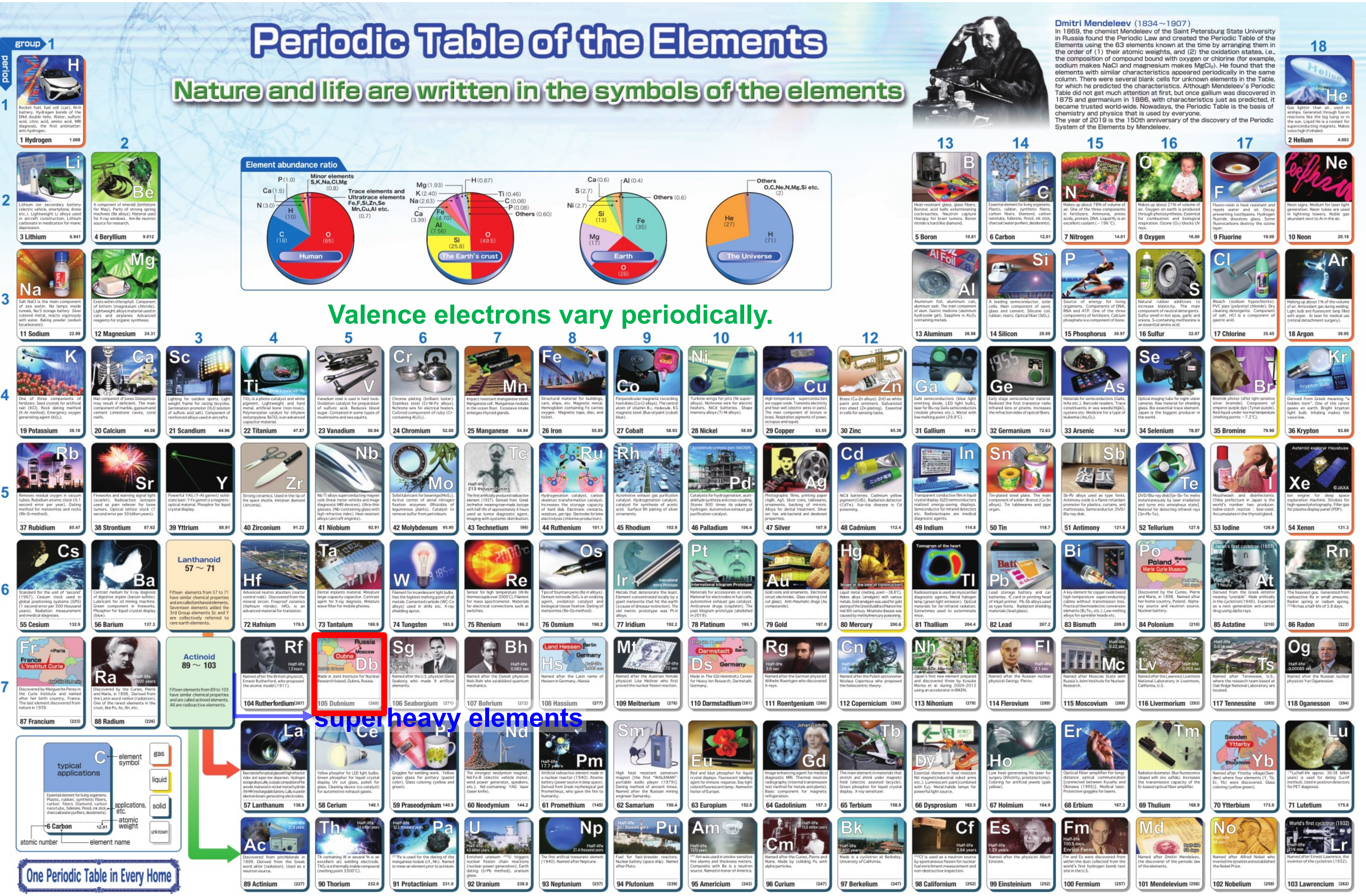
Relativistic effects and Db’s chemical character

2021.11.6.

Shu Nakamura

Contents

Periodic table

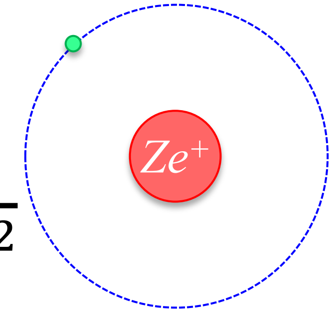


1) https://www.mext.go.jp/stw/series.html

Relativistic effects: classical model

Classically…(Bohr's model)

$$v_n = \frac{Ze^2}{4\pi\varepsilon_0\hbar n} \quad r_n = \frac{4\pi\varepsilon_0\hbar^2 n^2}{Ze^2 m_e} \quad E_n = -\frac{Z^2 e^4 m_e}{32\pi^2\varepsilon_0^2\hbar^2 n^2}$$



in the theory of relativity

$$\boxed{m_e^{rel} = \frac{m_e}{\sqrt{1-(v/c)^2}}}$$

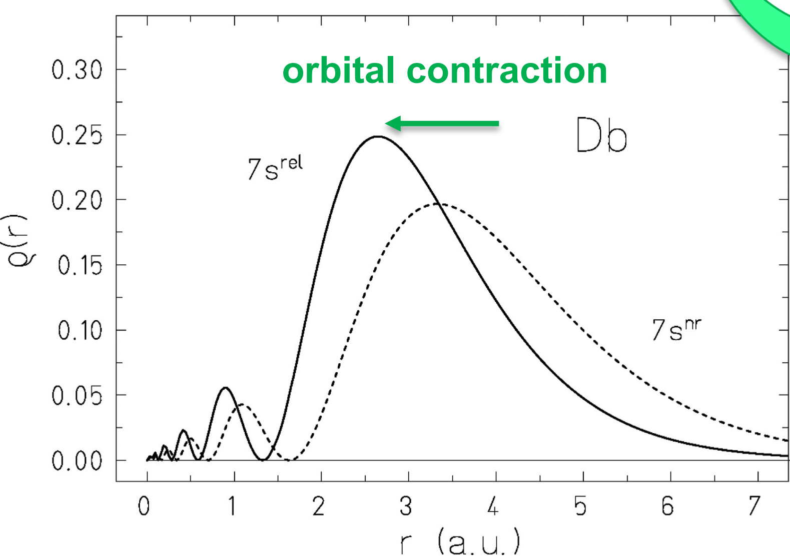
$$\left(m_e^{rel} \approx m_e \ (v \ll c)\right)$$

