a remote possibility that I might die, and it's ten percent, I get excited about it."* [68]

At that time however no experimental research has been done on the emission of secondary neutrons in the n-irradiation of uranium. For the first experiments about neutron production Fermi and Anderson use a fishpond,[‡‡] a tub of some 1m diameter and 1m high. It is filled with water and in the middle they hang a sphere of about 15cm diameter with a Rn-Be source. In the tub the emitted neutrons are moderated. Their number is counted by using the activation of a 42 second isomeric state in Rh^{104}. In the sphere later uranium oxide is added, in order to see whether *more neutrons* are produced, and if so, *how many*.

February - March 1939: Szilard is looking for radium. In 1939 the radium production in the USA is almost completely controlled by the *Radium Chemical Company of New York*, a subsidiary of our Belgian *Union Minière du Haut Katanga*. The company agrees to rent out two grams of radium, at 250 $ a month. In combination with a beryllium-disc from

---

[‡‡] Fermi had already used fish-ponds in experiments earlier, back in Rome: Pierre de Latil, *"Enrico Fermi, The Man, His Theories"*, 1964, p.76 (Professor Corbino's pond for goldfish was used on 22 October 1934 to place into it a Rn-Be source in order to measure the slow neutrons, by means of the activation of silver).

Clarendon lab in Oxford, were Szilard had worked before coming the USA, he can now set up his own neutron experiments.

Fermi's neutron source is based on radon, not radium. Szilard remarks that in beryllium radon produces faster neutrons than radium does. An increase in neutrons in Fermi's tub could come not from fission, but from a different reaction in Be. Fermi agrees to repeat his fishpond experiment with Szilard's 2g Ra-Be source. The set-up now consists of paraffin in which there is a beryllium cylinder with the 2 grams of radium; on top of that a box with uranium oxide. In the uranium oxide there is an ionisation chamber, linked to an oscilloscope. Their first results give an estimate for the production of secondary neutrons: per initial neutron 2 are generated.

February 1939, Paris: In Paris, in the last week of February 1939, Joliot, von Halban and Kowarski begin their experiments to detect secondary neutrons in fission experiments. They use a water-tank with a central neutron source and uranium dissolved in the water, not piled up around the source. They have a great advantage: direct access to the large stock of radium in the *Institut du Radium.* Their results come just one week prior to Fermi and Anderson's. They find there is "more than 1" secondary neutron.

17 March, 18 March and 22 April 1939: Wigner, Bohr, Rosenfeld, Szilard, Fermi and Teller meet in Washington. They want to deposit the results of the fission research with the Physical Review, *without publishing* them, in view of the Nazi-threat. The decision is taken on 17 March 1939: the majority does not want to publish, though Fermi does. He concedes to the majority.

Alas, on *18 March* Joliot, von Halban and Kowarski publish their results in Nature. Upon that Fermi says: not to publish makes no sense. On 22 April a second paper by Joliot, von Halban and Kowarski appears in Nature. There they claim *that 3.5 neutrons are liberated per fission.* Within a few days the whole world is aware of the explosive powers of a chain reaction in uranium.

29 April 1939 - June 1940: .As a consequence of this publication a conference is held in Nazi-Germany in Berlin on 29 April 1939. A research program is started, all exports of uranium products are forbidden, and all the radium reserves of St. Joachimsthal are impounded. It is almost unbelievable that in June 1940 the German journal Naturwissenschaften publishes a paper by Flugge, about the possibilities of nuclear energy. This

development causes great concern in the West. In 1942 Werner Heisenberg gives a talk in Berlin (for a small group of military and physicists, among which Otto Hahn) about the explosive possibilities of U^{235} but during the war-years little or nothing of this transpires to the rest of the world.

