Uranium

CHEM-E4130 - Chemistry of the Elements

Aalto-yliopisto
Kemian tekniikan
korkeakoulu

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General information

General information

- Discovered in 1789 by Martin Heinirch Klaproth
- Named after the then recently discovered planet Uranus
- Radioactive properties discovered in 1896
- Silvery-grey and weakly radioactive metal when refined
- Highest atomic weight of the primordially occurring elements
- Nuclear power and military applications [1]


[2]

[1] https://en.wikipedia.org/wiki/Uranium
[2] https://commons.wikimedia.org/wiki/File:Autunite_1(France).jpg

Chemistry of uranium

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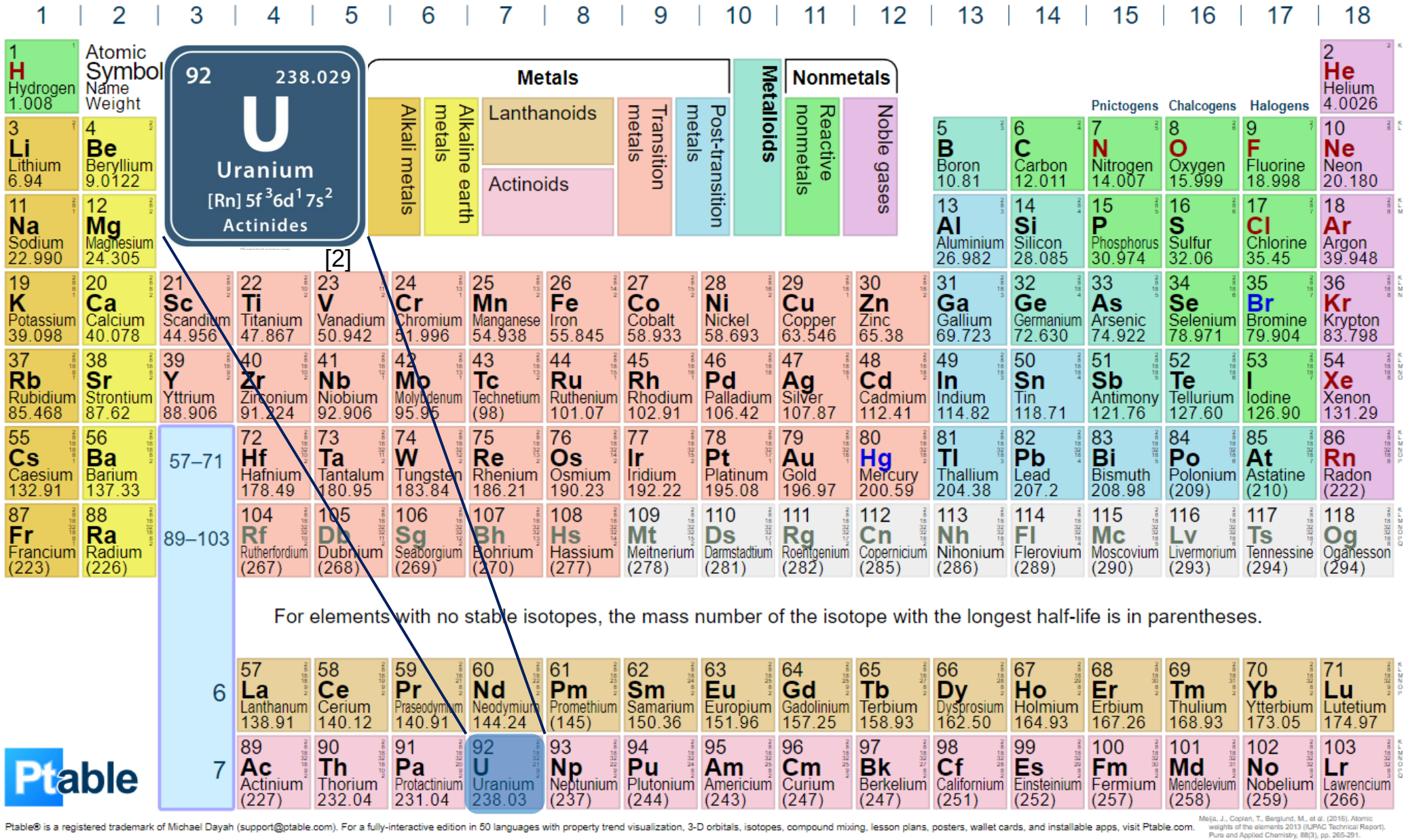
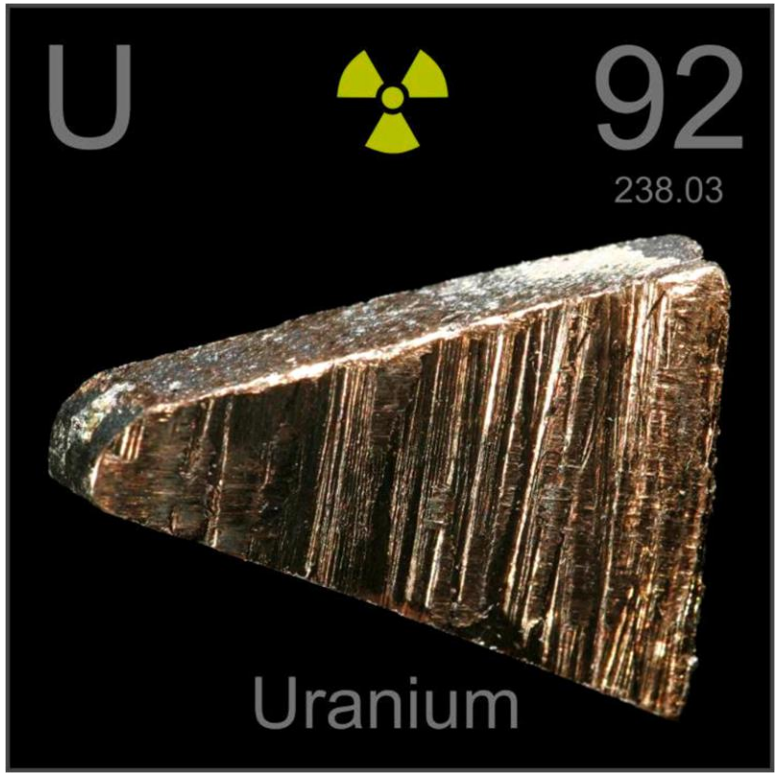


