

Radium

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Radium is a chemical element with symbol **Ra** and atomic number 88. It is the sixth element in group 2 of the periodic table, also known as the alkaline earth metals. Pure radium is silvery-white, but it readily combines with nitrogen (rather than oxygen) on exposure to air, forming a black surface layer of radium nitride (Ra_3N_2). All isotopes of radium are highly radioactive, with the most stable isotope being radium-226, which has a half-life of 1600 years and decays into radon gas (specifically the isotope radon-222). When radium decays, ionizing radiation is a product, which can excite fluorescent chemicals and cause radioluminescence.

Radium, in the form of radium chloride, was discovered by Marie and Pierre Curie in 1898. They extracted the radium compound from uraninite and published the discovery at the French Academy of Sciences five days later. Radium was isolated in its metallic state by Marie Curie and André-Louis Debierne through the electrolysis of radium chloride in 1911.^[1]

In nature, radium is found in uranium and (to a lesser extent) thorium ores in trace amounts as small as a seventh of a gram per ton of uraninite. Radium is not necessary for living organisms, and adverse health effects are likely when it is incorporated into biochemical processes because of its radioactivity and chemical reactivity. Currently, other than its use in nuclear medicine, radium has no commercial applications; formerly, it was used as a radioactive source for radioluminescent devices and also in radioactive quackery for its supposed curative powers. Today, these former applications are no longer in vogue because radium's toxicity has since become known, and less dangerous isotopes are used instead in radioluminescent devices.

Characteristics

Radium is the heaviest known alkaline earth metal and is the only radioactive member of its group. Its physical and chemical properties most closely resemble its lighter congener barium.

Radium, $_{88}\text{Ra}$



General properties

| | |
|---------------------|------------------------|
| Name, symbol | radium, Ra |
| Appearance | silvery white metallic |

Radium in the periodic table

| | |
|---|--|
| Atomic number (<i>Z</i>) | 88 |
| Group, block | group 2 (alkaline earth metals), s-block |
| Period | period 7 |
| Element category | ☐ alkaline earth metal |
| Standard atomic weight (<i>A</i> _r) | (226) |
| Electron configuration | [Rn] 7s ² |
| per shell | 2, 8, 18, 32, 18, 8, 2 |

Physical properties

| | |
|----------------------|-------------------------|
| Phase | solid |
| Melting point | 973 K (700 °C, 1292 °F) |

Physical

Pure radium is a volatile silvery-white metal, although its lighter congeners calcium, strontium, and barium have a slight yellow tint.^[2] Its color rapidly vanishes in air, yielding a black layer of radium nitride (Ra₃N₂).^[3] Its melting point is either 700 °C (1,292 °F) or 960 °C (1,760 °F)^[a] and its boiling point is 1,737 °C (3,159 °F). Both of these values are slightly lower than those of barium, confirming periodic trends down the group 2 elements.^[4] Like barium and the alkali metals, radium crystallizes in the body-centered cubic structure at standard temperature and pressure: the radium–radium bond distance is 514.8 picometers.^[5] Radium has a density of 5.5 g/cm³, higher than that of barium, again confirming periodic trends; the radium–barium density ratio is comparable to the radium–barium atomic mass ratio,^[6] due to the two elements' similar crystal structures.^{[6][7]}

Chemical

Radium, like barium, is a highly reactive metal and always exhibits its group oxidation state of +2.^[3] It forms the colorless Ra²⁺ cation in aqueous solution, which is highly basic and does not form complexes readily.^[3] Most radium compounds are therefore simple ionic compounds,^[3] though participation from the 6s and 6p electrons (in addition to the valence 7s electrons) is expected due to relativistic effects and would enhance the covalent character of radium compounds such as RaF₂ and RaAt₂.^[8] For this reason, the standard electrode potential for the half-reaction Ra²⁺ (aq) + 2e[−] → Ra (s) is −2.916 V, even slightly lower than the value −2.92 V for barium, whereas the values had previously smoothly increased down the group (Ca: −2.84 V; Sr: −2.89 V; Ba: −2.92 V).^[9] The values for barium and radium are almost exactly the same as those of the heavier alkali metals potassium, rubidium, and caesium.^[9]

Solid radium compounds are white as radium ions provide no specific coloring, but they gradually turn yellow and then dark over time due to self-radiolysis from radium's alpha decay.^[3] Insoluble radium compounds coprecipitate with

(disputed)

| | |
|-----------------------------|---------------------------|
| Boiling point | 2010 K (1737 °C, 3159 °F) |
| Density near r.t. | 5.5 g/cm ³ |
| Heat of fusion | 8.5 kJ/mol |
| Heat of vaporization | 113 kJ/mol |

Vapor pressure

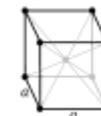
| P (Pa) | 1 | 10 | 100 | 1 k | 10 k | 100 k |
|-----------------|-----|-----|------|------|------|-------|
| at T (K) | 819 | 906 | 1037 | 1209 | 1446 | 1799 |