In June 1940 (Belgium is then occupied by the Nazis since a month), the Americans order 60 tons uranium oxide from Union Minière. Union Minière manages to ship *1250 tons of extremely rich pitchblende* (65% uranium oxide) to the USA. [69]

X. Radium and Fission

Rn-Be used to start the first reactor - Chicago CP1 - 1942

In 1939 Szilard suggest to use carbon as a moderator for the neutrons, and sais to Fermi *"... next best guess to heavy water..."*. Finding and purchasing a large quantity of *very pure* carbon is no small matter. In July 1939 Szilard buys 4 tons of high quality graphite from the National Carbon Company of New York. Thus the first experiment with carbon as a moderator can be set up. Fermi is very enthusiastic. They want to know how far the neutrons of the radon-beryllium source, placed in paraffin under the carbon mass will reach, after their collisions with the carbon. The farther they reach, the better carbon is as a moderator. The distribution of the neutrons is measured using the activation of Rh^{104} ($T_{1/2} = 42s.$). Fermi, a stop watch in hand, runs with the activated sample, to the Geiger counter in less than 20 seconds, to measure its activity. In the course of 1940 the necessary data are obtained to develop the theoretical model of a reactor. Unfortunately the data are precise only to 10% and more reliable measurements are needed for the construction of an experimental reactor. The first reactor, CP-1 (Chicago Pile Number 1), is built under Fermi's direction. It becomes critical on 2 December 1942. [70] The (Ra, Be) source plays an important role: it gives the starting neutrons.

Ra and Po in the neutron initiators of the first atomic bombs - Trinity 16 July 1945

As compared to the development of the atomic bomb, the development of its initiator can be seen as a *small* problem, albeit a very important one. The chain reaction needs a few (one or two) neutron to get started. No one wants to take the chance that the many billions invested in the production of plutonium and of the bomb, are be lost because of erratic neutrons. Since the time that Chadwick produced neutrons by the (α, n) reaction on beryllium, with radium, radon and polonium as α-emitters, everyone had his own neutron source. Making a neutron-source for research is no problem at all, but making one as an initiator for the bomb, that had never been done.

In Los Alamos in 1943, Robert Serber theoretically studies the possibilities of a Ra-Be source in the initiator of the bomb. In the *Los Alamos Primer*[§§] there is an extremely crude sketch of the two types of bombs (the *gun* and the *implosion* type) and their initiators.

For example to fire the gun-type the Ra (together with part of the U) is shot into the U-mass, in which there is also the Be. That way the critical mass is surpassed, and by means of the Ra-Be neutrons the chain reaction ignites. Radium however has the drawback that it produces intense gamma-radiation (we talk here about large amounts of radium, in order to have a strong enough neutron source), so Serber preferred Po as primary neutron source: *"some other source such as polonium ... will probably prove more satisfactory"*. [71] The challenge consists not only of making a neutron source as strong as possible, but also one that produces its neutrons at a precisely given moment.

[§§] The *Los Alamos Primer* is the nickname for the only document that the scientists received when entering the seclusion of the development centre (the *"Teac Area"* for which a *Secret Limited access pass* was needed). It contained a very succinct description of what they were expected to do there. One of the items on the list was "make an initiator for the bomb".

Fig.8: Schematic representation of the two types of atomic bombs, such as they were presented in the "Los Alamos Primer". Left: the "gun" type, right the "implosion" type.

This is of course not the finest application of radium and polonium, but one that is all important in writing a new chapter in history.

For the U^{235}-gun type, the procedure is fairly easy: the alpha-source is in the "projectile", the beryllium in the main U-mass; they are apart and come together when the projectile is fired into the U-mass. For the Pu-implosion type of bomb, it is more difficult. In the "Fat Man'" both Po and Be have to be in the center of the Pu-mass, but without producing any neutrons up till a fraction of a nanosecond prior to the implosion, in which the Pu-mass is pressed together and thus the critical mass is surpassed.

The range in a metal foil of the alphas from Po^{210} is just a few hundreds of a millimeter. They can therefore be easily screened between two foils. The source is spherical, with the Be on the outside, the whole has about 1 cm diameter. *A quantity of Po, alpha-emission wise equivalent to 32 grams of Ra***, is used to produce 9 to 10 neutrons within the time-window of the implosion-time.