$v_1(\mathrm{H}) \approx c/137$

$v_1(\mathrm{Hg}) \approx 0.6c$

$$r_n^{rel} = \sqrt{1-(v/c)^2}\, r_n$$ orbital contraction

$$E_n^{rel} = \frac{E_n}{\sqrt{1-(v/c)^2}} < E_n$$ stabilization



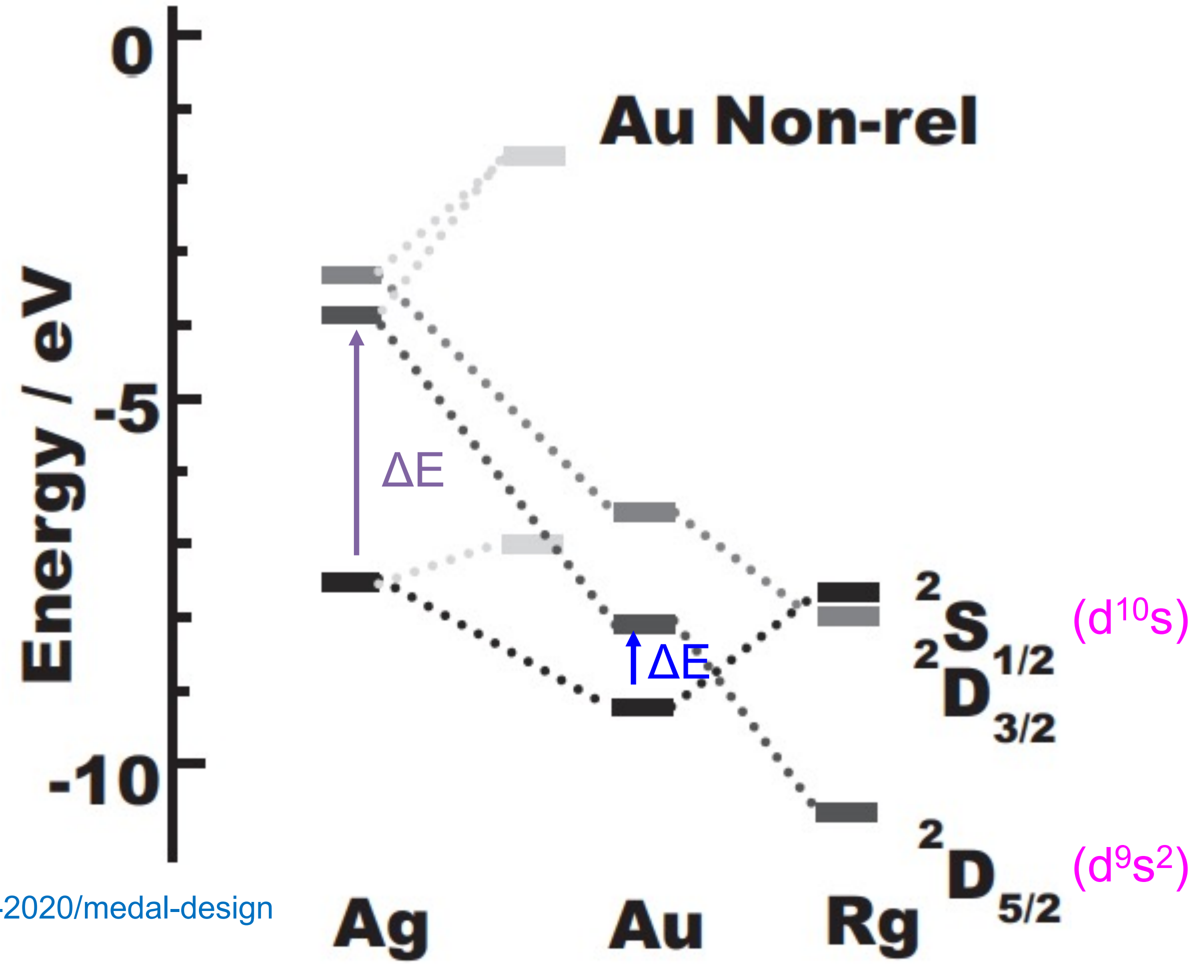
Only if Z does not change.

→ contraction and stabilization for s, p ($p_{1/2}$) orbitals
the opposites for d, f orbitals

1) Türler, A.; Pershina, V. *Chem. Rev.* **2013**, *113*, 1237.
2) 永 目 諭 一 郎（編著）『超重元素化学の最前線』、日本放射化学会、**2019**.

Relativistic effects: example

https://olympics.com/ja/olympic-games/tokyo-2020/medal-design



s Orbital of Au is stabilized.

→ ΔE decreases, absorbing blue light.

1) Pyykko, P.; Desclaux, J., P. *Acc. Chem. Res.* **1979**, *12*, 276.
2) 永 目 諭 一 郎（編著）『超重元素化学の最前線』、日本放射化学会、**2019**.

What makes elements metal?

- high electrical conductivity
- high thermal conductivity
- ductility

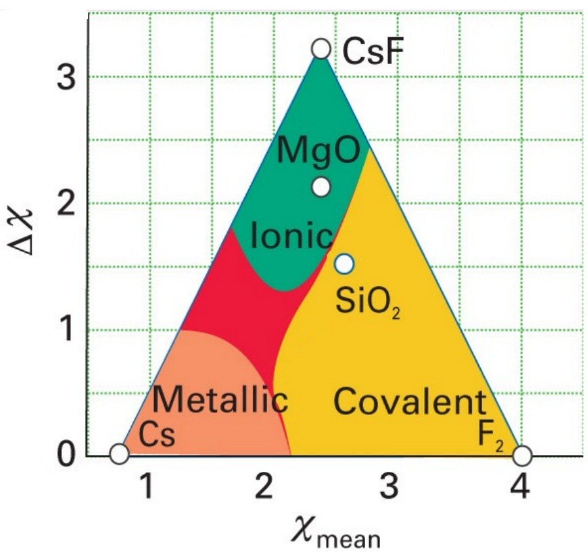
more strictly: the temperature dependence of the electrical conductivity

When temperature rises…

metals: lower conductivity

others: higher conductivity

characters of single substances



Ketelaar triangle

Metals easily become cation in compounds.

1) Hensel, F.; Slocombe, D., R.; Edwards, P. P. *Phil. Trans. R. Soc. A 373*, 20140477.

2) シュライバー・アトキンス無機化学（上）

Valence –価数–

a) Number of bonds (結合数)

* Coordinate bonds (*dashed bonds*) are not counted.

b) Valence (原子価)

the number of electrons that an atom uses in bonding

b = a + d

c) Oxidation number (酸化数)

the charge remaining on an atom if covalent electron pair are transferred to the more electronegative partner

→ionic character

c = (charge on compound) – (charge on ligands)

d) Formal charge (形式電荷)

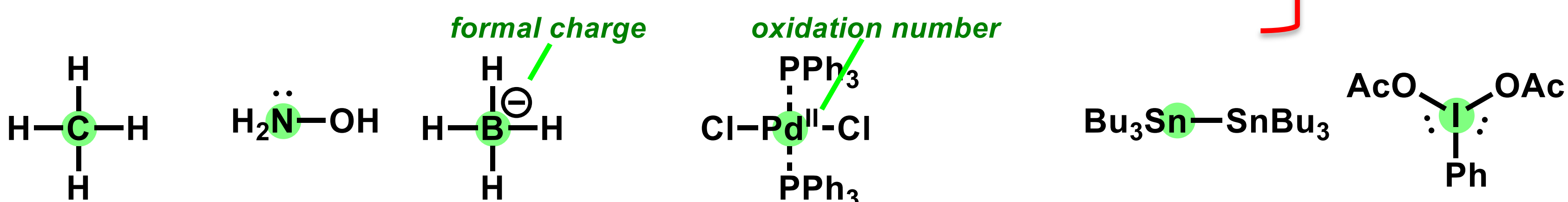
the charge remaining on an atom when all ligands are removed homolytically

→covalent character

e) Coordination number (配位数)

the number of atoms bonded to the atom of interest
(sometimes, number of atoms close to the atom)

sometimes called "価数"



a) 4	a) 3	a) 4	a) 2	a) 4	a) 3
b) 4	b) 3	b) 3	b) 2	b) 4	b) 3
c) -4	c) -1	c) +3	c) +2	c) +3	c) +1
d) 0	d) 0	d) -1	d) 0	d) 0	d) 0
e) 4	e) 3	e) 4	e) 4	e) 4	e) 3

1) Parkin, G. *J. Chem. Educ.* **2006**, *83*, 791.

