Mendelevium

Mendelevium is a synthetic element with chemical symbol Md (formerly Mv) and atomic number 101 . A metallic radioactive transuranic element in the actinide series , it is the first element that currently cannot be produced in macroscopic quantities through neutron bombardment of lighter elements . It is the antepenultimate actinide and the ninth transuranic element . It can only be produced in particle accelerators by bombarding lighter elements with charged particles . A total of sixteen mendelevium isotopes are known , the most stable being 258Md with a half @-@ life of 51 days ; nevertheless , the shorter @-@ lived 256Md (half @-@ life 1 @.@ 27 hours) is most commonly used in chemistry because it can be produced on a larger scale .

Mendelevium was discovered by bombarding einsteinium with alpha particles in 1955 , the same method still used to produce it today . It was named after Dmitri Mendeleev , father of the periodic table of the chemical elements . Using available microgram quantities of the isotope einsteinium @-@ 253 , over a million mendelevium atoms may be produced each hour . The chemistry of mendelevium is typical for the late actinides , with a preponderance of the + 3 oxidation state but also an accessible + 2 oxidation state . Owing to the small amounts of produced mendelevium and all of its isotopes having relatively short half @-@ lives , there are currently no uses for it outside of basic scientific research .

Discovery

Mendelevium was the ninth transuranic element to be synthesized . It was first synthesized by Albert Ghiorso , Glenn T. Seaborg , Gregory R. Choppin , Bernard G. Harvey , and team leader Stanley G. Thompson in early 1955 at the University of California , Berkeley . The team produced 256Md (half @-@ life of 87 minutes) when they bombarded an 253Es target consisting of only a billion (109) einsteinium atoms with alpha particles (helium nuclei) in the Berkeley Radiation Laboratory 's 60 @-@ inch cyclotron , thus increasing the target 's atomic number by two . 256Md thus became the first isotope of any element to be synthesized one atom at a time . In total , seventeen mendelevium atoms were produced . This discovery was part of a program , begun in 1952 , that irradiated plutonium with neutrons to transmute it into heavier actinides . This method was necessary as the previous method used to synthesize transuranic elements , neutron capture , could not work because of a lack of beta decaying isotopes of fermium that would produce isotopes of the next element , mendelevium , and also due to the very short half @-@ life to spontaneous fission of fermium @-@ 258 that thus constituted a hard limit to the success of the neutron capture process .

To predict if the production of mendelevium would be possible , the team made use of a rough calculation . The number of atoms that would be produced would be approximately equal to the product of the number of atoms of target material , the target 's cross section , the ion beam intensity , and the time of bombardment ; this last factor was related to the half @-@ life of the product when bombarding for a time on the order of its half @-@ life . This gave one atom per experiment . Thus under optimum conditions , the preparation of only one atom of element 101 per experiment could be expected . This calculation demonstrated that it was feasible to go ahead with the experiment . The target material , einsteinium @-@ 253 , could be produced readily from irradiating plutonium : one year of irradiation would give a billion atoms , and its three @-@ week half @-@ life meant that the element 101 experiments could be conducted in one week after the produced einsteinium was separated and purified to make the target . However , it was necessary to upgrade the cyclotron to obtain the needed intensity of 1014 alpha particles per second ; Seaborg applied for the necessary funds .

While Seaborg applied for funding , Harvey worked on the einsteinium target , while Thomson and Choppin focused on methods for chemical isolation . Choppin suggested using ? @-@ hydroxyisobutyric acid to separate the mendelevium atoms from those of the lighter actinides . The actual synthesis was done by a recoil technique , introduced by Albert Ghiorso . In this technique , the einsteinium was placed on the opposite side of the target from the beam , so that the recoiling mendelevium atoms would get enough momentum to leave the target and be caught on a catcher foil made of gold . This recoil target was made by an electroplating technique , developed by Alfred Chetham @-@ Strode . This technique gave a very high yield , which was absolutely necessary when working with such a rare and valuable product as the einsteinium target material . The recoil target consisted of 109 atoms of 253Es which were deposited electrolytically on a thin gold foil . It was bombarded by 41 MeV alpha particles in the Berkeley cyclotron with a very high beam density of 6 × 1013 particles per second over an area of 0 @.@ 05 cm2 . The target was cooled by water or liquid helium , and the foil could be replaced .

Initial experiments were carried out in September 1954 . No alpha decay was seen from mendelevium atoms ; thus , Ghiorso suggested that the mendelevium had all decayed by electron capture to fermium and that the experiment should be repeated to search instead for spontaneous fission events . The repetition of the experiment happened in February 1955 .