[3]

[3] https://ptable.com/image/periodic-table.svg
[4] https://www.chemistrylearner.com/uranium.html

General information



[3]

Properties of Uranium	
Atomic number	92
Atomic mass	238.029
Group	-
Period	7
Block	f-block
Electronic configuration	[Rn] $7s^2$ $5f^3$ $6d^1$
Melting point	1132.2 ℃
Boiling point	4131 ℃
At RT	Solid
Crystal stucture	Orthorombic (Cmcm)

[1,5]

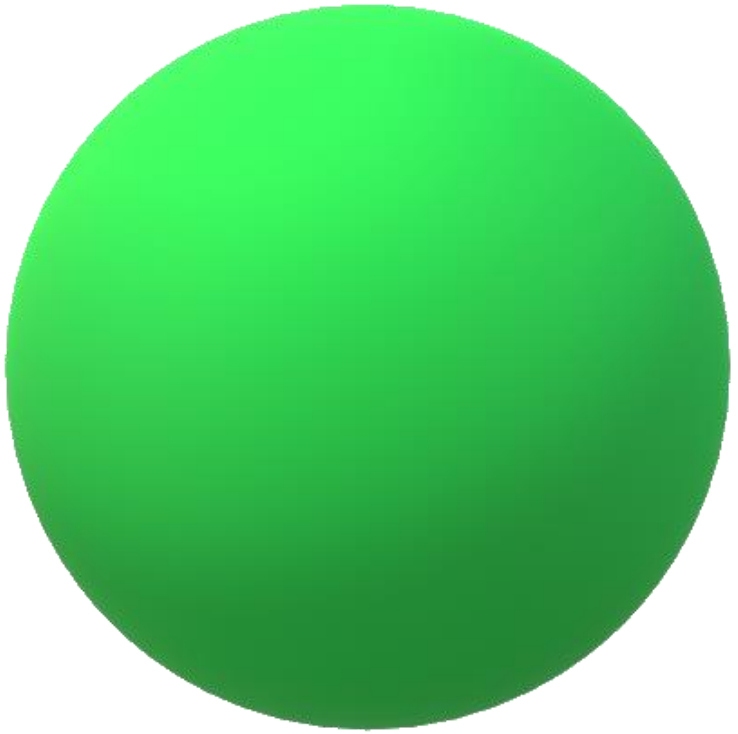
[1] https://en.wikipedia.org/wiki/Uranium
[5] https://www.chemistrylearner.com/uranium.html
[6] https://periodictable.com/Elements/092/index.html