Element 105: Dubnium

also called Hahnium (Ha) before 1997

belonging to group 5
[Rn] $5f^{14}$ $6d^{3}$ $7s^{2}$
→+V oxidation state favored

no stable isotopes

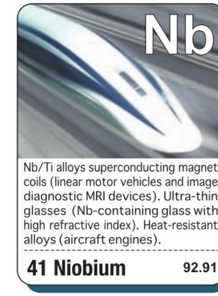
Synthesized:

1968 (JINR, in USSR)

$$^{243}_{95}\mathrm{Am}+^{22}_{10}\mathrm{Ne}\rightarrow^{261}_{105}\mathrm{Db}+5n$$

1970 (LBNL, in US)

$$^{249}_{98}\mathrm{Cf}+^{15}_{7}\mathrm{N}\rightarrow^{260}_{105}\mathrm{Db}+4n$$



1) Barber, R. C.; Greenwood, N. N.; Hrynkiewicz, A. Z. et al. *Pure & Appl. Chem.* **1993**, *85*, 1757.
2) Türler, A.; Pershina, V. *Chem. Rev.* **2013**, *113*, 1237.

Contents

Introduction

Prof. Tetsuya K. Sato

2003 Researcher @ Japan Atomic Energy Agency (JAEA)
2015-Assistant Principal Researcher @ JAEA
2017 Invited Researcher @ Helmholtz-Institut Mainz
2018 Invited Researcher @ Paul Schrerrer Institute
2019-Visiting Associate Professor@ Ibaraki University
2019-Visiting Associate Professor@ Tohoku University
2020-Visiting Scientist @ RIKEN

Research topic: Nuclear and radiochemistry
Superheavy element chemistry

Tandem Accelerator of JAEA
@Tokai-mura, Naka-gun, Ibaraki-ken
- One of the largest electrostatic particle accelerators

①accelerating anion → ②stripping electron (making cation)
→ ③accelerating cation (same electric field; opposite direction)

1982 Operation started
1993 The superconducting booster was completed

1) https://asrc.jaea.go.jp/soshiki/gr/HENS-gr/member.html
2) https://researchmap.jp/tetsuyaks
3) https://ttandem.jaea.go.jp/index.html

Pershina's calculation (1)
- introduction of relativistic effects -

Dirac equation

$$\widehat{\boldsymbol{H}}\psi = E\psi \qquad \widehat{\boldsymbol{H}} = c\boldsymbol{\alpha}\hat{\boldsymbol{p}} + \beta mc^2 + V(\boldsymbol{r})$$

$$\boldsymbol{\alpha} = \begin{bmatrix} 0 & \sigma \\ \sigma & 0 \end{bmatrix}$$ σ: Pauli spin matrices

$$\beta = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

in a spherical potential

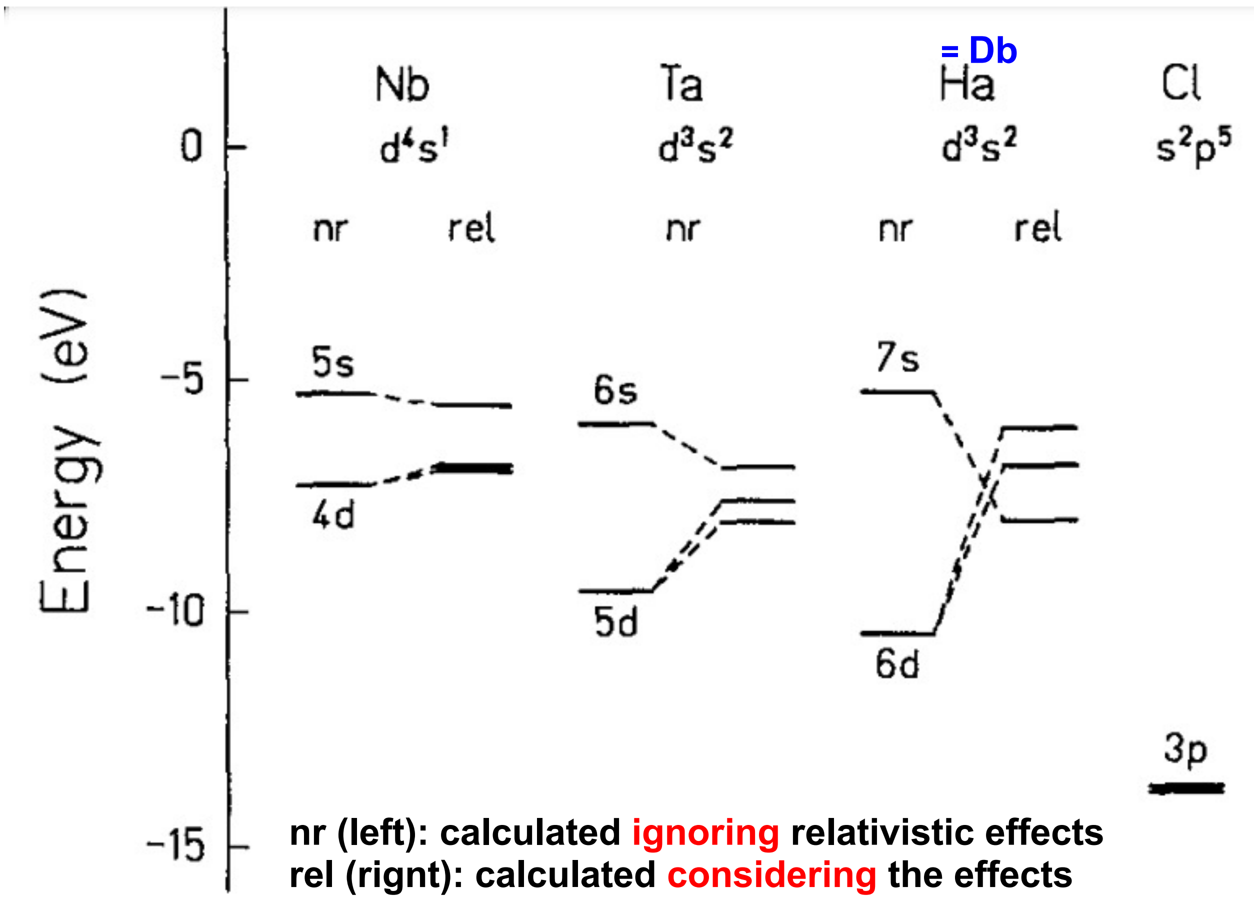
$$\psi_{n\kappa m} = \begin{bmatrix} \varphi \\ \overline{\varphi} \end{bmatrix} = \begin{bmatrix} \dfrac{P_{n\kappa}(r)}{r} y_{\kappa m}(\theta,\ \phi,\ s) \\ -i\dfrac{Q_{n\kappa}(r)}{r} y_{-\kappa m}(\theta,\ \phi,\ s) \end{bmatrix}, \kappa = \begin{cases} -l-1\ (j = l + \frac{1}{2}) \\ l\ \ (j = l - \frac{1}{2}) \end{cases}$$

$$\begin{cases} c\left(\dfrac{d}{dr} - \dfrac{\kappa}{r}\right) Q_i(r) + V(r)P_i(r) = \epsilon_i P_i(r) \\ c\left(-\dfrac{d}{dr} - \dfrac{\kappa}{r}\right) P_i(r) - 2c^2 Q_i(r) + V(r)Q_i(r) = \epsilon_i Q_i(r) \end{cases} \qquad (\epsilon_i \equiv E_i - mc^2)$$

1) Rosen, A.; Ellis, D., E. *J. Chem. Phys.* **1975**, *62*, 3039.
2） 永 目 諭 一 郎（編著）『超重元素化学の最前線』、日本放射化学会、**2019**.

Pershina's calculation (2)
- calculation of relativistic effects -

Relativistic effects on AOs



nr (left): calculated ignoring relativistic effects
rel (rignt): calculated considering the effects

1) Pershina, V.; Fricke, B. *J. Chem. Phys.* **1993**, *99*, 9720.

