

Dubnium

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Dubnium is a chemical element with symbol **Db** and atomic number 105. A transactinide element, dubnium is highly radioactive: the most stable known isotope, dubnium-268, has a half-life of just above a day. This greatly limits the extent of possible research on dubnium.

Dubnium does not occur naturally on Earth and is produced artificially. The first discovery of the element was claimed by the Soviet Joint Institute for Nuclear Research (JINR) in 1968, followed in 1970 by the American University of California. Both teams proposed a name for the new element, and used it without formal approval. The long-standing dispute was resolved in 1997, when the element was officially named *dubnium* after Dubna, the site of the JINR.

In the periodic table of the elements, dubnium is located in period 7, in d-block, thus being a transactinide element. Dubnium belongs to group 5 as the third member of the 6d series of transition metals. The limited investigation on chemistry of dubnium has demonstrated that behavior of dubnium is typical for group 5, and the element is established as the heavier homologue to tantalum in group 5; however, some deviations, particularly those from the periodic trends, occur due to relativistic effects.

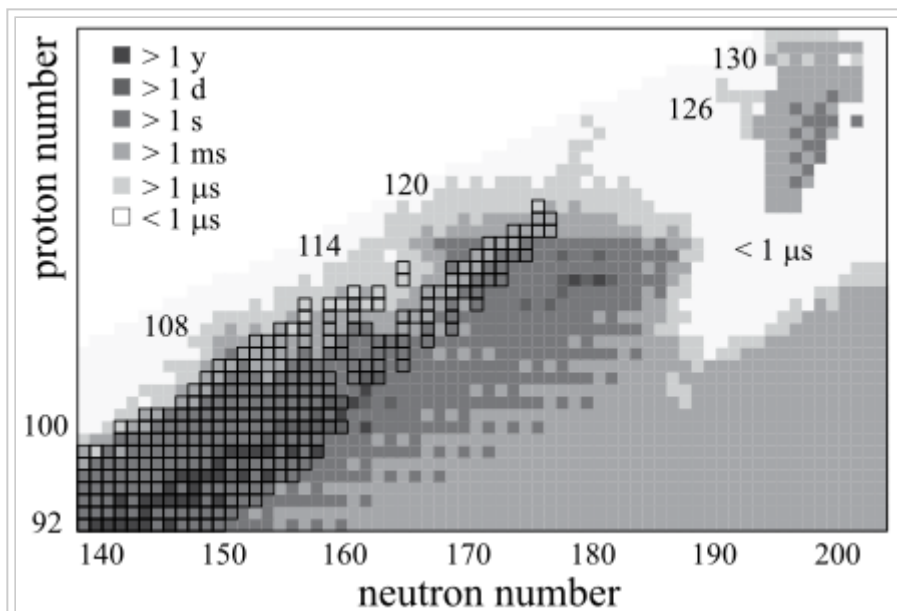
Isotopes

Dubnium, having atomic number 105, is a superheavy element, and as such is unstable. The most stable known isotope of dubnium, ²⁶⁸Db, has a half-life of around a day. Thus, even if it had once existed on Earth, it would have decayed completely long ago and can only be produced artificially.^[a]

The short half-live of dubnium limits the scope of experimentation. This is amplified by the neutron-to-proton ratio of the most stable isotopes of an element growing with the atomic number, a trend that is expected to continue to the superheavy elements;^[20] this complicates synthesis of the most stable isotopes as the isotopes in question will have more neutrons per proton than both the target and beam nuclei that could be employed. (Although a different technique based on rapid neutron capture is being

Dubnium, ¹⁰⁵Db

General properties	
Name, symbol	dubnium, Db
Dubnium in the periodic table	
Atomic number (<i>Z</i>)	105
Group, block	group 5, d-block
Period	period 7
Element category	 ▮ transition metal
Standard atomic weight (<i>A</i> _r)	[268]
Electron configuration	[Rn] 5f ¹⁴ 6d ³ 7s ² ^[1]
per shell	2, 8, 18, 32, 32, 11, 2
Physical properties	
Phase	solid <i>(predicted)</i> ^[2]
Density near r.t.	29.3 g/cm ³ <i>(predicted)</i> ^{[1][3]}
Atomic properties	
Oxidation states	5 , (4), (3) ^{[1][3]} (parenthesized oxidation states are predictions)
Ionization energies	1st: 656.1 kJ/mol 2nd: 1546.7 kJ/mol 3rd: 2378.4 kJ/mol



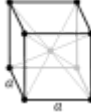
A chart of nuclide stability as used by the Dubna team in 2012. Characterized isotopes are shown with borders.^[17]

richness of nuclei with the increase in atomic number. Some of those isotopes have been produced since then with other fusion reactions. However, as research on superheavy nuclei moved on, the heaviest isotopes of dubnium were produced only indirectly, but rather as the daughters of heavier nuclei that would decay via consecutive alpha decays to dubnium.

