Lawrencium

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Lawrencium is a synthetic chemical element with chemical symbol **Lr** (formerly **Lw**) and atomic number 103. It is named in honor of Ernest Lawrence, inventor of the cyclotron, a device that was used to discover many artificial radioactive elements. A radioactive metal, lawrencium is the eleventh transuranic element and is also the final member of the actinide series. Like all elements with atomic number over 100, lawrencium can only be produced in particle accelerators by bombarding lighter elements with charged particles. Twelve isotopes of lawrencium are currently known; the most stable is ²⁶⁶Lr with a half-life of 11 hours, but the shorter-lived ²⁶⁰Lr (half-life 2.7 minutes) is most commonly used in chemistry because it can be produced on a larger scale.

Chemistry experiments have confirmed that lawrencium behaves as a heavier homolog to lutetium in the periodic table, and is a trivalent element. It thus could also be classified as the first of the 7th-period transition metals: however, its electron configuration is anomalous for its position in the periodic table, having an s²p configuration instead of the s²d configuration of its homolog lutetium. This means that lawrencium may be more volatile than expected for its position in the periodic table and have a volatility comparable to that of lead.

In the 1950s, 1960s, and 1970s, many claims of the synthesis of lawrencium of varying quality were made from laboratories in the Soviet Union and the United States. The priority of the discovery and therefore the naming of the element was disputed between Soviet and American scientists, and while the International Union of Pure and Applied Chemistry (IUPAC) established lawrencium as the official name for the element and gave the American team credit for the discovery, this was reevaluated in 1997, giving both teams shared credit for the discovery but not changing the element's name.

Characteristics

Physical

Lawrencium, ₁₀₃Lr

General properties

Name, symbol lawrencium, Lr

Appearance silvery (predicted)^[1]

Lawrencium in the periodic table

Atomic number (Z) 103

Group, block group n/a, d-block

Period period 7

Element category \square actinide, sometimes

considered a transition

metal

Standard atomic

weight (A_r)

Electron [Rn] $5f^{14} 7s^2 7p^1$

configuration

per shell 2, 8, 18, 32, 32, 8, 3

Physical properties

Phase solid (predicted)

Melting point 1900 K (1627 °C,

2961 °F) (predicted)

Density near r.t. $\sim 15.6-16.6 \text{ g/cm}^3$

(predicted)[2][3]

Atomic properties

Oxidation states 3

Ionization $1st: 478.6 \text{ kJ/mol}^{[4]}$ energies2nd: 1428.0 kJ/mol

to be a group 3 element, along with scandium, yttrium, and lutetium, as its filled fshell is expected to make it resemble the 7th-period transition metals. In the periodic table, it is located to the right of the actinide nobelium, to the left of the 6d transition metal rutherfordium, and under the lanthanide lutetium with which it shares many physical and chemical properties. Lawrencium is expected to be a solid under normal conditions and assume a hexagonal close-packed crystal structure ($^{c}/_{a} = 1.58$), similar to its lighter congener lutetium, though this is not yet known experimentally.^[5] The enthalpy of sublimation of lawrencium is estimated to be 352 kJ·mol⁻¹, close to the value of lutetium and strongly suggesting that metallic lawrencium is trivalent with the 7s and 6d electrons delocalized, a prediction also supported by a systematic extrapolation of the values of heat of vaporization, bulk modulus, and atomic volume of neighboring elements to lawrencium.[15] Specifically, lawrencium is expected to be a trivalent, silvery metal, easily oxidized by air, steam, and acids, [16] and having an atomic volume similar to that of lutetium and a trivalent metallic radius of 171 pm. [15] It is expected to be a rather heavy metal with a density of around 15.6 to 16.6 g·cm $^{-3}$.[2][3] It is also predicted to have a melting point of around 1900 K (1627 °C), not far from the value for lutetium (1925 K).[17]

Lawrencium is the final member of the actinide series and is sometimes considered

Chemical

In 1949, Glenn T. Seaborg, who devised the actinide concept that elements 89 to 103 formed an actinide series homologous to the lanthanide series from elements 57 to 71, predicted that element 103 (lawrencium) should be its final member and that the ${\rm Lr}^{3+}$ ion should be about as stable as ${\rm Lu}^{3+}$ in aqueous solution. It was not until decades later that element 103 was finally conclusively synthesized and this prediction was experimentally confirmed. [18]

1969 studies on the element showed that lawrencium reacted with chlorine to form a product that was most likely the trichloride LrCl₃. Its volatility was found to be similar to that of the chlorides of curium, fermium, and nobelium and much less than that of rutherfordium chloride. In 1970, chemical studies were performed on 1500 atoms of the isotope ²⁵⁶Lr, comparing it with divalent (No, Ba, Ra), trivalent