Pershina's calculation (3)
- covalency of $DbCl_5$ -

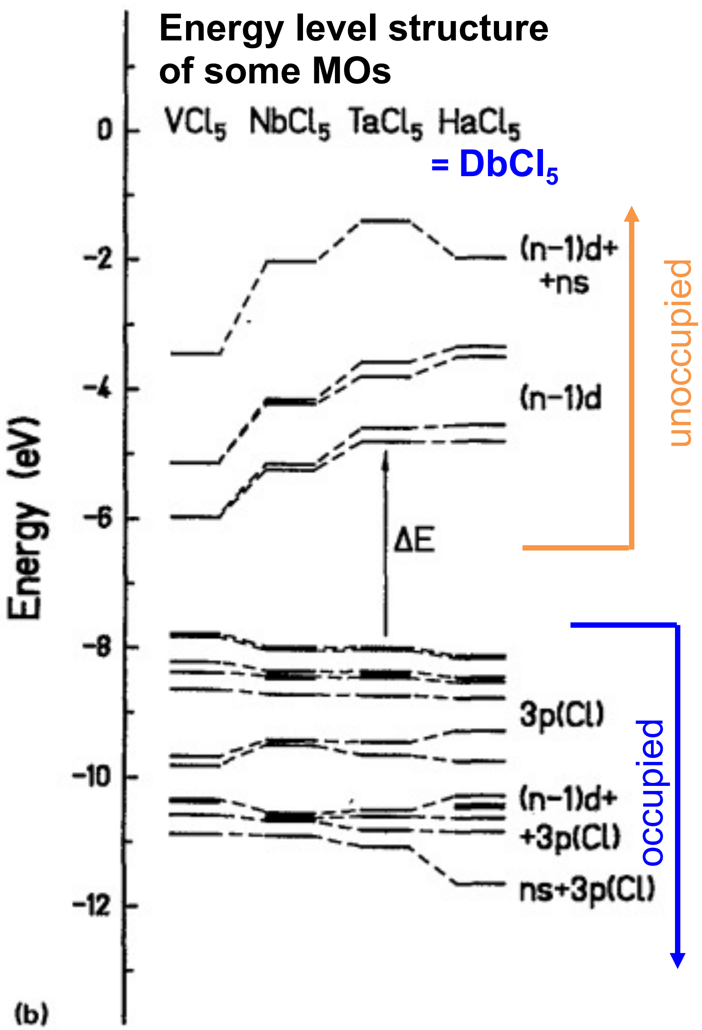


TABLE IV. Effective charges on atoms (Q) and atomic orbital populations (q_l) for MCl_5.

Molecule	$R_{M\text{-}Cl_{ax}}$ (Å) / $R_{M\text{-}Cl_{eq}}$ (Å)	Q	q_s	q_p	q_d	q_f	ΔE (eV)
VCl_5[a]	2.21 / 2.18	1.12	0.24	0.36	3.27	···	1.81
$NbCl_5$	2.338 / 2.241	0.93	0.20	0.22	3.65	···	2.70
$TaCl_5$	2.369 / 2.227	0.95	0.35	0.33	3.37	13.99	3.10
$HaCl_5$ = $DbCl_5$	2.42 / 2.28	0.81	0.55	0.33	3.32	13.99	3.36
$HaCl_5$	2.45 / 2.31	0.80	0.58	0.34	3.29	13.99	3.25
$HaCl_5$	2.47 / 2.32	0.79	0.60	0.35	3.27	13.99	3.18
$PaCl_5$	2.44	0.98	0.13	0.13	2.09	1.70	2.68

The charge on Db (≒Q) decreases.

→Db-Cl bond is predicted to be less ionic.

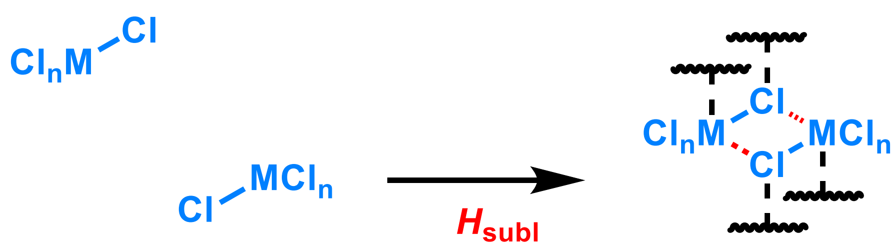
1) Pershina, V.; Sepp, W.-D.; Fricke, B. *J. Chem. Phys.* **1992**, *96*, 8367.

To measure the chemical character of Db

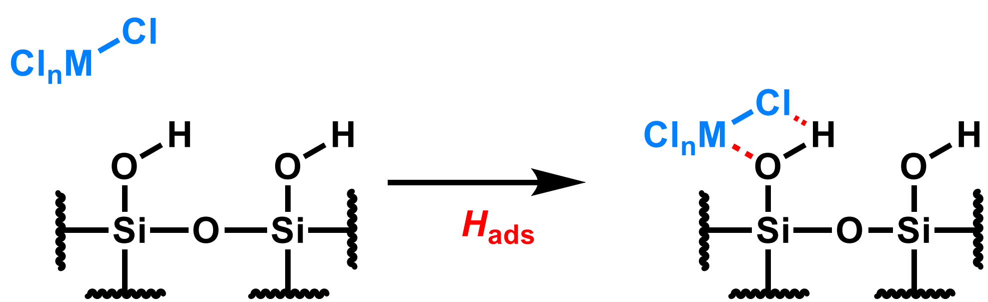
A trace amount of Db compounds will be available.

→ Only physicochemical parameters could be obtained.