Atomic properties

| | |
|-----------------------------|--|
| Oxidation states | 2 (expected to have a strongly basic oxide) |
| Electronegativity | Pauling scale: 0.9 |
| Ionization energies | 1st: 509.3 kJ/mol 2nd: 979.0 kJ/mol |
| Covalent radius | 221±2 pm |
| Van der Waals radius | 283 pm |

Miscellanea

Crystal structure body-centered cubic (bcc)



| | |
|-------------------------------|-------------------|
| Thermal conductivity | 18.6 W/(m·K) |
| Electrical resistivity | 1 μΩ·m (at 20 °C) |
| Magnetic ordering | nonmagnetic |
| CAS Number | 7440-14-4 |

History

| | |
|------------------------|-------------------------------|
| Discovery | Pierre and Marie Curie (1898) |
| First isolation | Marie Curie (1910) |

all barium, most strontium, and most lead compounds.^[10]

Radium oxide (RaO) has not been characterized, despite oxides being common compounds for the other alkaline earth metals. Radium hydroxide (Ra(OH)₂) is the most readily soluble among the alkaline earth hydroxides and is a stronger base than its barium congener, barium hydroxide.^[11] It is also more soluble than actinium hydroxide and thorium hydroxide: these three adjacent hydroxides may be separated by precipitating them with ammonia.^[11]

Radium chloride (RaCl₂) is a colorless, luminous compound. It becomes yellow after some time due to self-damage by the alpha radiation given off by radium when it decays. Small amounts of barium impurities give the compound a rose color.^[11] It is soluble in water, though less so than barium chloride, and its solubility decreases with increasing concentration of hydrochloric acid. Crystallization from aqueous solution gives the dihydrate RaCl₂·2H₂O, isomorphous with its barium analog.^[11]

Radium bromide (RaBr₂) is also a colorless, luminous compound.^[11] In water, it is more soluble than radium chloride. Like radium chloride, crystallization from aqueous solution gives the dihydrate RaBr₂·2H₂O, isomorphous with its barium analog. The ionizing radiation emitted by radium bromide excites nitrogen molecules in the air, making it glow. The alpha particles emitted by radium quickly gain two electrons to become neutral helium, which builds up inside and weakens radium bromide crystals. This effect sometimes causes the crystals to break or even explode.^[11]

Radium nitrate (Ra(NO₃)₂) is a white compound that can be made by dissolving radium carbonate in nitric acid. As the concentration of nitric acid increases, the solubility of radium nitrate decreases, an important property for the chemical purification of radium.^[11]

Radium forms much the same insoluble salts as its lighter congener barium: it forms the insoluble sulfate (RaSO₄, the most insoluble known sulfate), chromate (RaCrO₄), carbonate (RaCO₃), iodate (Ra(IO₃)₂), tetrafluoroberyllate (RaBeF₄), and nitrate (Ra(NO₃)₂). With the exception of the carbonate, all of these are less soluble in water than the corresponding barium salts. Additionally, radium phosphate, oxalate, and sulfite are probably also insoluble, as they coprecipitate with the corresponding insoluble barium salts.^[12] The great insolubility of radium sulfate (at 20 °C, only 2.1 mg will dissolve in 1 kg of water) means that it is one of the less biologically dangerous radium compounds.^[13]

Most stable isotopes of radium

| iso | NA | half-life | DM | DE (MeV) | DP |
|--------------|-------|-----------|----------------|----------|-------|
| 223Ra | trace | 11.43 d | α | 5.99 | 219Rn |
| 224Ra | trace | 3.6319 d | α | 5.789 | 220Rn |
| 225Ra | trace | 14.9 d | β ⁻ | 0.356 | 225Ac |
| 226Ra | trace | 1600 y | α | 4.871 | 222Rn |
| 228Ra | trace | 5.75 y | β ⁻ | 0.046 | 228Ac |

Isotopes

Radium has 33 known isotopes, with mass numbers from 202 to 234: all of them are radioactive.^[14] Four of these – ^{223}Ra (half-life 11.4 days), ^{224}Ra (3.64 days), ^{226}Ra (1600 years), and ^{228}Ra (5.75 years) – occur naturally in the decay chains of primordial thorium-232, uranium-235, and uranium-238 (^{223}Ra from uranium-235, ^{226}Ra from uranium-238, and the other two from thorium-232). These isotopes nevertheless still have half-lives too short to be primordial radionuclides and only exist in nature from these decay chains.^[15] Together with the artificial ^{225}Ra (15 d), these are the five most stable isotopes of radium.^[15] All other known radium isotopes have half-lives under two hours, and the majority have half-lives under a minute.^[14] At least 12 nuclear isomers have been reported; the most stable of them is radium-205m, with a half-life of between 130 and 230 milliseconds, which is still shorter than thirty-four ground-state radium isotopes.^[14]

In the early history of the study of radioactivity, the different natural isotopes of radium were given different names. In this scheme, ^{223}Ra was named actinium X (AcX), ^{224}Ra thorium X (ThX), ^{226}Ra radium (Ra), and ^{228}Ra mesothorium 1 (MsTh₁).^[15] When it was realized that all of these are isotopes of radium, many of these names fell out of use, and "radium" came to refer to all isotopes, not just ^{226}Ra .^[15] Some of radium-226's decay products received historical names including "radium", ranging from radium A to radium G.^[15]

