

Molybdenum

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Molybdenum is a chemical element with symbol **Mo** and atomic number 42. The name is from Neo-Latin *molybdaenum*, from Ancient Greek Μόλυβδος *molybdos*, meaning lead, since its ores were confused with lead ores.^[5] Molybdenum minerals have been known throughout history, but the element was discovered (in the sense of differentiating it as a new entity from the mineral salts of other metals) in 1778 by Carl Wilhelm Scheele. The metal was first isolated in 1781 by Peter Jacob Hjelm.

Molybdenum does not occur naturally as a free metal on Earth; it is found only in various oxidation states in minerals. The free element, a silvery metal with a gray cast, has the sixth-highest melting point of any element. It readily forms hard, stable carbides in alloys, and for this reason most of world production of the element (about 80%) is used in steel alloys, including high-strength alloys and superalloys.

Most molybdenum compounds have low solubility in water, but when molybdenum-bearing minerals contact oxygen and water, the resulting molybdate ion MoO_4^{2-} is quite soluble. Industrially, molybdenum compounds (about 14% of world production of the element) are used in high-pressure and high-temperature applications as pigments and catalysts.

Molybdenum-bearing enzymes are by far the most common bacterial catalysts for breaking the chemical bond in atmospheric molecular nitrogen in the process of biological nitrogen fixation. At least 50 molybdenum enzymes are now known in bacteria and animals, although only bacterial and cyanobacterial enzymes are involved in nitrogen fixation. These nitrogenases contain molybdenum in a form different from other molybdenum enzymes, which all contain fully oxidized molybdenum in a molybdenum cofactor. These various molybdenum cofactor enzymes are vital to the organisms, and molybdenum is an essential element for life in all higher eukaryote organisms, though not in all bacteria.

Characteristics

Molybdenum, $_{42}\text{Mo}$



General properties

| | |
|---------------------|----------------|
| Name, symbol | molybdenum, Mo |
| Appearance | gray metallic |

Molybdenum in the periodic table

| | |
|---|--------------------------------------|
| Atomic number (<i>Z</i>) | 42 |
| Group, block | group 6, d-block |
| Period | period 5 |
| Element category | ▣ transition metal |
| Standard atomic weight (\pm) (<i>A</i> _r) | 95.95(1) ^[1] |
| Electron configuration | [Kr] 4d ⁵ 5s ¹ |
| per shell | 2, 8, 18, 13, 1 |

Physical properties

| | |
|--------------------------|---------------------------|
| Phase | solid |
| Melting point | 2896 K (2623 °C, 4753 °F) |
| Boiling point | 4912 K (4639 °C, 8382 °F) |
| Density near r.t. | 10.28 g/cm ³ |
| when liquid, at m.p. | 9.33 g/cm ³ |

Physical properties

In its pure form, molybdenum is a silvery-grey metal with a Mohs hardness of 5.5. It has a melting point of 2,623 °C (4,753 °F); of the naturally occurring elements, only tantalum, osmium, rhenium, tungsten, and carbon have higher melting points.^[5] Weak oxidation of molybdenum starts at 300 °C (572 °F). It has one of the lowest coefficients of thermal expansion among commercially used metals.^[6] The tensile strength of molybdenum wires increases about 3 times, from about 10 to 30 GPa, when their diameter decreases from ~50–100 nm to 10 nm.^[7]

Isotopes

There are 35 known isotopes of molybdenum, ranging in atomic mass from 83 to 117, as well as four metastable nuclear isomers. Seven isotopes occur naturally, with atomic masses of 92, 94, 95, 96, 97, 98, and 100. Of these naturally occurring isotopes, only molybdenum-100 is unstable.^[8]

Molybdenum-98 is the most abundant isotope, comprising 24.14% of all molybdenum. Molybdenum-100 has a half-life of about 10¹⁹ y and undergoes double beta decay into ruthenium-100. Molybdenum isotopes with mass numbers from 111 to 117 all have half-lives of approximately 150 ns.^{[8][9]} All unstable isotopes of molybdenum decay into isotopes of niobium, technetium, and ruthenium.^[9]

As also noted below, the most common isotopic molybdenum application involves molybdenum-99, which is a fission product. It is a parent radioisotope to the short-lived gamma-emitting daughter radioisotope technetium-99m, a nuclear isomer used in various imaging applications in medicine.^[10] In 2008, the Delft University of Technology applied for a patent on the molybdenum-98-based production of molybdenum-99.^[11]

Compounds and chemistry

| | |
|-----------------------------|-----------------|
| Heat of fusion | 37.48 kJ/mol |
| Heat of vaporization | 598 kJ/mol |
| Molar heat capacity | 24.06 J/(mol·K) |

Vapor pressure

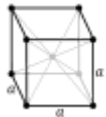
| P (Pa) | 1 | 10 | 100 | 1 k | 10 k | 100 k |
|----------|------|------|------|------|------|-------|
| at T (K) | 2742 | 2994 | 3312 | 3707 | 4212 | 4879 |