a) Sublimation enthalpy: macroscopic parameter



b) Adsorption enthalpy: microscopic parameter



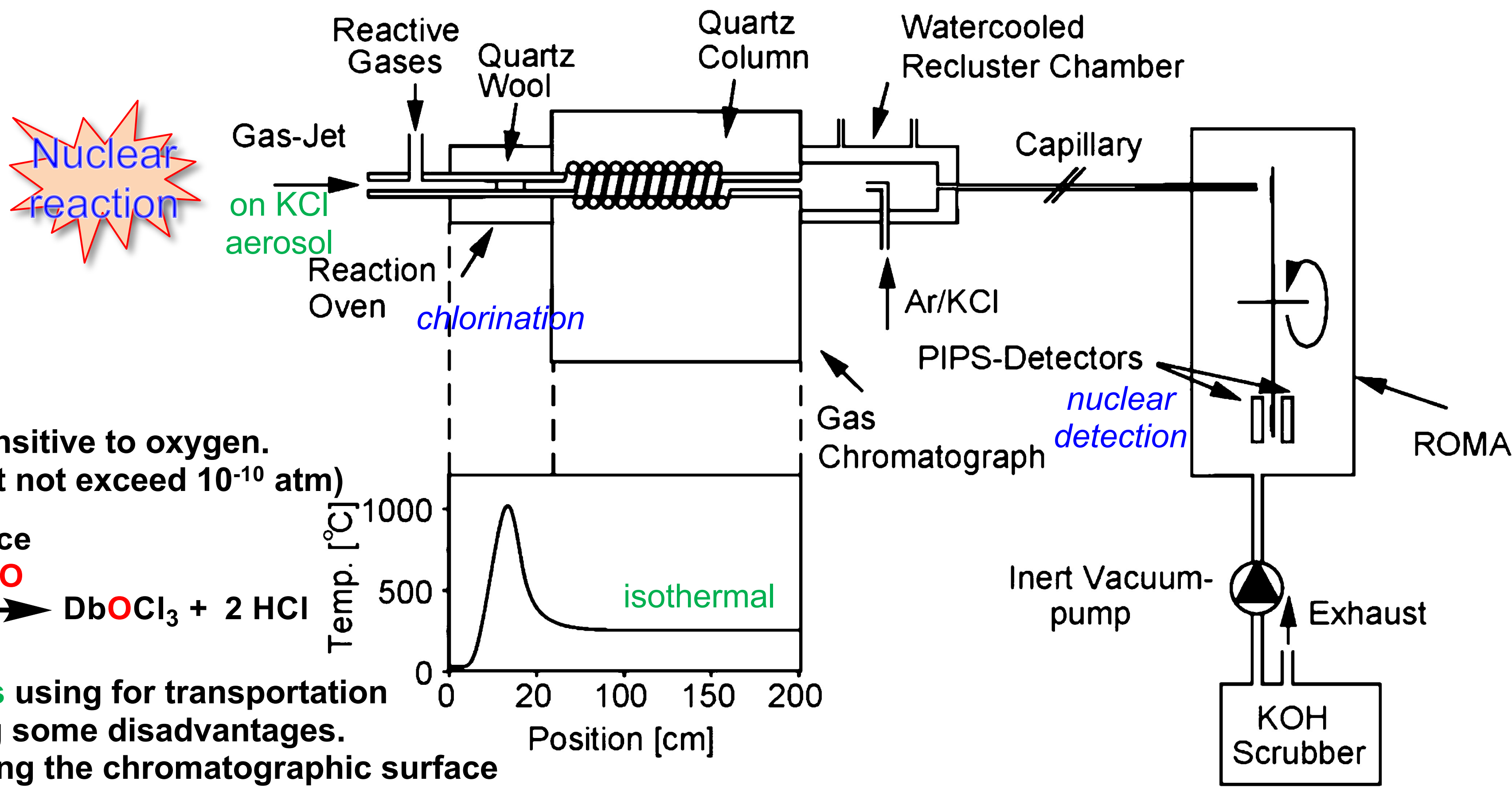
There should be a correlation.

1) Chiera, N., M.; Sato, T., K.; Tomitsuka, T.; Asai, M.; Suzuki, H.; Tokoi, K.; Toyoshima, A.; Tsukada, K.; Nagame, Y. *Inorg. Chim. Acta* **2019**, *486*, 361.

2) 永 目 諭 一 郎（編著）『超重元素化学の最前線』、日本放射化学会、**2019**.

Isothermal Gas-Chromatography (IGC)
- Measurement of $DbCl_5$ -

Ordinal set-up for measurement of volatilities



problems

1) Db is sensitive to oxygen.
($p(O_2)$ must not exceed 10^{-10} atm)

$$DbCl_5 \xrightarrow{\text{trace } H_2O} DbOCl_3 + 2\,HCl$$

2) Aerosols using for transportation of Db bring some disadvantages.

a) affecting the chromatographic surface

b) contamination of non-volatile nuclear byproducts

c) deposition of aerosol particles if charged

1) Chiera, N., M.; Sato, T., K.; Tomitsuka, T.; Asai, M.; Ito, Y.; Shirai, K.; Suzuki, H.; Tokoi, K.; Toyoshima, A.; Tsukada, K.; Nagame, Y. *J. Radioanaly. Nucl. Chem.* **2019**, *320*, 633.

2) Türler, A.; Eichler, R.; Yakushev, A. *Nucl. Phys. A* **2015**, *944*, 640.

Model experiment (1)