The most stable isotope of dubnium is ^{268}Db . By 2016, only a few atoms were available each time, and thus the half-lives changed significantly during the process. During three experiments, 23 atoms were created in total, with a resulting half-life of 28^{+11}_{-4} hours.^[22] The second most stable isotope, ^{270}Db , has been produced in even smaller quantities: three atoms in total, with lifetimes of 33.4 h,^[23] 1.3 h, and 1.6 h.^[24] These two are the heaviest isotopes of dubnium to date, and both were produced as a result of decay of heavier nuclei rather than directly. The reason for is that the experiments that yielded were originally designed in Dubna for using ^{48}Ca beams.^[25]

considered,^[21] the ones based on collision of a big and a small nucleus dominate research in the area nowadays.)

The first nuclei of dubnium were produced by reactions of direct nuclear fusion, in which two nuclei fused into one, possibly emitting a few neutrons. These first nuclei were very unstable, lasting often less than a second. However, more stable isotopes of dubnium heavier than those first synthesized should exist, as the nuclear drip line moves towards greater relative neutron-

	(more) <i>(all but first estimated)</i> ^[1]
Atomic radius	empirical: 139 pm <i>(estimated)</i> ^[1]
Covalent radius	149 pm <i>(estimated)</i> ^[4]
Miscellanea	
Crystal structure	body-centered cubic (bcc) <i>(predicted)</i> ^[2]
	
CAS Number	53850-35-4
History	
Naming	after Dubna, Moscow Oblast, Russia, site of the Joint Institute for Nuclear Research
Discovery	independently by the University of California and the Joint Institute for Nuclear Research (1970)
Most stable isotopes of dubnium	

For its mass, ⁴⁸Ca has by far the greatest neutron excess of all practically stable nuclei, both quantitative and relative,^[26] which, correspondingly, helps synthesize superheavy nuclei with more neutrons.

While it yet remains to be seen if there are principally more stable isotopes, there has not any theoretical, let alone practical, suggestion this could be the case. In a 2012 calculation from Dubna, it was suggested that the half-lives of all dubnium isotopes, synthesized or not, did not actually significantly exceed a day.^{[17][b]}

Predicted properties

According to the periodic law, dubnium should belong to group 5, under vanadium, niobium, and tantalum. Several studies investigated the properties of element 105 and found a general agreement with the predictions from the periodic law. Significant deviations may nevertheless occur, due to relativistic effects, which dramatically change physical properties on both atomic and macroscopic scales. These properties have remained challenging to measure: only gas-phase studies have been performed on singular atoms, and generally prove the assignment of dubnium to the position under tantalum in the periodic table.

Atomic and physical

Relativistic effects arise when an object moves on velocities comparable to the speed of light. For example, as velocity of an object increases, so does its mass, which leads to decrease of the mean distance between the electron and the nucleus.

A direct relativistic effect is that as atomic numbers of elements increase, the innermost electrons begin to revolve faster around the nucleus as a result of the increase of the electromagnetic attraction between an electron and a nucleus. Similar effects have been found for s orbitals (and p_{1/2} ones, though this is not quite applicable for dubnium): for example, the 7s orbital is contracted by 25% in size and stabilized by 2.6 eV.^[1]