Atomic properties

| | |
|----------------------------|--|
| Oxidation states | 6, 5, 4, 3, 2, 1, ^[2] −1, −2, −4 (a strongly acidic oxide) |
| Electronegativity | Pauling scale: 2.16 |
| Ionization energies | 1st: 684.3 kJ/mol 2nd: 1560 kJ/mol 3rd: 2618 kJ/mol |
| Atomic radius | empirical: 139 pm |
| Covalent radius | 154±5 pm |

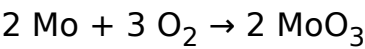
Miscellanea

| | |
|--------------------------|---------------------------|
| Crystal structure | body-centered cubic (bcc) |
|--------------------------|---------------------------|



| | |
|-----------------------------------|---|
| Speed of sound thin rod | 5400 m/s (at r.t.) |
| Thermal expansion | 4.8 μm/(m·K) (at 25 °C) |
| Thermal conductivity | 138 W/(m·K) |
| Thermal diffusivity | 54.3 mm ² /s (at 300 K) ^[3] |
| Electrical resistivity | 53.4 nΩ·m (at 20 °C) |
| Magnetic ordering | paramagnetic ^[4] |

Molybdenum is a transition metal with an electronegativity of 2.16 on the Pauling scale and a standard atomic weight of 95.95 g/mol.^{[13][14]} It does not visibly react with oxygen or water at room temperature, and the bulk oxidation occurs at temperatures above 600 °C, resulting in molybdenum trioxide:



The trioxide is volatile and sublimates at high temperatures. This prevents formation of a continuous protective (passivating) oxide layer, which would stop the bulk oxidation of metal.^[15] Molybdenum has several oxidation states, the most stable being +4 and +6 (bolded in the table at left). The chemistry and the compounds show more similarity to tungsten than to chromium; the instability of molybdenum(III) and tungsten(III) compounds, for example, contrasts with the stability of the chromium(III) compounds. The highest oxidation state is seen in molybdenum(VI) oxide (MoO₃), while the normal sulfur compound is molybdenum disulfide MoS₂.^[16]

Molybdenum(VI) oxide is soluble in strong alkaline water, forming molybdates (MoO₄^{2−}). Molybdates are weaker oxidants than chromates, but they show a similar tendency to form complex oxyanions by condensation at lower pH values, such as [Mo₇O₂₄]^{6−} and [Mo₈O₂₆]^{4−}. Polymolybdates can incorporate other ions, forming polyoxometalates.^[17] The dark-blue phosphorus-containing heteropolymolybdate P[Mo₁₂O₄₀]^{3−} is used for the spectroscopic detection of phosphorus.^[18] The broad range of oxidation states of molybdenum is reflected in various molybdenum chlorides:^[16]

- Molybdenum(II) chloride MoCl₂ (yellow solid)
- Molybdenum(III) chloride MoCl₃ (dark red solid)
- Molybdenum(IV) chloride MoCl₄ (black solid)
- Molybdenum(V) chloride MoCl₅ (dark green solid)
- Molybdenum(VI) chloride MoCl₆ (brown solid)

The structure of the MoCl₂ is clusters of Mo₆Cl₈⁴⁺ and four chloride ions compensating the charge.^[16]

| Young's modulus | 329 GPa | | | | |
|---|-----------------------------|----------------------------|-------------------------------|------------------------|-------------------|
| Shear modulus | 126 GPa | | | | |
| Bulk modulus | 230 GPa | | | | |
| Poisson ratio | 0.31 | | | | |
| Mohs hardness | 5.5 | | | | |
| Vickers hardness | 1400–2740 MPa | | | | |
| Brinell hardness | 1370–2500 MPa | | | | |
| CAS Number | 7439-98-7 | | | | |
| History | | | | | |
| Discovery | Carl Wilhelm Scheele (1778) | | | | |
| First isolation | Peter Jacob Hjelm (1781) | | | | |
| Most stable isotopes of molybdenum | | | | | |
| iso | NA | half-life | DM | DE (MeV) | DP |
| 92Mo | 14.65% | is stable with 50 neutrons | | | |
| 93Mo | syn | 4×10 ³ y | ε | – | ⁹³ Nb |
| 94Mo | 9.19% | is stable with 52 neutrons | | | |
| 95Mo | 15.87% | is stable with 53 neutrons | | | |
| 96Mo | 16.67% | is stable with 54 neutrons | | | |
| 97Mo | 9.58% | is stable with 55 neutrons | | | |
| 98Mo | 24.29% | is stable with 56 neutrons | | | |
| 99Mo | syn | 65.94 h | β [−] | 0.436, 1.214 | ^{99m} Tc |
| | | | γ | 0.74, 0.36, 0.14 | – |
| 100Mo | 9.74% | 7.8×10 ¹⁸ y | β [−] β [−] | 3.04 | ¹⁰⁰ Ru |

Like chromium and some other transition metals, molybdenum forms quadruple bonds, such as in $\text{Mo}_2(\text{CH}_3\text{COO})_4$. This compound can be transformed into $\text{Mo}_2\text{Cl}_8^{4-}$, which also has a quadruple bond.^[16]

The oxidation state 0 is possible with carbon monoxide as ligand, such as in molybdenum hexacarbonyl, $\text{Mo}(\text{CO})_6$.^[16]

External links

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