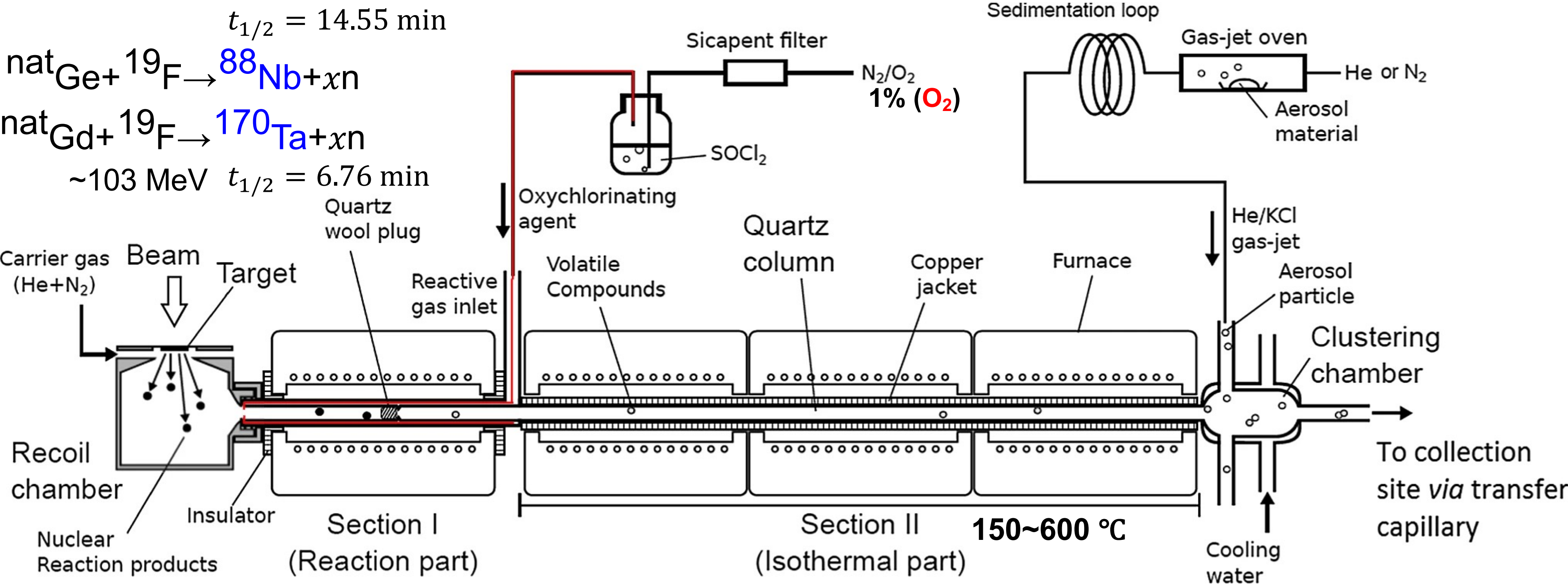
Improved set-up

$t_{1/2} = 14.55$ min

$^{nat}Ge + ^{19}F \rightarrow ^{88}Nb + xn$

$^{nat}Gd + ^{19}F \rightarrow ^{170}Ta + xn$

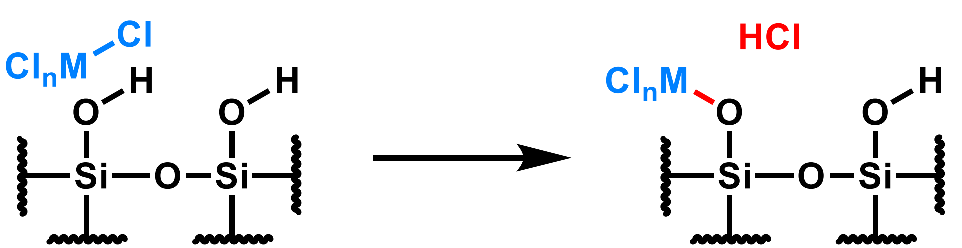
~103 MeV $t_{1/2} = 6.76$ min



without aerosols ***$MOCl_3$ formation***

800~1000 ℃

*** pre-treated with chlorination gas**

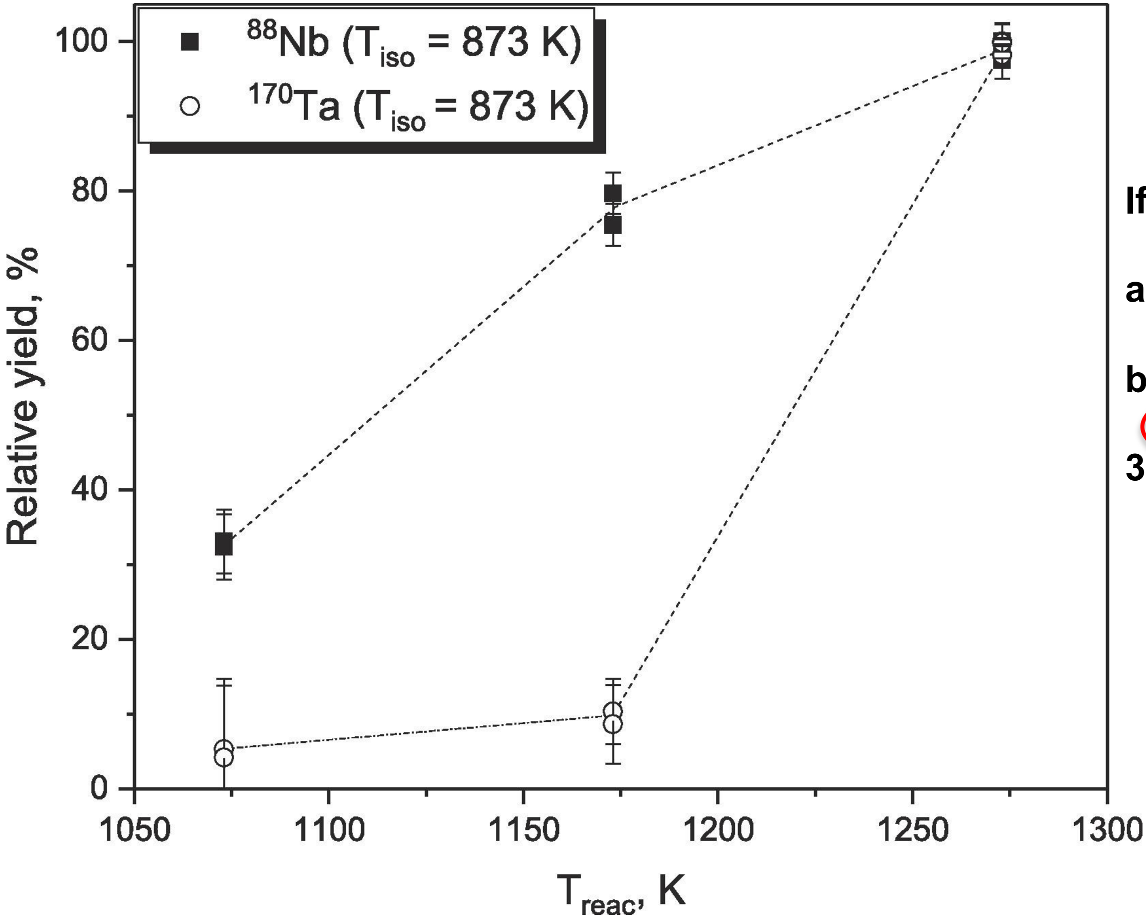


1) Chiera, N., M.; Sato, T., K.; Tomitsuka, T.; Asai, M.; Suzuki, H.; Tokoi, K.; Toyoshima, A.; Tsukada, K.; Nagame, Y. *Inorg. Chim. Acta* **2019**, *486*, 361.

2) Chiera, N., M.; Sato, T., K.; Tomitsuka, T.; Asai, M.; Ito, Y.; Shirai, K.; Suzuki, H.; Tokoi, K.; Toyoshima, A.; Tsukada, K.; Nagame, Y. *J. Radioanaly. Nucl. Chem.* **2019**, *320*, 633.

Section I: Reaction temperature

Relative yields of volatile Nb/Ta compounds



If T_{reac} < 1273 K

a) Formation of $MOCl_3$ was too slow.

b) Cl_2 pressure was too low.

$$3\ SOCl_2 + 2\ O_2 \rightarrow SO_3 + 2\ SO_2 + 3\ Cl_2$$

→ T_{reac} is set at 1273 K.

1) Chiera, N., M.; Sato, T., K.; Tomitsuka, T.; Asai, M.; Suzuki, H.; Tokoi, K.; Toyoshima, A.; Tsukada, K.; Nagame, Y. *Inorg. Chim. Acta* **2019**, *486*, 361.

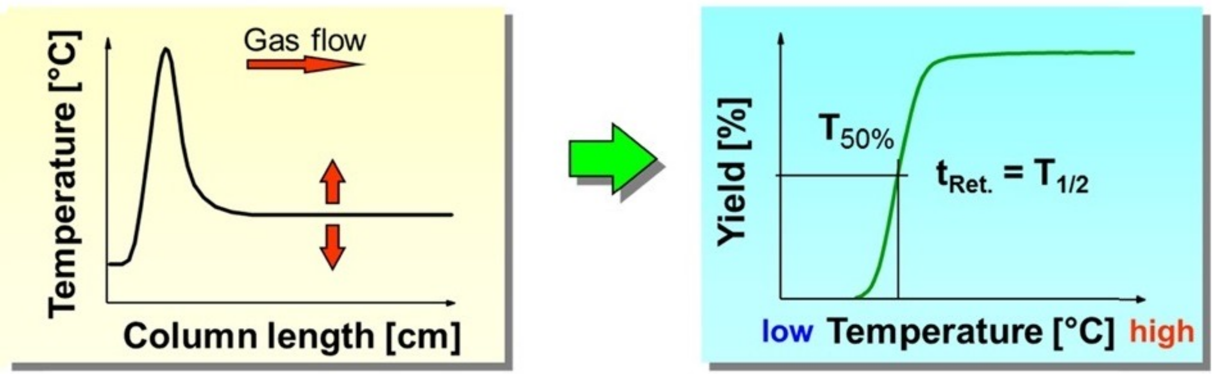
2) Chiera, N., M.; Sato, T., K.; Tomitsuka, T.; Asai, M.; Ito, Y.; Shirai, K.; Suzuki, H.; Tokoi, K.; Toyoshima, A.; Tsukada, K.; Nagame, Y. *J. Radioanaly. Nucl. Chem.* **2019**, *320*, 633.

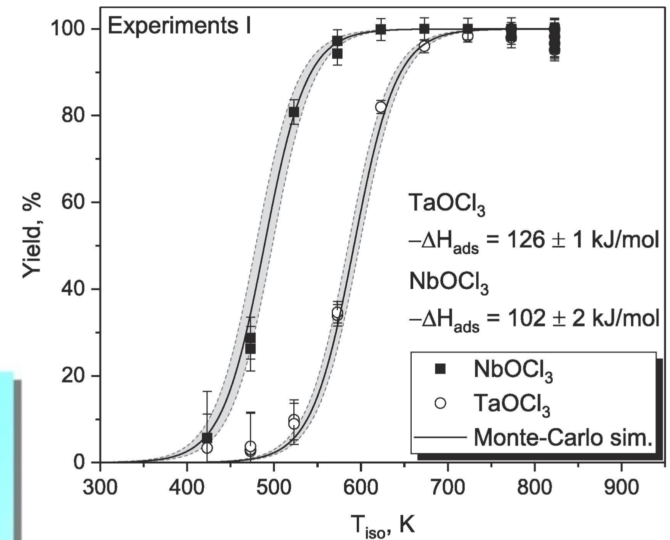
Section II: Gas-chromatography temperature