A more indirect effect would be that the contracted s and p_{1/2} orbitals shield (take on themselves) the charge of the nucleus more effectively, leaving even less for the outer d and f electrons, which therefore move on larger orbitals. Dubnium is greatly affected by this: unlike the previous group 5 members, its 7s electrons are more difficult to extract from an atom than the 6d electrons, though these energy levels remain close to each other.^[1]

iso	NA	half-life	DM	DE (MeV)	DP
262Db	syn	34 s ^{[5][6]}	67% α	8.66, 8.45	258Lr
			33% SF		
263Db	syn	27 s ^[6]	56% SF		
			41% α	8.36	259Lr
			3% ε		263mRf
266Db	syn	22 min ^[6]	SF		
			ε		266Rf
267Db	syn	1.2 h ^[6]	SF		
268Db	syn	29 h ^[6]	SF		
			ε		268Rf
270Db	syn	23.15 h ^[7]	17% SF		
			83% α		266Lr

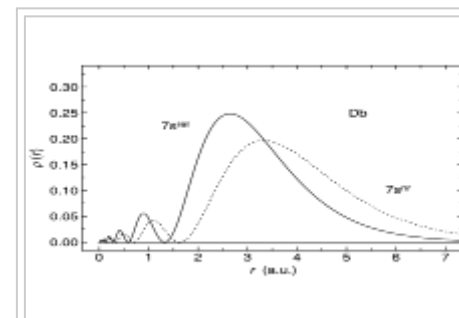
A third effect is the spin-orbit (SO) interaction, particularly, the SO splitting, which, in application to dubnium, splits the 6d subshell—the azimuthal quantum number ℓ for a d shell is 2—into two subshells, with four of the ten orbitals having its ℓ lowered to 3/2 and six raised to 5/2. While all ten energy levels are actually raised (lowered in absolute values), making them less stable energetically, four of them are more stable than the other six. (The three 6d electrons normally assume the energy levels of lowest energy, $6d_{3/2}$.)^[1]

While after a removal of a single electron from a neutral dubnium atom, the remaining valence electrons in a singly ionized ion (Db^+) should organize themselves in a $6d^2 7s^2$ configuration, the doubly (Db^{2+}) or triply (Db^{3+}) ionized atoms eliminate the 7s electrons: this is the opposite order to that of its lighter homologs. Despite the changes, however, dubnium is still expected to use five electrons as its valence electrons; 7p energy levels have not been shown to influence dubnium and its properties. As the 6d orbitals are further destabilized compared to 5d ones of tantalum, and Db^{3+} is expected to have two d, rather than s, electrons remaining, the resulting oxidation state is expected to be unstable and even rarer than that of tantalum. The ionization potential of dubnium in its maximum oxidation state should be slightly lower than that of tantalum and the ionic radius of dubnium should increase compared to tantalum; this has a significant effect on dubnium's chemistry (see below).^[1]

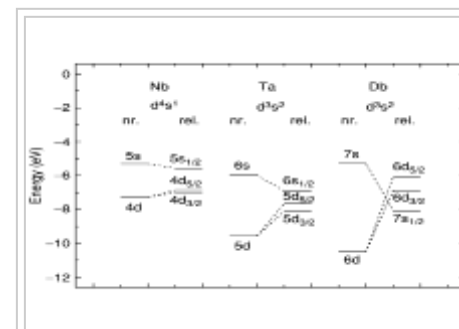
Dubnium atoms, when in quantity and in a free state, should arrange themselves in a body-centered cubic configuration, like the previous group 5 elements.^[2] The predicted density of dubnium is 29 g/cm^3 .^[1]

Chemical

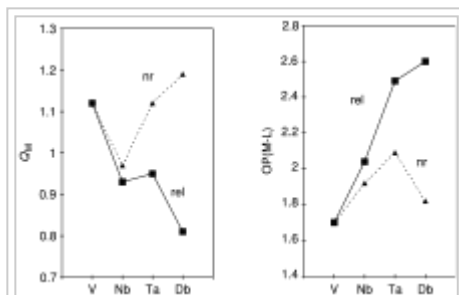
The simplest case for computational chemistry is the gas-phase chemistry, in which a substance is treated as if it was a gas to eliminate the necessity to take interactions between molecules in account. Research by multiple authors^[1] has been undertaken on the expected highest chloride of dubnium, DbCl_5 : it has been calculated to be consistent with the periodic laws by exhibiting properties of a compound of a d-block element, for example, the molecular orbital levels indicate dubnium uses three 6d electron levels, just as it would be expected. One property DbCl_5 is expected to show is its increased (compared to TaCl_5) covalence: a decrease in the effective charge on an atom and an increase in the overlap population (between orbitals of dubnium and chlorine).^[1]



Relativistic (solid line) and nonrelativistic (dashed line) radial distribution of the 7s valence electrons in dubnium.