Chemistry of uranium

- **Oxidation states: +VI,** V**,** IV**,** III
- **Isotopes: all of them are radioactive:**
  - Most common ^{238}U (99.3 %)
  - Others: ^{235}U, ^{234}U

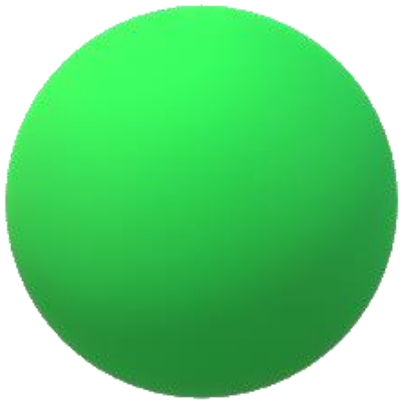
[1,7]

U 156 pm



or U 156-175 pm

U^{6+} 73 pm

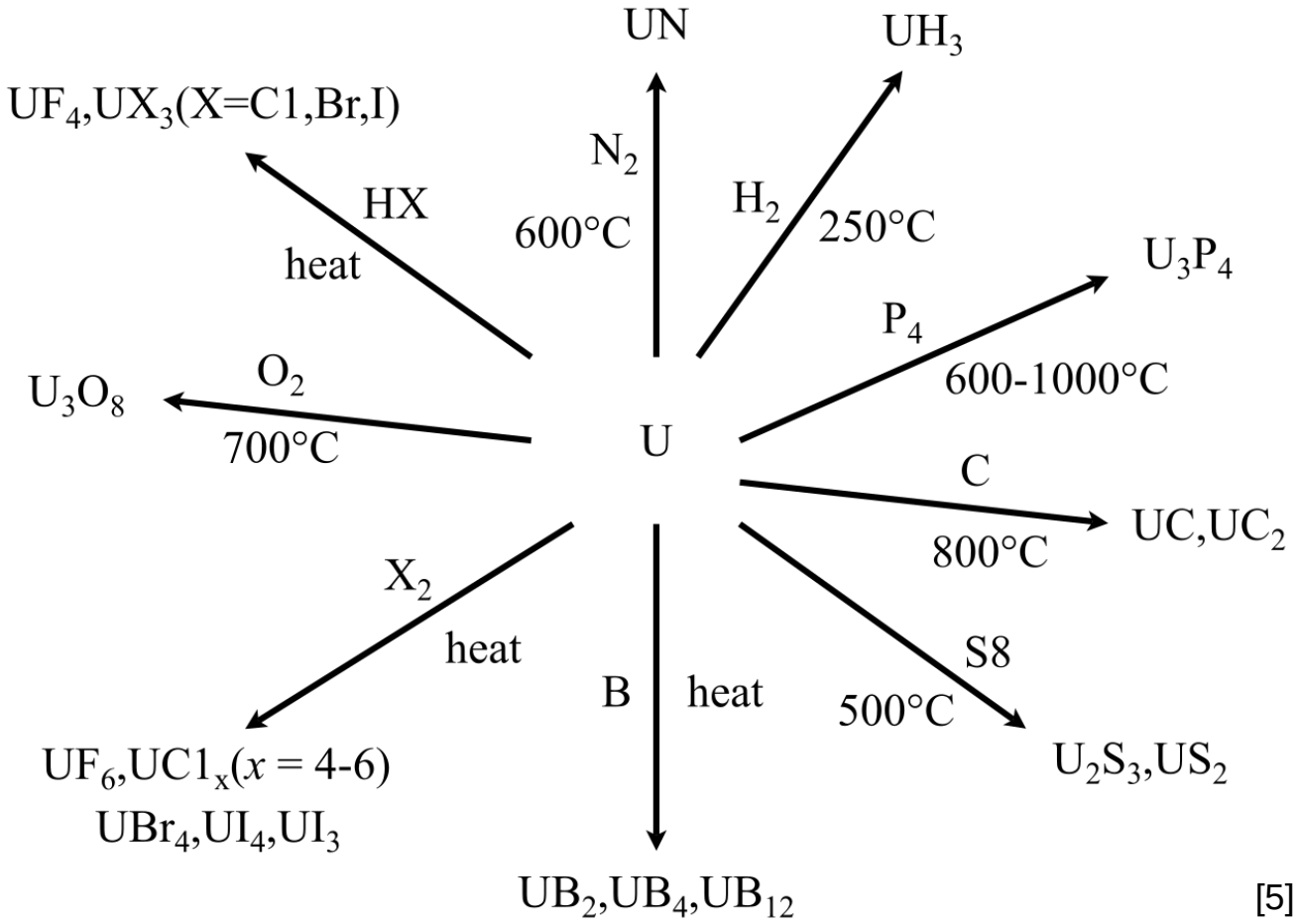


or U^{6+} 45-86 pm

[1] https://en.wikipedia.org/wiki/Uranium
[7] http://abulafia.mt.ic.ac.uk/shannon/radius.php?Element=U

Reactivity of uranium

Electron configuration [Rn] $7s^2$ $5f^3$ $6d^1$ → +VI preferred oxidation state



[5]

Uranium compounds

Examples of uranium compounds

- **Uranium forms several oxides [8, 11]**
  - Uranium dioxide UO_2 (reactor fuel)
  - Diuranium pentoxide U_2O_5
  - Uranium trioxide UO_3
  - Triuranium octoxide U_3O_8 (most stable)
  - Uranyl peroxide UO_4

- **Uranium carbides [9]**
  - Uranium methanide UC
  - Uranium sesquicarbide U_2C_3
  - Uranium acetylide UC_2

- **Uranium tetrachloride UCl_4 [10]**

[8] https://en.wikipedia.org/wiki/Uranium_oxide
[9] https://en.wikipedia.org/wiki/Uranium_carbide
[10] https://en.wikipedia.org/wiki/Uranium_tetrachloride
[11] "The Actinide and Transactinide Elements (Z = 90–103 and 104–112)", Chemistry of the Elements, Elsevier, 1997, P. 1250-1284. DOI: 10.1016/B978-0-7506-3365-9.50037-7

Tiruranium octoxodie U_3O_8

- **Most stable uranium oxide**
- **Olive green to black solid, odorless [11]**
- **”Yellowcake” uranium concentrate powder contains around 70% - 90% U_3O_8 by weight**
- **Coarse powder that has a pungent odor**
- **Intermediate step in processing uranium ores [12]**