Isothermal Gas-Chromatography

high temperature → weak adsorption on quartz → short retention

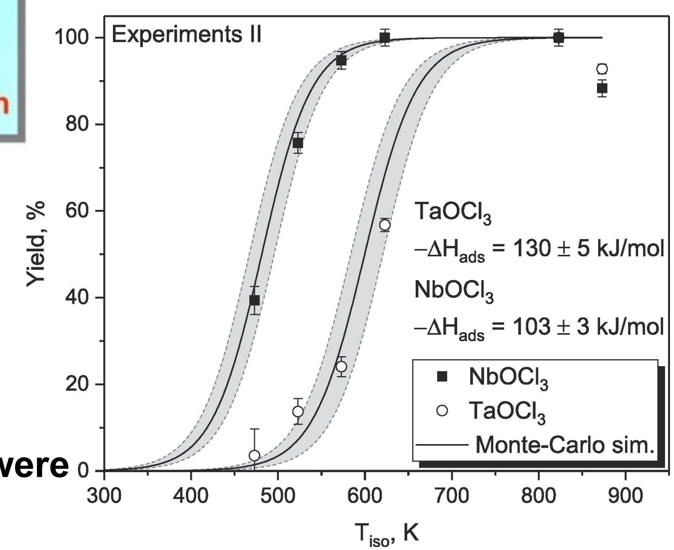
This correlation depends on *ΔH*$_{ads}$.





Chemical species	$-\Delta H_{ads}$ (this work) kJ/mol		$-\Delta H_{ads}$ (literature) kJ/mol	
$NbOCl_3$	102 ± 2	(a)	99 ± 1	[12]
	103 ± 3	(b)	92	[32]
	102 ± 4	average	94 ± 13	[33]
			96 ± 3	[34]
			63	[35]
			74 ± 2	[36]
$TaOCl_3$	126 ± 1	(a)	157 ± 12	(c)
	130 ± 5	(b)	133 ± 20	[37]
	128 ± 5	average	60	[35]
			149 ± 5	[38]

Two sets of experiments (I, II) were performed.

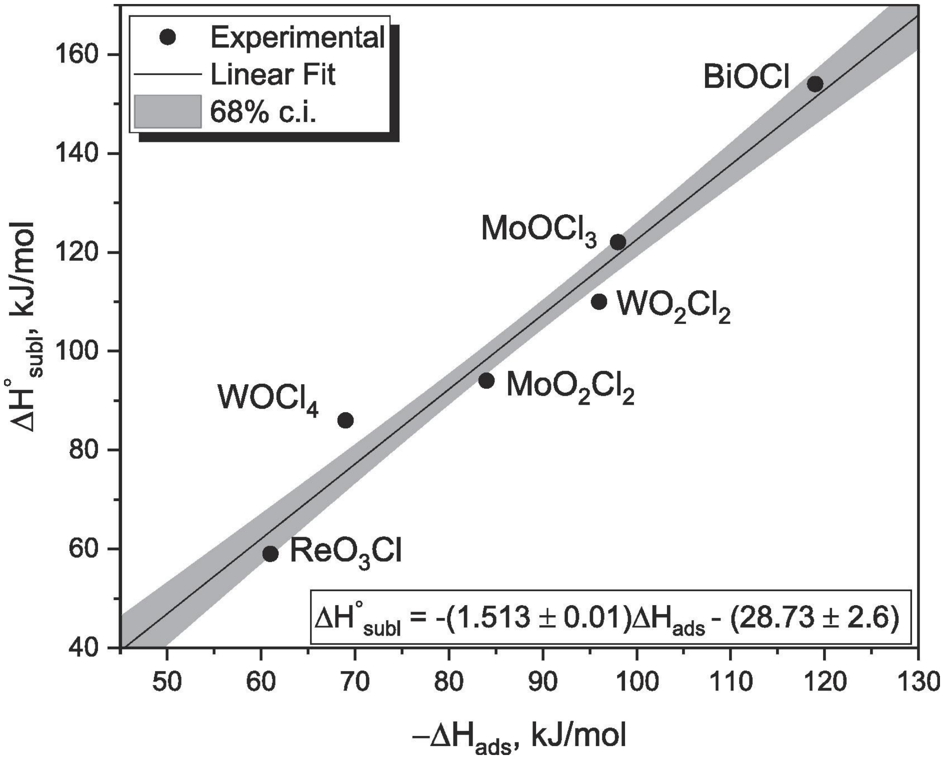


1) Chiera, N., M.; Sato, T., K.; Tomitsuka, T.; Asai, M.; Suzuki, H.; Tokoi, K.; Toyoshima, A.; Tsukada, K.; Nagame, Y. *Inorg. Chim. Acta* **2019**, *486*, 361.

2) Türler, A.; Eichler, R.; Yakushev, A. *Nucl. Phys. A* **2015**, *944*, 640.

Conversion to ΔH_{subl}

A semi-empirical correlation between ΔH_{ads} and ΔH_{subl} can be obtained using similar chemical species (oxychlorides).



literature data

$$\Delta H^0_{subl}\,(\mathrm{NbOCl_3}) = 128.5\ [\mathrm{kJ/mol}]$$

$$\Delta H^0_{subl}\,(\mathrm{TaOCl_3}) = 170\ [\mathrm{kJ/mol}]$$

$$\Delta H^0_{subl}\,(\mathrm{NbOCl_3}) = 126 \pm 10\ [\mathrm{kJ/mol}]$$

$$\Delta H^0_{subl}\,(\mathrm{TaOCl_3}) = 165 \pm 11\ [\mathrm{kJ/mol}]$$

extrapolation

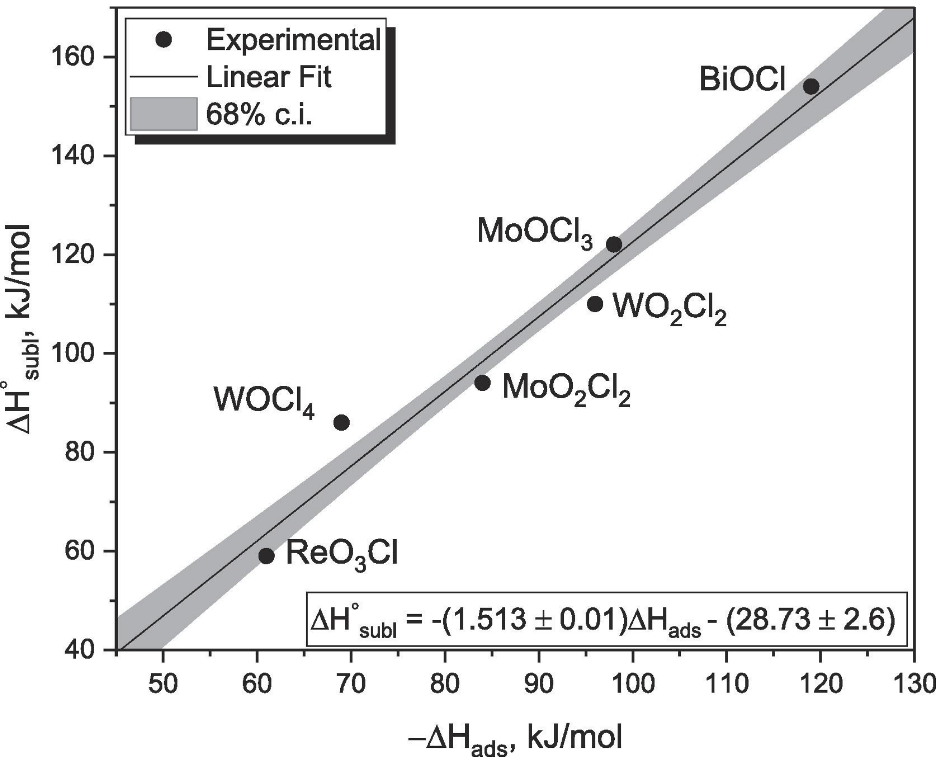
$$\Delta H^0_{subl} \approx -(1.513 \pm 0.01)\Delta H_{ads} - (28.73 \pm 2.6)\ [\mathrm{kJ/mol}]$$