^{226}Ra is the most stable isotope of radium and is the last isotope in the $(4n + 2)$ decay chain of uranium-238 with a half-life of over a millennium: it makes up almost all of natural radium. Its immediate decay product is the dense radioactive noble gas radon, which is responsible for much of the danger of environmental radium.^[16] It is 2.7 million times more radioactive than the same molar amount of natural uranium (mostly uranium-238), due to its proportionally shorter half-life.^{[17][18]}

A sample of radium metal maintains itself at a higher temperature than its surroundings because of the radiation it emits – alpha particles, beta particles, and gamma rays. More specifically, natural radium (which is mostly ^{226}Ra) emits mostly alpha particles, but other steps in its decay chain (the uranium or radium series) emit alpha or beta particles, and almost all particle emissions are accompanied by gamma rays.^[19]

Occurrence

All isotopes of radium have half-lives much shorter than the age of the Earth, so that any primordial radium would have decayed long ago. Radium nevertheless still occurs in the environment, as the isotopes ^{223}Ra , ^{224}Ra , ^{226}Ra , and ^{228}Ra are part of the decay chains of natural thorium and uranium isotopes.^[15] Of these four isotopes, the most long-lived is ^{226}Ra (half-life 1600 years), a decay product of natural uranium. Because of its relative longevity, ^{226}Ra is the most common isotope of the element, making up about one part per trillion of the Earth's crust; essentially all natural radium is ^{226}Ra .^[20] Thus, radium is

found in tiny quantities in the uranium ore uraninite and various other uranium minerals, and in even tinier quantities in thorium minerals. One ton of pitchblende typically yields about one seventh of a gram of radium.^[21] One kilogram of the Earth's crust contains about 900 picograms of radium, and one liter of sea water contains about 89 femtograms of radium.^[22]

Production

Uranium had no large scale application in the late 19th century and therefore no large uranium mines existed. In the beginning the only larger source for uranium ore was the silver mines in Joachimsthal, Austria-Hungary (now Jáchymov, Czech Republic).^[23] The uranium ore was only a by-product of the mining activities.^[24]

In the first extraction of radium Curie used the residues after extraction of uranium from pitchblende. The uranium had been extracted by dissolution in sulfuric acid leaving radium sulfate, which is similar to barium sulfate but even less soluble in the residues. The residues also contained rather substantial amounts of barium sulfate which thus acted as a carrier for the radium sulfate. The first steps of the radium extraction process involved boiling with sodium hydroxide followed by hydrochloric acid treatment to remove as much as possible of other compounds. The remaining residue was then treated with sodium carbonate to convert the barium sulfate into barium carbonate carrying the radium, thus making it soluble in hydrochloric acid. After dissolution the barium and radium are reprecipitated as sulfates and this was repeated one or few times, for further purification of the mixed sulfate. Some impurities, that form insoluble sulfides, were removed by treating the chloride solution with hydrogen sulfide followed by filtering. When the mixed sulfate were pure enough they were once more converted to mixed chloride and barium and radium were separated by fractional crystallisation while monitoring the progress using a spectroscope (radium gives characteristic red lines in contrast to the green barium lines), and the electroscope.^[25]

After the isolation of radium by Marie and Pierre Curie from uranium ore from Joachimsthal several scientists started to isolate radium in small quantities. Later small companies purchased mine tailings from Joachimsthal mines and started isolating radium. In 1904 the Austrian government nationalised the mines and stopped exporting raw ore. For some time the radium availability was low.^[26]

The formation of an Austrian monopoly and the strong urge of other countries to have access to radium led to a worldwide search for uranium ores. The United States took over as leading producer in the early 1910s. The Carnotite sands in Colorado provide some of the element, but richer ores are found in the Congo and the area of the Great Bear Lake and the Great Slave Lake of northwestern Canada.^{[23][27]} Neither of the deposits is mined for radium but the uranium content makes mining profitable.

The Curies' process was still used for industrial radium extraction in 1940, but mixed bromides were then used for the fractionation.^[28] If the barium content of the uranium ore is not high enough it is easy to add some to carry the radium. These processes were applied to high grade uranium ores but may not work well with low grade ores.

Small amounts of radium were still extracted from uranium ore by this method as late as the 1990s,^[20] but today they are extracted only from spent nuclear fuel.^[29] and it is still in this range today, while the annual production of pure radium compounds is only about 100 g in total today.^[20] The chief radium-producing countries are Belgium, Canada, the Czech Republic, Slovakia, the United Kingdom, and Russia.^[20] The amounts of radium produced were and are always relatively small; for example, in 1918, 13.6 g of radium were produced in the United States.^[30] In 1954, the total worldwide supply of purified radium amounted to about 5 pounds (2.3 kg).^[31]

Source

- Wikipedia: Radium (<https://en.wikipedia.org/wiki/Radium>)