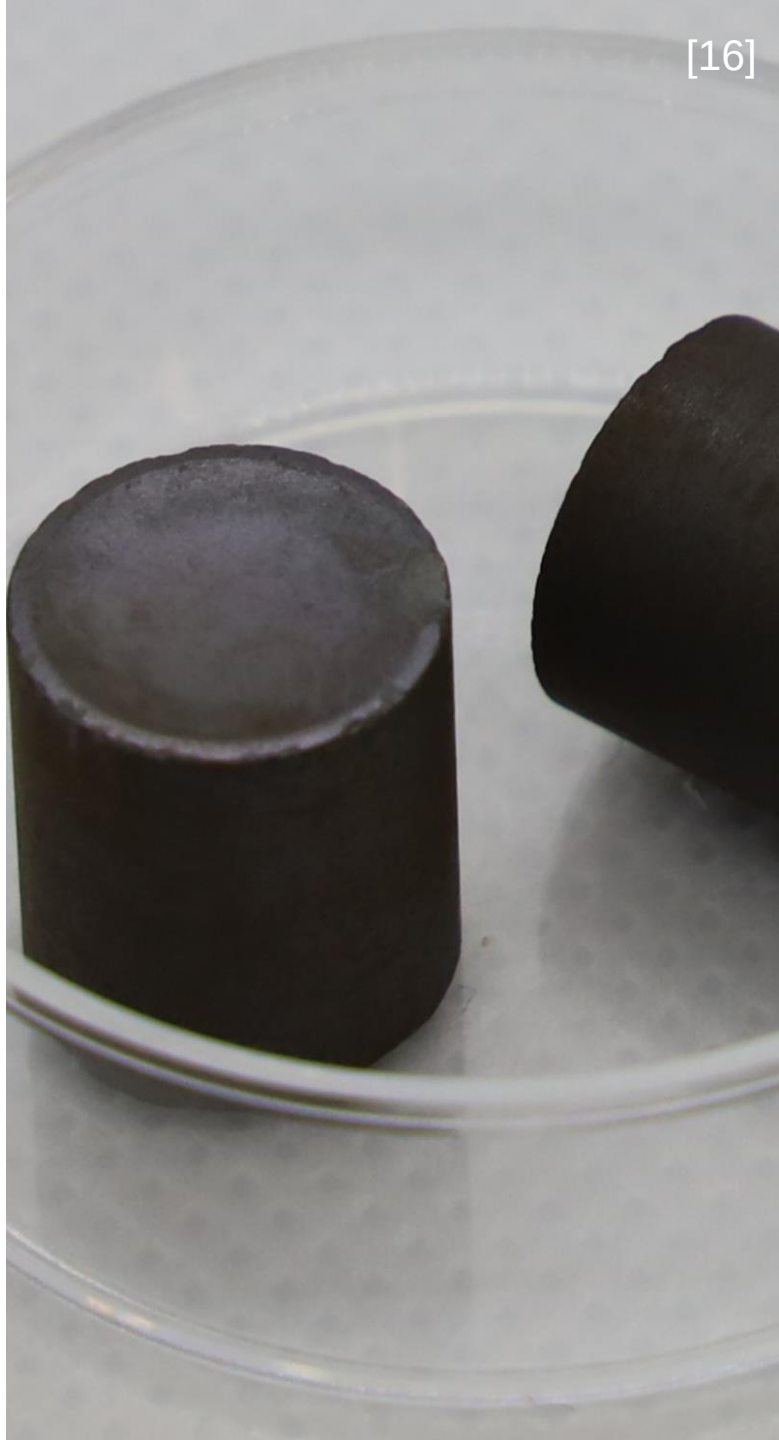

[13]


[14]

[11] https://en.wikipedia.org/wiki/Triuranium_octoxide
[12] https://en.wikipedia.org/wiki/Yellowcake
[13] https://en.wikipedia.org/wiki/File:UO2_Pellet.jpg
[14] https://commons.wikimedia.org/wiki/File:Triuranium_octoxide.JPG

Uranium dioxide UO_2

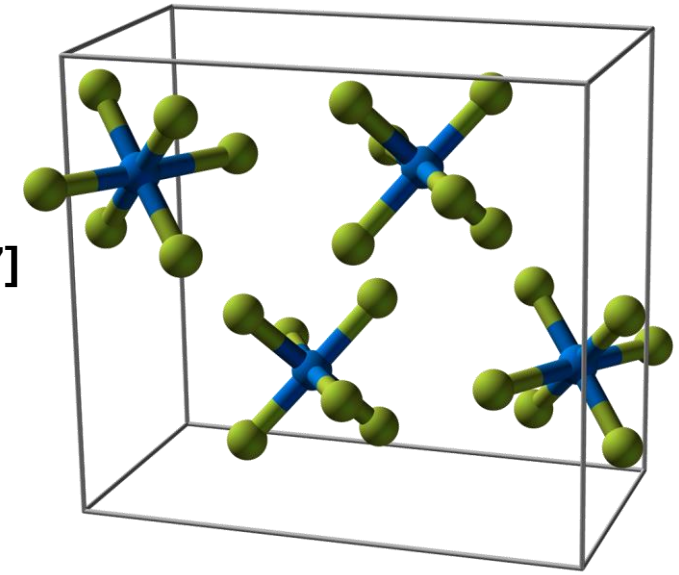
- Used as nuclear fuel rods in nuclear rods
- Black, radioactive and crystalline powder
- Naturally occurs in the mineral uranitite
- Was used to colour glass and ceramics [15]


[16]

[15] https://en.wikipedia.org/wiki/Uranium_dioxide
[16] https://en.wikipedia.org/wiki/File:UO2_Pellet.jpg