On the day of discovery , 19 February , alpha irradiation of the einsteinium target occurred in three three @-@ hour sessions . The cyclotron was in the University of California campus , while the Radiation Laboratory was on the next hill . To deal with this situation , a complex procedure was used : Ghiorso took the catcher foils (there were three targets and three foils) from the cyclotron to Harvey , who would use aqua regia to dissolve it and pass it through an anion @-@ exchange resin column to separate out the transuranium elements from the gold and other products . The resultant drops entered a test tube , which Choppin and Ghiorso took in a car to get to the Radiation Laboratory as soon as possible . There Thompson and Choppin used a cation @-@ exchange resin column and the ? @-@ hydroxyisobutyric acid . The solution drops were collected on platinum disks and dried under heat lamps . The three disks were expected to contain respectively the fermium , no new elements , and the mendelevium . Finally , they were placed in their own counters , which were connected to recorders such that spontaneous fission events would be recorded as huge deflections in a graph showing the number and time of the decays . There thus was no direct detection , but by observation of spontaneous fission events arising from its electron @-@ capture daughter 256Fm . The first one was identified with a " hooray " followed by a " double hooray " and a " triple hooray " . The fourth one eventually officially proved the chemical identification of the 101st element , mendelevium . In total , five decays were reported up till 4 a.m. Seaborg was notified and the team left to sleep . Additional analysis and further experimentation showed the produced mendelevium isotope to have mass 256 and to decay by electron capture to fermium @-@ 256 with a half @-@ life of 1 @.@ 5 h .

We thought it fitting that there be an element named for the Russian chemist Dmitri Mendeleev , who had developed the periodic table . In nearly all our experiments discovering transuranium elements , we 'd depended on his method of predicting chemical properties based on the element 's position in the table . But in the middle of the Cold War , naming an element for a Russian was a somewhat bold gesture that did not sit well with some American critics .

Being the first of the second hundred of the chemical elements , it was decided that the element would be named " mendelevium " after the Russian chemist Dmitri Mendeleev , father of the periodic table . Due to the fact that this discovery came during the Cold War , Seaborg had to request permission of the government of the United States to propose that the element be named for a Russian , but it was granted . The name " mendelevium " was accepted by the International Union of Pure and Applied Chemistry (IUPAC) in 1955 with symbol " Mv " , which was changed to " Md " in the next IUPAC General Assembly (Paris , 1957) .

= = Characteristics = =

= = = Physical = = =

In the periodic table , mendelevium is located to the right of the actinide fermium , to the left of the actinide nobelium , and below the lanthanide thulium . Mendelevium metal has not yet been prepared in bulk quantities , and bulk preparation is currently impossible . Nevertheless , a number

of predictions and some preliminary experimental results have been done regarding its properties .
The lanthanides and actinides , in the metallic state , can exist as either divalent (such as europium and ytterbium) or trivalent (most other lanthanides) metals . The former have fnd1s2 configurations , whereas the latter have fn + 1s2 configurations . In 1975 , Johansson and Rosengren examined the measured and predicted values for the cohesive energies (enthalpies of crystallization) of the metallic lanthanides and actinides , both as divalent and trivalent metals . The conclusion was that the increased binding energy of the [Rn] 5f126d17s2 configuration over the [Rn] 5f137s2 configuration for mendelevium was not enough to compensate for the energy needed to promote one 5f electron to 6d , as is true also for the very late actinides : thus einsteinium , fermium , mendelevium , and nobelium were expected to be divalent metals . The increasing predominance of the divalent state well before the actinide series concludes is attributed to the relativistic stabilization of the 5f electrons , which increases with increasing atomic number . Thermochromatographic studies with trace quantities of mendelevium by Zvara and Hübener from 1976 to 1982 confirmed this prediction . In 1990 , Haire and Gibson estimated mendelevium metal to have an enthalpy of sublimation between 134 and 142 kJ · mol ? 1 . Divalent mendelevium metal should have a metallic radius of around (194 ± 10) pm . Like the other divalent late actinides (except the once again trivalent lawrencium) , metallic mendelevium should assume a face @-@ centered cubic crystal structure . Mendelevium 's melting point has been estimated at 827 ° C , the same value as that predicted for the neighboring element nobelium . Its density is predicted to be around 10 @.@ 3 ± 0 @.@ 7 g · cm ? 3 .

