

Closing in on radium

Marie Curie determines its relative atomic mass

In 1907, Marie Curie publishes an experimental determination of the relative atomic mass (formerly called atomic weight) of a radioactive element that she has been studying for a few years – radium. Curie has no doubts that radium is a well-defined chemical element. In 1902, she reported an average value of 225.0 for its relative atomic mass, but this came from an experiment using only 0.09 g of radium chloride. The results she publishes five years later are based on over four times as much: 0.4 g of “perfectly pure” radium chloride. She also improves the experimental conditions.

Curie’s successful isolation of radium as a pure salt followed a method of fractional crystallisation of radium chloride obtained from purifying tens of kilograms of barium sulphate. In the first part of this fractional crystallisation, radium chloride is dissolved in water mixed with hydrochloric acid: evaporation of this solution leads to the formation of needle-like crystals. The remaining liquid is decanted to recover the small quantity of radium salt in it. As fractionation progresses, photographs of spark spectra taken with Demarçay’s spectrograph allow comparison of the relative intensities of the 4554.2 Å line corresponding to barium and the 4533.3 Å line of radium: successful fractionation brings down the intensity of the former. When the barium line does not get any dimmer, Curie resorts to fractional precipitation: she adds drops of alcohol to the constantly stirred aqueous solution until the salt precipitates and the remaining liquid can be decanted again. Curie observes that the barium line never disappears entirely, and doubts that she could achieve this result with the sample she had available.

To determine the relative atomic mass of radium, Curie proceeds in 1907 as she had done in 1902. The crystallised radium chloride, placed in a previously weighed crucible, is dried and heated above 100 °C so that it loses all water and its mass is unchanged on further heating. The constant mass of the radium chloride sample is determined by letting the crucible cool down in a desiccator. As radium chloride salt easily absorbs water vapour, the weighing operation must be fast and is thus performed with the aperiodic balance devised by Pierre Curie, with direct readings for masses below 0.1 g.

The radium chloride salt (which has the chemical formula RaCl_2), is then dissolved in water in which a warm solution of silver nitrate – together with a small quantity of nitric acid – has been added. When the warm, stirred solution is clear, it is possible to collect the precipitated silver chloride by filtration. Dried silver chloride detached from the filter (which is itself burnt and accounted for when weighing the dry silver chloride) is heated until it reaches its point of fusion. Once cooled, silver chloride is weighed on the same aperiodic balance.



Assuming that radium is a divalent metal and the relative atomic masses of silver and chlorine are 107.8 and 35.4 respectively, the relative atomic mass of radium is determined in three consecutive experiments. The values found are 226.35, 226.04 and 226.15 giving an average of 226.18. Therefore, Curie concludes that the relative atomic mass of radium is 226.2. The three experimental values are remarkably close, which was not the case in the 1902 investigation.

Could the disagreement about a unit between the average values obtained in 1902 and 1907 be due to the different purity of the radium chloride samples? Curie is satisfied with the purity of the salt isolated in 1907, but she thinks that the source of disagreement must be the higher precision of her latest experiment rather than increased purity. To test this hypothesis, she takes a few milligrams of radium chloride and adds a known quantity of barium chloride. With this known proportion of barium chloride, Curie observes that the intensity of the 4554.2 Å barium line is almost as strong as that of the 4533.3 Å radium line; nevertheless, the corresponding change in relative atomic mass is smaller than a unit. This confirms to Curie that it is the improved precision of the experimental method that is responsible for the discrepancy between the 1902 and 1907 values. Being able to work with a larger quantity of radium salt made an important contribution to this improvement, as did careful handling of all reagents in better conceived conditions.

Indeed, Curie dedicates a whole section of her paper to the experimental issues she encountered in the laboratory. One difficulty has to do with the chemical composition of the substances used as reagents. Eventually, Curie prepares her own distilled water, later used to produce hydrochloric acid, and redistils the alcohol. This helps reduce the amount of spurious residues (especially sulphates) in the solutions she processes. Having realised that other such residues come from radium chloride attacking her glass containers, Curie switches to platinum containers but observes that operating quickly remains the only way to prevent substantial damage caused by radium chloride.

The importance of Curie's determination of the relative atomic mass of radium cannot be overstated. In 1911, upon accepting the Nobel Prize in Chemistry, Curie herself comments that "the task of isolating radium is the cornerstone of the edifice of the science of radioactivity". The ability to prepare pure radium salts and to establish its relative atomic mass prove that radium is a new element, deserving its own place in the periodic table. In her 1911 Nobel lecture, Curie also stresses how crucial it was to her study of radium to hypothesise that radioactivity – a term she coined – is an atomic property of a substance. Based on this assumption, each step of the fractionation process is accompanied by activity measurements, where the intensity of one of radium's spectral line increases as the substance's activity becomes more concentrated. This kind of procedure marks an entirely new way of searching for new chemical elements.



In Curie's time, not all scientists were as ready to embrace the existence of radioactive substances such as radium as she and her husband Pierre were. Notably, Lord Kelvin, inventor of the absolute temperature scale that bears his name, expressed scepticism about radium's status as a genuine chemical element. Marie and Pierre Curie's pioneering study of radioactive substances proved Kelvin wrong. More important, their work laid strong foundations for a field of study that would profoundly change scientific disciplines ranging from geology – with the first radiometric estimates for the age of the earth taking place around 1907 – to medicine. Regarding radioactivity as an atomic property of a substance and studying the source of the energy observed in radioactive phenomena led to the theory of atomic disintegration, which correctly predicted that helium gas is a product of radium's radioactive decay.

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