Keeping the Po and Be separate is no problem, but making them merge at the exact time during the implosion is quite another matter. Many versions were tested in the course of 1944-45.

On 10 July 1945, on the MacDonald Ranch near Trinity Site, the three elements of the puzzle are assembled on a table covered with brown paper, in a room that has been sealed off, the doors masked with sticky tape against dust. These three elements are the two nickel-covered half-spheres of plutonium and a small glistening ball, the (Po, Be) initiator.

*** Polonium emits about 5000 times more alphas than the same mass of radium.

In the first official report (the "Smyth Report) [72] [‡‡‡] , there is no mention of the initiating mechanism. It still is *classified information*. Today research into the atomic bomb still continues in the Nevada desert in the USA. It is concerned with what goes on within the fraction of a nano-second (10^{-10} to 10^{-12} s.), just before the implosion takes place. Under strict surveillance you can tour through the test site by bus, but no one tells you much, and not much can be seen, since everything goes on underground.

XI. Conclusion

After World War II, radium rapidly loses its interest for research in physics, as well as for medical applications. In medicine it is replaced by ^{60}Co, ^{137}Cs, ^{198}Au,... In physics its main application, i.e. producing neutrons, is quickly taken over by reactors, where an initial (thermal) flux of some 10^7 neutrons/s would quickly reach 10^{12} or 10^{13} n/s. To day radium only has historical interest. The reserves of radium are so big, and its half-life is so long, that in any respect the world-wide demands can be met. These demands grow smaller and smaller over the years, and it is highly improbable that in the future any radium will ever be produced from ores, as it was done in the first half of this century. In the currently applied uranium purification processes radium is considered simply waste-material. It is collected and buried together with other long-lived waste. Landa [21] concludes rightly: *"In less than a century radium has evolved from the status of buried treasure to that of buried waste."*

[‡‡‡] This report known as the "Smyth report", was the very first information that came through after the publication stop for fission-related data of 1940. The 143 pages long text was literally devoured by all physicists around the world. In Denmark, in Bohr's laboratory, the text was cut out and pinned on the wall, in order that several people be able to read it at the same time. 50 years later each student handbook contains more information than this report. A second (extended) "Smyth report", "Atomic Energy for Military Purposes", (Princeton University Press, 1946), has 308 pages. Yet it does not mention anything about the initiating-mechanism.

References

1. See for example: G. Amaldi: *"The Nature of Matter. Physical Theory from Thales to Fermi"*, The University of Chicago Press, 1966.
2. A. de Rassenfosse en G. Guében *"Des Alchimistes aux Briseurs d'Atomes"*, G.Thone, Liège, 1936, p.39.
3. See for example:A.Pais: *"Inward Boun"d*, Oxford University Press, 1994
4. F. Soddy *"Radio-Activity: an Elementary Treatise, from the Standpoint of the Disintegration Theory"*, "The Electrician" Printing & Publ. C°, Ltd., London, 1904, p.1 (referred to further on as "Soddy").
5. W. Crookes, *"Radiant Matter"*, etc., a series of 8 publications in Chemical News, Nature en Am. J. of Science, 1879.
6. A very complete survey of the history of cathodic rays can be found in: Per F. Dahl, *"Flash of the Cathode Rays - A History of J.J. Thomson's Electron"*, Institute of Physics Publ., Bristol, 1997.
7. In 1896 6 papers by Becquerel appreared one after the other in the Comptes Rendus CXXII: p.420, 501, 559, 609, 762 and 1086.
8. Roberto de Andrade Martins, *"A critical analysis of Becquerel's early experiments"*, Congrès S.F.P., Paris 1997, Communication Radioactivité N°15.04
9. Soddy, p.11
10. See a very complete analysis by A. Pais in *"Inward Bound"* (cfr. ref. 3) (Chapter 4: The discovery of the electron).
11. Mme Sklodowska Curie, *"Recherches sur les substances radioactives"*, Thèses présentées à la Faculté des Sciences de Paris pour obtenir le grade de Docteur ès Sciences Physiques. Paris, Gauthier-Villars, 1903. p.14 e.v.
12. M. Curie,*"Traité de Radioactivité"*, Gauthier-Villars, Paris, 1910, t1. p.142 - Congrès international de Physique 1900, t.3, p.79.