Uranium hexafluoride UF_6

- Used in the process of enriching uranium
- A volatile white solid
- Relatively convenient to process
- Used in both main uranium enrichment methods: the gas centrifuge method and gaseous diffusion [17]



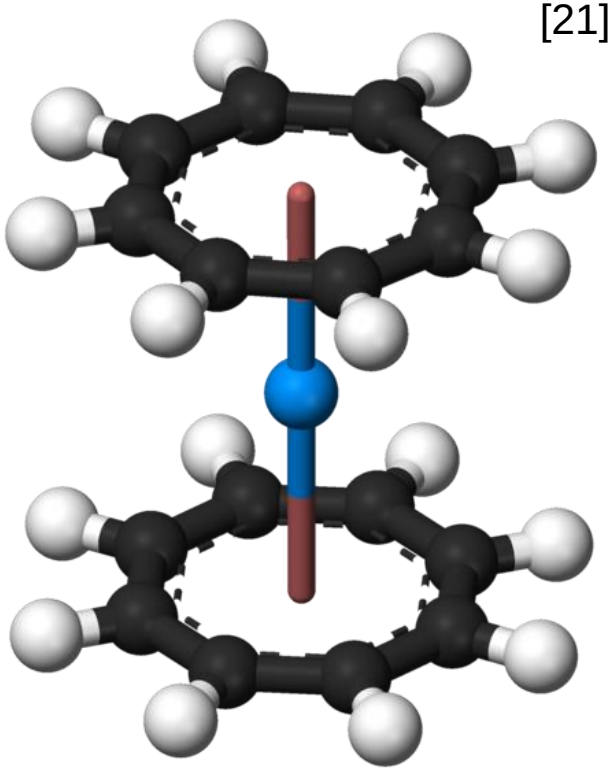
[18]

[17] https://en.wikipedia.org/wiki/Uranium_hexafluoride
[18] https://commons.wikimedia.org/wiki/File:Uranium-hexafluoride-unit-cell-3D-balls.png

Organouranium compounds: Uranocene

- Organouranium compounds are organometallic compounds containing a carbon to uranium chemical bond
- Somewhat important to the nuclear industry [19]
- Uranocene $U(C_8H_8)_2$
- Uranium atom sandwiched between two cyclooctatetraenide rings
- No known practical applications [20]

[21]



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[19] https://en.wikipedia.org/wiki/Organouranium_chemistry
[20] https://en.wikipedia.org/wiki/Uranocene
[21] https://commons.wikimedia.org/wiki/File:Uranocene-3D-balls.png

Applications

Applications of uranium

- **Historically used for pottery and photographics chemicals**
- **Nuclear fuel and weapons [1]**
- **Depleted uranium as kinetic energy penetrator (military use) [22]**

- **Uranium dioxide as a semiconductor material?**
- **Band gap comparable to silicon [15]**
- **A p-n-p transistor of UO2 was manufactured in a lab [23]**

[1] https://en.wikipedia.org/wiki/Uranium
[15] https://en.wikipedia.org/wiki/Uranium_dioxide
[22] https://en.wikipedia.org/wiki/Depleted_uranium