= = = Chemical = = =

The chemistry of mendelevium is mostly known only in solution , in which it can take on the + 3 or + 2 oxidation states . The + 1 state has also been reported , but has not yet been confirmed .
Before mendelevium 's discovery , Seaborg and Katz predicted that it should be predominantly trivalent in aqueous solution and hence should behave similarly to other tripositive lanthanides and actinides . After the synthesis of mendelevium in 1955 , these predictions were confirmed , first in the observation at its discovery that it eluted just after fermium in the trivalent actinide elution sequence from a cation @-@ exchange column of resin , and later the 1967 observation that mendelevium could form insoluble hydroxides and fluorides that coprecipitated with trivalent lanthanide salts . Cation @-@ exchange and solvent extraction studies led to the conclusion that mendelevium was a trivalent actinide with an ionic radius somewhat smaller than that of the previous actinide , fermium . Mendelevium can form coordination complexes with 1 @,@ 2 @-@ cyclohexanedinitrilotetraacetic acid (DCTA) .
In reducing conditions , mendelevium (III) can be easily reduced to mendelevium (II) , which is stable in aqueous solution . The standard reduction potential of the E ° (Md3 + ? Md2 +) couple has been variously estimated as ? 0 @.@ 10 V or ? 0 @.@ 20 V. In comparison , E ° (Md3 + ? Md0) should be around ? 1 @.@ 74 V , and E ° (Md2 + ? Md0) should be around ? 2 @.@ 5 V. Mendelevium (II) ' s elution behavior has been compared with that of strontium (II) and europium (II) .
In 1973 , mendelevium (I) was reported to have been produced by Russian scientists , who obtained it by reducing higher oxidation states of mendelevium with samarium (II) . It was found to be stable in neutral water ? ethanol solution and be homologous to caesium (I) . However , later experiments found no evidence for mendelevium (I) and found that mendelevium behaved like divalent elements when reduced , not like the monovalent alkali metals . Nevertheless , the Russian team conducted further studies on the thermodynamics of cocrystallizing mendelevium with alkali metal chlorides , and concluded that mendelevium (I) had formed and could form mixed crystals with divalent elements , thus cocrystallizing with them . The status of the + 1 oxidation state is still tentative .
Although E ° (Md4 + ? Md3 +) was predicted in 1975 to be + 5 @.@ 4 V , suggesting that mendelevium (III) could be easily oxidized to mendelevium (IV) , 1967 experiments with the strong oxidizing agent sodium bismuthate were unable to oxidize mendelevium (III) to

mendelevium (IV) .

= = = Atomic = = =

A mendelevium atom has 101 electrons , of which at least three (and perhaps four) can act as valence electrons . They are expected to be arranged in the configuration [Rn] 5f137s2 (ground state term symbol 2F7 / 2) , although experimental verification of this electron configuration had not yet been made as of 2006 . In forming compounds , three valence electrons may be lost , leaving behind a [Rn] 5f12 core : this conforms to the trend set by the other actinides with their [Rn] 5fn electron configurations in the tripositive state . The first ionization potential of mendelevium was measured to be at most (6 @.@ 58 ± 0 @.@ 07) eV in 1974 , based on the assumption that the 7s electrons would ionize before the 5f ones ; this value has since not yet been refined further due to mendelevium 's scarcity and high radioactivity . The ionic radius of hexacoordinate Md3 + had been preliminarily estimated in 1978 to be around 91 @.@ 2 pm ; 1988 calculations based on the logarithmic trend between distribution coefficients and ionic radius produced a value of 89 @.@ 6 pm , as well as an enthalpy of hydration of ? (3654 ± 12) kJ · mol ? 1 . Md2 + should have an ionic radius of 115 pm and hydration enthalpy ? 1413 kJ · mol ? 1 ; Md + should have ionic radius 117 pm .

= = = Isotopes = = =

Sixteen isotopes of mendelevium are known , with mass numbers from 245 to 260 ; all are radioactive . Additionally , five nuclear isomers are known : 245mMd , 247mMd , 249mMd , 254mMd , and 258mMd . Of these , the longest @-@ lived isotope is 258Md with a half @-@ life of 51 @.@ 5 days , and the longest @-@ lived isomer is 258mMd with a half @-@ life of 58 @.@ 0 minutes . Nevertheless , the slightly shorter @-@ lived 256Md (half @-@ life 1 @.@ 27 hours) is more often used in chemical experimentation because it can be produced in larger quantities from alpha particle irradiation of einsteinium . After 258Md , the next most stable mendelevium isotopes are 260Md with a half @-@ life of 31 @.@ 8 days , 257Md with a half @-@ life of 5 @.@ 52 hours , 259Md with a half @-@ life of 1 @.@ 60 hours , and 256Md with a half @-@ life of 1 @.@ 27 hours . All of the remaining mendelevium isotopes have half @-@ lives that are less than an hour , and the majority of these have half @-@ lives that are less than 5 minutes .

The half @-@ lives of mendelevium isotopes mostly increase smoothly from 245Md onwards , reaching a maximum at 258Md . Experiments and predictions suggest that the half @-@ lives will then decrease , apart from 260Md with a half @-@ life of 31 @.@ 8 days , as spontaneous fission becomes the dominant decay mode due to the mutual repulsion of the protons posing a limit to the island of relative stability of long @-@ lived nuclei in the actinide series .