13. E. Rutherford, Phil.Mag. 47 (1899) (january) 116. and alsdo ref. 14, p.109

14. E. Rutherford, *"Radio-Activity"*, Cambridge Physical Series, 2nd edition, 1905, p.18.(hereafter referred to as "Rutherford 1905")

15. M. Curie, *"Traité de Radioactivité"*, Gauthier-Villars, Paris, 1910, t1. p.136 (hereafter referred to as "M.Curie, Traité"

16. P. en M. Curie, C.R., 127, (1898), (18 juillet), 175.

17. P. Curie, Mme. P. Curie en G. Bémont, C.R. 127, (1898), (26 décembre), 1215.

18. M. Curie Traîté, Chapter III.

19. M. Curie Traité, p.151.

20. Susan Quinn, *"Marie Curie"*, Traduit de l'anglais par Laurent Muhleisen, Ed. Odile Jacob, 1996, p.183. In 1903 four members of the Académie (among whom Mascart and Poincaré) wrote a letter in which it can be read that Pierre Curie alone had studied several uranium and thorium minerals and had -alone- separated two new elements, polonium and radium.

21. E. R. Landa, *"The First Nuclear Industry"*, Sci. Am. 247 (1982) 154.

22. Demarçay, C.R. 127, (1898), (décembre), 1218 - C.R. 129, (1899), (novembre), 716 - C.R. 131, (1900), (juillet), 258. The results of Demarçay are cited several times in the publications of P. and M. Curie; a summary can be found in Congrès international de Physique 1900, t.3, 79 *" Les nouvelles substances radioactives et les rayons qu'elles émettent"*.

23. M. Curie Traîté, p. 164. See also the papers by M. Curie in C.R. 129 (1899) (novembre), 760 and C.R.131, (1900), (août), 382; P.en M. Curie, Congrès international de Physique, 1900, t.3, 79.

24. See the papers by M. Curie in the Comptes Rendus of the years 1899, 1900, 1902 and 1907.

25. Thorpe, Proc.Roy.Soc., A81 (1908) in ref. 3, p. 173.

26. E. Rutherford, in 1905, refers to Runge and Precht in Phil.Mag. (1903); M. Curie in her Traité refers (1910) naar the review paper by Runge and Precht in Phys.Zeit. (1903), which describes the spectroscopic research by Runge and Precht, Exner and Haschek and Crookes.

27. Rutherford 1905, p.18.

28. P.Curie, *"Oeuvres de Pierre Curie publiés par les soins de la Société Française de Physique"*, Gauthier-Villars, Paris 1908, p. 530 en p. 549 (with explanations by the instrumentmaker).
29. M. Curie, Traîté , p.177.
30. Soddy, p.18.
31. A. Debierne, C.R. 129, octobre 1899 and C.R. 130, avril 1900.
32. Rutherford 1905, p. 328.
33. E. Rutherford and F. Soddy, Phil. Mag. 4 (1902) 370, 569.
34. P.Curie, *"Recherches récentes sur la radioactivité"*, J. de Chimie physique 1 (1903) 409.
35. P. Curie and J. Danne, C.R. 138 (1904) (14 mars) 683.
36. P. Curie and J. Dewar, C.R. 138 (1904) (25 janvier) 190.
37. P. Curie and J. Danne, C.R. 138 (1904) (21 mars) 748.
38. Rutherford 1905, p.442.
39. McLennan, Phys.Rev. 4, (1903),
40. P. Curie and A. Laborde, C.R. 136 (1903) 673.
41. One of the many papers concerning the Kelvin-problem: Kelvin, Phil.Mag. 7, (1904), 220. The story is amply described by A. Pais in *"Inward Bound"* Oxford University Press, 1994, p. 110.
42. M. Curie Traîté, p.153-155.
43. M. Curie Traîté, nr.42.
44. M. Curie Traité, p 158.
45. M. CurieTraité p.168.
46. J. Vanderlinden, *"Marie Curie et le radium "belge"*, in *"Marie Curie et la Belgique"*, ULB, 1990, p. 92
47. E. R. Landa, Sci. Am. 247 (1982) 154.
48. *"Radium. Production, Propriétés générales, Ses applications en thérapeuthique, Appareils, Union Minière du Haut Katanga"*, Dept. Radium, 8, Montagne du Parc, Bruxelles, 1931.
49. Maurice Curie, *"Le radium et les radio-éléments"*, Libr. J.-B. Baillière et fils, Paris 1925.
50. M. Curie Traîté, p,153 e.v.
51. E. Rutherford, J. Chadwick and C. Ellis, Radiations from radioactive Substances, Cambridge University Press, 1930 §130, p.567.
52. E. Marsden, Phil.Mag. 27 (1914) 824.
53. E. Rutherford, Collected Papers, v.II, Interscience, 1963, p.547.