(predicted)

3rd: 2219.1 kJ/mol

(predicted)

Miscellanea

Crystal structure hexagonal close-packed

(hcp)

(predicted)^[5]

CAS Number 22537-19-5

History

Naming after Ernest Lawrence

Discovery Lawrence Berkeley

National Laboratory and Joint Institute for Nuclear

Research (1961–1971)

Most stable isotopes of lawrencium

(Fm, Cf, Cm, Am, Ac), and tetravalent (Th, Pu) elements. It was found that lawrencium coextracted with the trivalent ions, but the short half-life of the ²⁵⁶Lr isotope precluded a confirmation that it eluted ahead of Md³⁺ in the elution sequence.[18] Lawrencium occurs as the trivalent Lr³⁺ ion in aqueous solution and hence its compounds should be similar to those of the other trivalent actinides: for example, lawrencium(III) fluoride (LrF₃) and hydroxide (Lr(OH)₃) should both be insoluble in water. [18] Due to the actinide contraction, the ionic radius of Lr³⁺ should be smaller than that of Md³⁺, and that it should elute ahead of Md³⁺ when ammonium α -hydroxyisobutyrate (ammonium α -HIB) is used as an eluant. [18] Later 1987 experiments on the longer-lived isotope ²⁶⁰Lr confirmed lawrencium's trivalency and that it eluted in roughly the same place as erbium, and found that lawrencium's ionic radius was (88.6 \pm 0.3) pm, larger than would be expected from simple extrapolation from periodic trends. [18] Later 1988 experiments with more lawrencium atoms refined this value to (88.1 \pm 0.1) pm and calculated an enthalpy of hydration value of $-(3685 \pm 13) \text{ kl·mol}^{-1}$. It was also pointed out that the actinide contraction at the end of the actinide series was larger than the analogous lanthanide contraction, with the exception of the last actinide, lawrencium: the cause was speculated to be relativistic effects.[18]

iso	NA	half- life	DM	DE (MeV)	DP
²⁶⁶ Lr	syn	11 h	SF		
²⁶² Lr	syn	3.6 h	ε		²⁶² No
²⁶¹ Lr	syn	44 min	SF/ ε?		
²⁶⁰ Lr	syn	2.7 min	α	8.04	²⁵⁶ Md
²⁵⁹ Lr	syn	6.2 s	78% α 22%	8.44	²⁵⁵ Md
²⁵⁶ Lr	syn	27 s	SF α	8.62,8.52,8.32	²⁵² Md
²⁵⁵ Lr	syn	21.5 s	α	8.43,8.37	²⁵¹ Md
²⁵⁴ Lr	syn	13 s	α	8.46,8.41	²⁵⁰ Md
			22% ε		²⁵⁴ No

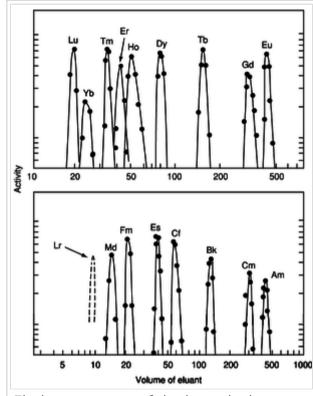
It has been speculated that the 7s electrons are relativistically stabilized, so that in reducing conditions, only the $7p_{1/2}$ or 6d electron would be ionized, leading to the monovalent Lr^+ ion. However, all experiments to reduce Lr^{3+} to Lr^{2+} or Lr^+ in aqueous solution were unsuccessful. On the basis of this, the standard electrode potential of the $E^{\circ}(Lr^{3+}\to Lr^+)$ couple was calculated to be less than -1.56 V, indicating that the existence of Lr^+ ions in aqueous solution was unlikely. The upper limit for the $E^{\circ}(Lr^{3+}\to Lr^{2+})$ couple was predicted to be -0.44 V: the values for $E^{\circ}(Lr^{3+}\to Lr)$ and $E^{\circ}(Lr^{4+}\to Lr^{3+})$ are predicted to be -2.06 V and +7.9 V. $^{[18]}$ The stability of the group oxidation state in the 6d transition series decreases as Rf^{4+} > Db^{5+} > Sg^{6+} , and lawrencium continues the trend with Lr^{3+} being more stable than Rf^{4+} . $^{[19]}$