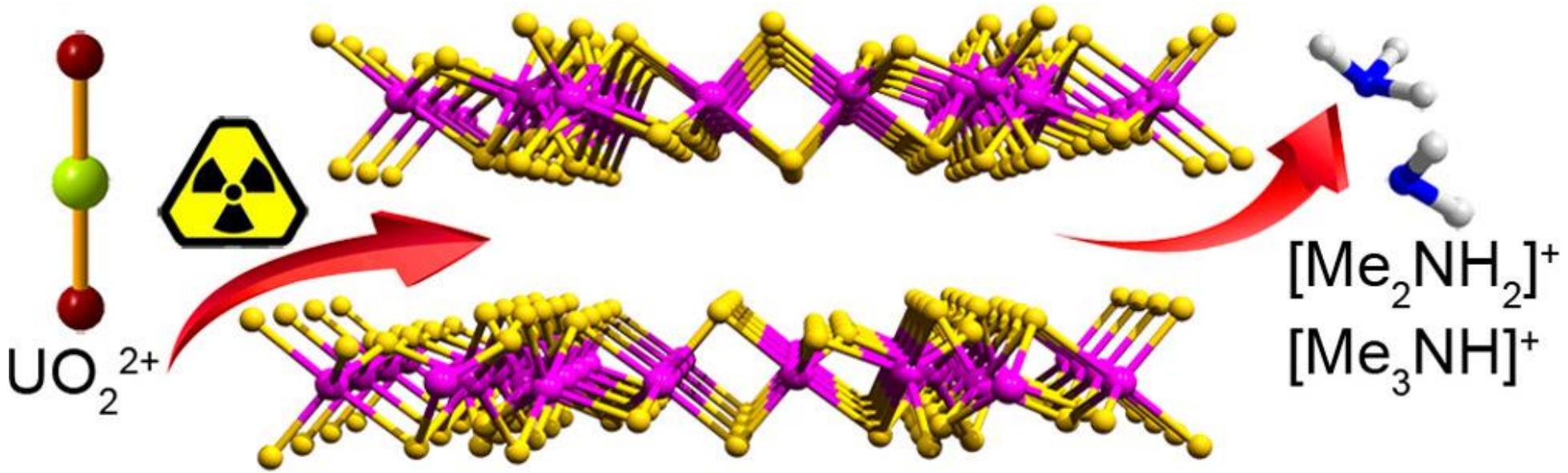
[23] Meek, T. & von Roedern, B. Semiconductor devices fabricated from actinide oxides. Vacuum. Vol. 83. 2008. P. 226-228. DOI: 10.1016/j.vacuum.2008.04.005

Recovery of Uranium by a Layered Organic–Inorganic Hybrid Thiostannate (1)

- **Uranium is still left in nuclear waste**
- $(Me_2NH_2)_{1.33}(Me_3NH)_{0.67}Sn_3S_7 \cdot 1.25\ H_2O$ **(FJSM-SnS) is used for recovery of uranium**
- **Ion exchange with FJSM-SnS where UO_2^{2+} are exchanged for $[Me_2NH_2]^+$ and $[Me_3NH]^+$ ions**

M.-L. Feng, D. Sarma, X.-H. Qi, et al. Efficient Removal and Recovery of Uranium by a Layered Organic–Inorganic Hybrid Thiostannate Journal of the American Chemical Society, 2016, 138 (38), 12578-12585. DOI: 10.1021/jacs.6b07351

Recovery of Uranium by a Layered Organic–Inorganic Hybrid Thiostannate (2)



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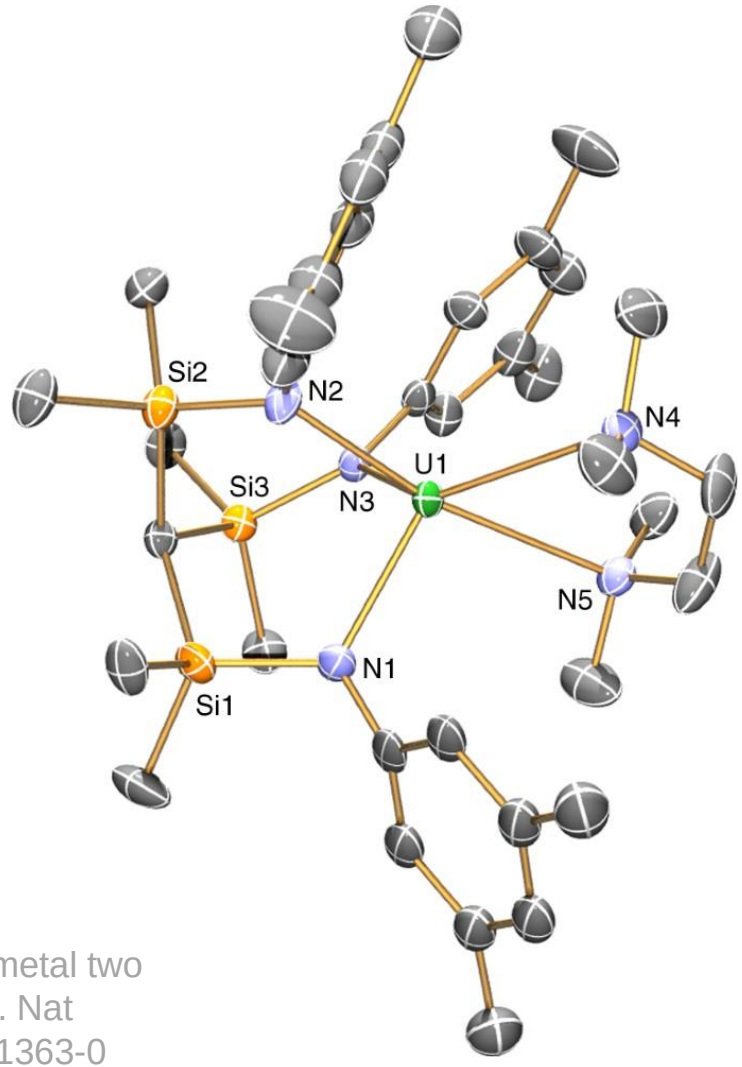
Single-metal two-electron oxidative addition and reductive elimination at uranium