54. N. Bohr, *"Essays on Atomic Physics and Human Knowledge, 1958-1963"*. Interscience, 1963, p.50.

55. Rutherford 1930 p.253 (scattering) and p. 283 (disintegration)

56. N. Bohr, *"Essays on Atomic Physics and Human Knowledge, 1958-1963"*. Interscience, 1963, p.589.

57. E. Rutherford, Phil.Mag. 37, 581 (1919)

58. E. Rutherford, *"The Bakerian Lecture: Nuclear Constitution of Atoms"*, Collected Papers v.III, Interscience 1965, p.14.

59. M. Oliphant, *"Rutherford Recollections of the Cambridge Days"*, Elsevier Publ. Co., 1972, p.40

60. A. Brown, *"The Neutron and the Bomb - A Biography of Sir James Chadwick"*, Oxford University Press, 1997, p.87 - 88.

61. I. Curie and F. Joliot, *"La projection de noyaux atomiques par un rayonnement pénétrant - L'existence du neutron"*, Actualités Scientifiques et Industrielles, Vol. XXXII, Exposés de Physique Théorique publiés sous la direction de M. Louis de Broglie, 1932. and also: I. Curie et F. Joliot, C.R. 194 (1932) 273, and C.R. 194 (1932) 847.

62. E. Segrè, *"From X-rays to Quarks, Modern Physicists and their Discoveries"*, University of California , Berkeley - 1980, p.183-84.

63. J. Chadwick, *"The existence of a neutron."* Proc.Roy.Soc.136A (1932) 692. See also ref. 69 p. 162 and A. Brown, *"The Neutron and the Bomb"*, A Biography of Sir James Chadwick, Oxford University Press, 1997, Chapter 6.

64. J. Chadwick, *"Possible existence of a Neutron"*, Nature 129 (1932) 312

65. Pierre de Latil, *"Enrico Fermi, The Man and his Theories"*, Profiles in Science, Souvenir Press, 1965 and Laura Fermi in Selected Writings - The Nobel Prize, p.143 and also p. 61.

66. The first announcement was made on March 25 1934 in the Ricerca Scientifica (p.283); the second announcement was by a whole group, dated 10 May 1934. The group would publish another 5 papers together.

67. F. Joliot and I. Curie, *"Artificial Production of a New Kind of Radio-Element"*, Nature 10 Februari 1934

68. R. Rodes, *"The Making of the Atomic Bomb"*, Penguin Books 1988, p.280. (hereafter referred to as "Atomic Bomb")
69. Atomic Bomb p.427
70. E. Fermi, *"The development of the first chain reacting pile"* , Proceedings of the American Phil. Soc. 90 (1946) 20 (Read November 17, 1945, in the Symposium on Atomic Energy and its Implications).
71. Atomic Bomb, p. 578.
72. H.D. Smyth, *"A General Account of the Development of Methods of Using Atomic Energy for Military Purposes under the Auspics of The United States Government. 1940 - 1945., Written at the request of Major General L.R. Groves, United States Army, Publication authorized August 1945."*