Mendelevium @-@ 256 , the chemically most important isotope of mendelevium , decays through electron capture 90 @.@ 7 % of the time and alpha decay 9 @.@ 9 % of the time . It is most easily detected through the spontaneous fission of its electron @-@ capture daughter fermium @-@ 256 , but in the presence of other nuclides that undergo spontaneous fission , alpha decays at the characteristic energies for mendelevium @-@ 256 (7 @.@ 205 and 7 @.@ 139 MeV) can provide more useful identification .

= = Production and isolation = =

The lightest mendelevium isotopes (245Md to 247Md) are mostly produced through bombardment of bismuth targets with heavy argon ions , while slightly heavier ones (248Md to 253Md) are produced by bombarding plutonium and americium targets with lighter ions of carbon and nitrogen . The most important and most stable isotopes are in the range from 254Md to 258Md and are produced through bombardment of einsteinium isotopes with alpha particles : einsteinium @-@ 253 , -254 , and -255 can all be used . 259Md is produced as a daughter of 259No , and 260Md can be produced in a transfer reaction between einsteinium @-@ 254 and oxygen @-@ 18 . Typically , the most commonly used isotope 256Md is produced by bombarding either einsteinium @-@ 253 or -254 with alpha particles : einsteinium @-@ 254 is preferred when available because it has a longer half @-@ life and therefore can be used as a target for longer . Using available microgram quantities of einsteinium , femtogram quantities of mendelevium @-@ 256 may be produced .

The recoil momentum of the produced mendelevium @-@ 256 atoms is used to bring them physically far away from the einsteinium target from which they are produced , bringing them onto a thin foil of metal (usually beryllium , aluminium , platinum , or gold) just behind the target in a vacuum . This eliminates the need for immediate chemical separation , which is both costly and prevents reusing of the expensive einsteinium target . The mendelevium atoms are then trapped in a gas atmosphere (frequently helium) , and a gas jet from a small opening in the reaction chamber carries the mendelevium along . Using a long capillary tube , and including potassium chloride aerosols in the helium gas , the mendelevium atoms can be transported over tens of meters to be chemically analyzed and have their quantity determined . The mendelevium can then be separated from the foil material and other fission products by applying acid to the foil and then coprecipitating the mendelevium with lanthanum fluoride , then using a cation @-@ exchange resin column with a 10 % ethanol solution saturated with hydrochloric acid , acting as an eluant . However , if the foil is made of gold and thin enough , it is enough to simply dissolve the gold in aqua regia before separating the trivalent actinides from the gold using anion @-@ exchange chromatography , the eluant being 6 M hydrochloric acid .

Mendelevium can finally be separated from the other trivalent actinides using selective elution from a cation @-@ exchange resin column , the eluant being ammonia ? @-@ HIB . Using the gas @-@ jet method often renders the first two steps unnecessary . The above procedure is the most commonly used one for the separation of transeinsteinium elements .

Another possible way to separate the trivalent actinides is via solvent extraction chromatography using bis- (2 @-@ ethylhexyl) phosphoric acid (abbreviated as HDEHP) as the stationary organic phase and nitric acid as the mobile aqueous phase . The actinide elution sequence is reversed from that of the cation @-@ exchange resin column , so that the heavier actinides elute later . The mendelevium separated by this method has the advantage of being free of organic complexing agent compared to the resin column ; the disadvantage is that mendelevium then elutes very late in the elution sequence , after fermium .

Another method to isolate mendelevium exploits the distinct elution properties of Md2 + from those of Es3 + and Fm3 + . The initial steps are the same as above , and employs HDEHP for extraction chromatography , but coprecipitates the mendelevium with terbium fluoride instead of lanthanum fluoride . Then , 50 mg of chromium is added to the mendelevium to reduce it to the + 2 state in 0 @.@ 1 M hydrochloric acid with zinc or mercury . The solvent extraction then proceeds , and while the trivalent and tetravalent lanthanides and actinides remain on the column , mendelevium (II) does not and stays in the hydrochloric acid . It is then reoxidized to the + 3 state using hydrogen peroxide and then isolated by selective elution with 2 M hydrochloric acid (to remove impurities , including chromium) and finally 6 M hydrochloric acid (to remove the mendelevium) . It is also possible to use a column of cationite and zinc amalgam , using 1 M hydrochloric acid as an eluant , reducing Md (III) to Md (II) where it behaves like the alkaline earth metals . Thermochromatographic chemical isolation could be achieved using the volatile mendelevium hexafluoroacetylacetonate : the analogous fermium compound is also known and is also volatile .