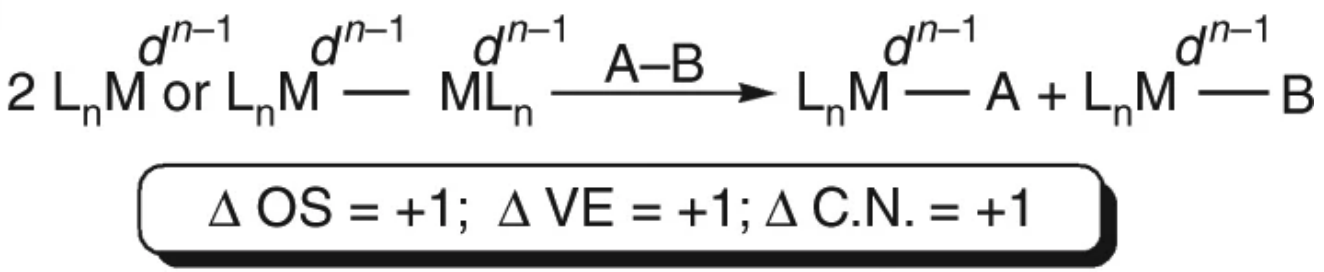
- Single-metal two-electron oxidative addition possible for d-block metals
- Only one- or multi-electron oxidation or reduction reactions for f-block metals
- Possibility to oxidize uranium(III) complexes to uranium(V) complexes



Gardner, B.M., Kefalidis, C.E., Lu, E. et al. Evidence for single metal two electron oxidative addition and reductive elimination at uranium. Nat Commun 8, 1898 (2017). https://doi.org/10.1038/s41467-017-01363-0

Single-metal two-electron oxidative addition and reductive elimination at uranium

a



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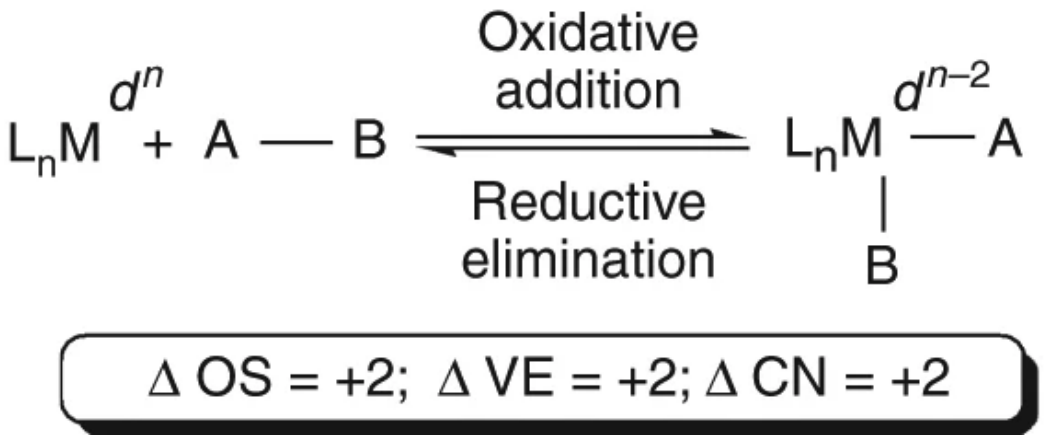

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