Atomic

A lawrencium atom has 103 electrons, of which three can act as valence electrons. In 1970, it was predicted that the groundstate electron configuration of lawrencium was $[Rn]5f^{14}6d^{1}7s^{2}$ (ground state term symbol $^{2}D_{3/2}$), following the Aufbau principle and conforming to the $[Xe]4f^{14}5d^{1}6s^{2}$ configuration of lawrencium's lighter homolog lutetium. [20] However, the next year, calculations were published that questioned this prediction, instead expecting an anomalous [Rn]5f¹⁴7s²7p¹ configuration. [20] Though early calculations gave conflicting results, [21] more recent studies and calculations confirm the s²p suggestion. [22][23] 1974 relativistic calculations concluded that the energy difference between the two configurations was small and that it was uncertain which was the ground state. [20] Later 1995 calculations concluded that the s²p configuration should be energetically favored, because the spherical s and p_{1/2} orbitals are nearest to the atomic nucleus and thus move quickly enough that their relativistic mass increases significantly. [20]

In 1988, a team of scientists led by Eichler calculated that lawrencium's enthalpy of adsorption on metal sources would differ enough depending on its electron configuration that it would be feasible to carry out experiments to exploit this fact to measure lawrencium's electron configuration. The s^2p configuration was expected to be more volatile than the s^2d configuration, and be more similar to that of the p-block element lead. No evidence for lawrencium being volatile was obtained and the lower limit for the enthalpy of adsorption of lawrencium on quartz or platinum was significantly higher than the estimated value for the s^2p configuration.

In 2015, the first ionization energy of lawrencium was measured, using the isotope 256 Lr. $^{[24]}$ The measured value, $4.96^{+0.08}_{-0.07}$ eV, agreed very well with the relativistic theoretical prediction of 4.963(15) eV, and also provided a first step into measuring the first ionization energies of the transactinides. $^{[24]}$ This value is the lowest among all the lanthanides and actinides, and supports the s²p configuration as the $7p_{1/2}$ electron is



Elution sequence of the late trivalent lanthanides and actinides, with ammonium α -HIB as eluant: the broken curve for lawrencium is a prediction.

expected to be only weakly bound. This suggests that lutetium and lawrencium behave similarly to the d-block elements (and hence being the true heavier congeners of scandium and yttrium, instead of lanthanum and actinium), and also that lawrencium may behave similarly to the alkali metals sodium and potassium in some ways. [25] Given that the s^2p configuration is correct, then lawrencium cannot be regarded as a transition metal under the IUPAC definition ("An element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell"), [26] unlike its lighter homolog lutetium and the group 3 elements, with which lutetium and lawrencium are sometimes classified. [27] It is nevertheless quite likely that metallic lawrencium will behave similarly to curium and show the expected [Rn]5f¹⁴6d¹7s² configuration, which is supported by the earlier volatility experiments. [28]

Isotopes

Twelve isotopes of lawrencium are known, with mass numbers 252–262 and 266; all are radioactive. [29][30] Additionally, one nuclear isomer is known, with mass number 253. [29] The longest-lived lawrencium isotope, ²⁶⁶Lr, has a half-life of 11 hours and is one of the longest lived superheavy isotopes known to date, suggesting that it is perhaps on the shore of the island of stability of superheavy nuclei. [31] However, shorter-lived isotopes are usually used in chemical experiments because ²⁶⁶Lr currently can only be produced as a final decay product of even heavier and harder-to-synthesize elements: it was discovered in 2014 in the decay chain of tennessine-294. [29][30] The isotope ²⁵⁶Lr (half-life 27 seconds) was used in the first chemical studies on lawrencium: currently, the slightly longer lived isotope ²⁶⁰Lr (half-life 2.7 minutes) is usually used for this purpose. [29] After ²⁶⁶Lr, the longest-lived lawrencium isotopes are ²⁶²Lr (3.6 h), ²⁶¹Lr (44 min), ²⁶⁰Lr (2.7 min), ²⁵⁶Lr (27 s), and ²⁵⁵Lr (22 s). [29][32][33] All other known lawrencium isotopes have half-lives under 20 seconds, and the shortest-lived of them (²⁵²Lr) has a half-life of only 390 milliseconds. [29][32][33] However, the undiscovered isotopes with mass numbers 263 to 265 are expected to have longer half-lives (²⁶³Lr, 5 h; ²⁶⁴Lr and ²⁶⁵Lr, 10 h). [32][33] The half-lives of lawrencium isotopes mostly increase smoothly from ²⁵²Lr to ²⁶⁶Lr, with a dip from ²⁵⁷Lr to ²⁵⁹Lr to ²⁵⁹Lr [29][32][33]

Source

Wikipedia: Lawrencium.