Relativistic stabilization of the ns orbitals, the destabilization of the (n-1)d orbitals and their SO splitting for the group 5 elements.



Relativistic (rel) and nonrelativistic (nr) values of the effective charge (Q_M) and overlap population (OP) in MCl_5 , where $M = V, Nb, Ta$, and Db

Calculations for solution chemistry indicate that again, the maximum oxidation state, +5, will be more stable than that of niobium and tantalum, and the +3 state will be less stable than those of niobium and tantalum. Hydrolysis of cations of +5 is expected to continue to decrease within group 5; however, it is still expected to be quite rapid. Complexation of dubnium is expected to follow group 5 trends in its richness; calculations for hydroxo-chlorido- complexes have been conducted; they show reversal in the trend in the complex formation and extraction of group 5 elements, with dubnium being more prone to do so than tantalum.^[1]

Experimental chemistry

Early experimental results of studies of the chemistry of element 105 date back to 1974 and 1976. Dubna researchers used a thermochromatographic system, and concluded that the volatility of dubnium bromide was less than that of niobium bromide and about the same as that of hafnium bromide. It is not certain, however, that the detected fission products confirmed that the parent was indeed element 105. This may imply that the new element behaved more like

hafnium than niobium.^[1]

Further studies of the chemistry of element 105 were reported over a decade later, in 1988. Studies at Berkeley examined whether the most stable oxidation state of element 105 in aqueous solution is 5+. Sorption of element 105 on glass cover slips after fuming twice and washing with concentrated nitric acid, was compared with that of tracers of the group 5 elements niobium and tantalum and the group 4 elements zirconium and hafnium produced on-line under similar conditions. The group 5 elements are known to sorb on glass surfaces while the group 4 elements do not. Element 105 was confirmed as a group 5 member. However, it was surprising that extraction behavior into methyl isobutyl ketone from mixed HNO_3/HF solutions differed between element 105, tantalum, and niobium. Element 105 did not extract and its behavior resembled niobium more closely than tantalum, indicating that details of complexing behavior cannot be predicted based only on simple extrapolations of trends within a group in the periodic table.^[1]

This prompted further exploration of the chemical behavior of complexes of element 105. Thousand of repetitive chromatographic experiments were performed jointly in various labs in the period 1988–93. All group 5 elements and protactinium were extracted from concentrated hydrochloric acid; at lower concentrations of HCl , small amounts of HF were added to start selective re-extraction. Element 105 showed a behavior unlike tantalum at concentrations of HCl below 12 M, following the behavior of niobium and the pseudohomolog protactinium. Because of this similarity to these two elements, the research suggested that the formed complex was either $DbOX_4^-$ or $[Db(OH)_2X_4]^-$. After extraction experiments of Db from HBr into diisobutyl carbinol, a specific extractant for protactinium, with subsequent elutions with mixed HCl/HF and HCl , the obtained extraction sequence $Pa > Nb > Db$ was determined. It was explained as an increasing tendency to form non-extractable complexes of multiple negative charges. Further experiments in 1992 confirmed the stability of the +5 state: $Db(V)$ was shown to

be extractable from cation-exchange columns with α -hydroxyisobutyrate, similarly to other group 5 elements and protactinium; Db(III) and Db(IV) were not. In 1998 and 1999, new predictions yielded the sequence $\text{Pa} \gg \text{Nb} \geq \text{Db} > \text{Ta}$ for extraction from halide solutions, which was later confirmed.^[1]

The first isothermal gas chromatography experiments were performed in 1992 with ^{262}Db ($t_{1/2} = 35$ s). The volatilities for niobium and tantalum were similar within error limits, but dubnium appeared to be significantly less volatile. It was postulated that traces of oxygen in the system might have led to formation of DbOBr_3 , which was predicted to be less volatile than DbBr_5 . Later experiments in 1996 showed that group 5 chlorides were more volatile than the corresponding bromides, with the exception of tantalum, presumably due to formation of TaOCl_3). Later volatility studies of chlorides of dubnium and niobium as a function of controlled partial pressures of oxygen, showed that formation of oxychlorides and general volatility are dependent on concentrations of oxygen. The oxychlorides were shown to be less volatile than the chlorides.^[1]

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