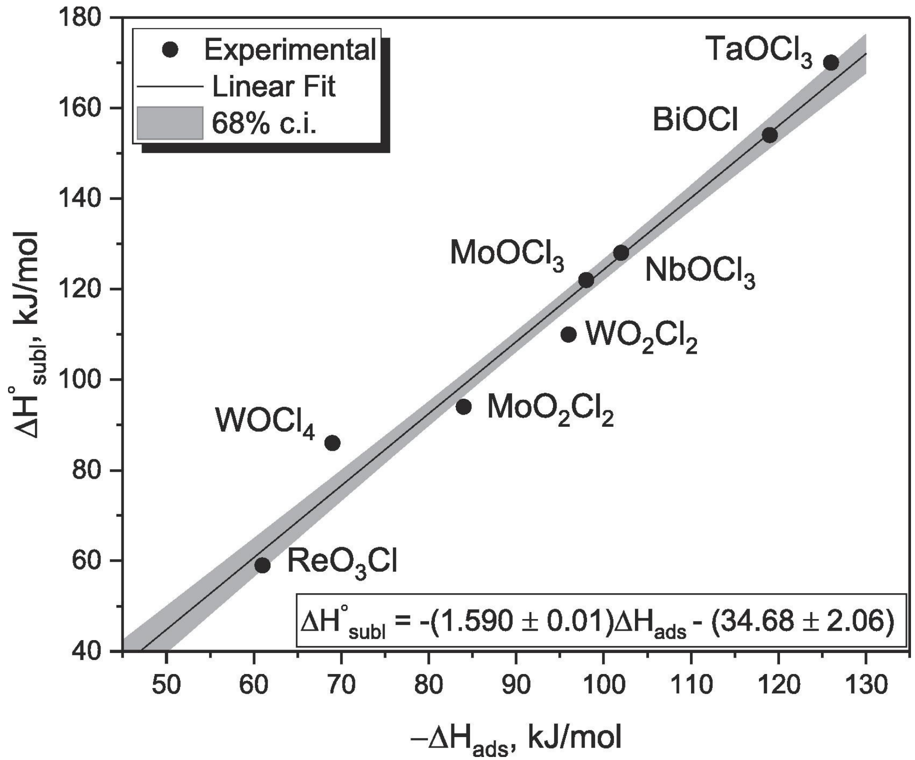
1) Chiera, N., M.; Sato, T., K.; Tomitsuka, T.; Asai, M.; Suzuki, H.; Tokoi, K.; Toyoshima, A.; Tsukada, K.; Nagame, Y. *Inorg. Chim. Acta* **2019**, *486*, 361.

2) Chiera, N., M.; Sato, T., K.; Tomitsuka, T.; Asai, M.; Ito, Y.; Shirai, K.; Suzuki, H.; Tokoi, K.; Toyoshima, A.; Tsukada, K.; Nagame, Y. *J. Radioanaly. Nucl. Chem.* **2019**, *320*, 633.

Optimization of correlation

Obtained ΔH_{ads} were added to the dataset.





$$\Delta H^0_{subl} \approx -(1.590 \pm 0.01)\Delta H_{ads} - (34.68 \pm 2.06)\ [\mathrm{kJ/mol}]$$

This would be useful to extrapolate $\Delta H_{subl}(DbOCl_3)$.

1) Chiera, N., M.; Sato, T., K.; Tomitsuka, T.; Asai, M.; Suzuki, H.; Tokoi, K.; Toyoshima, A.; Tsukada, K.; Nagame, Y. *Inorg. Chim. Acta* **2019**, *486*, 361.
2) Chiera, N., M.; Sato, T., K.; Tomitsuka, T.; Asai, M.; Ito, Y.; Shirai, K.; Suzuki, H.; Tokoi, K.; Toyoshima, A.; Tsukada, K.; Nagame, Y. *J. Radioanaly. Nucl. Chem.* **2019**, *320*, 633.

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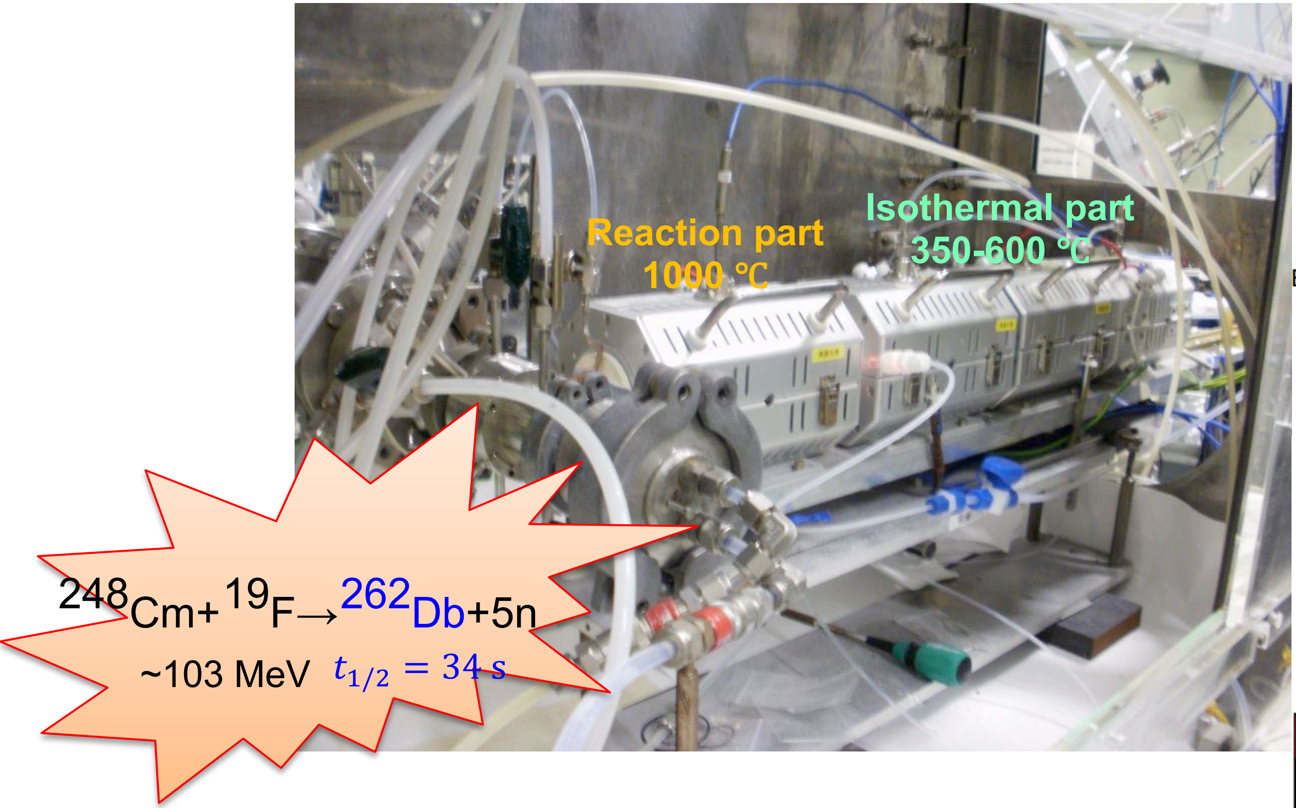
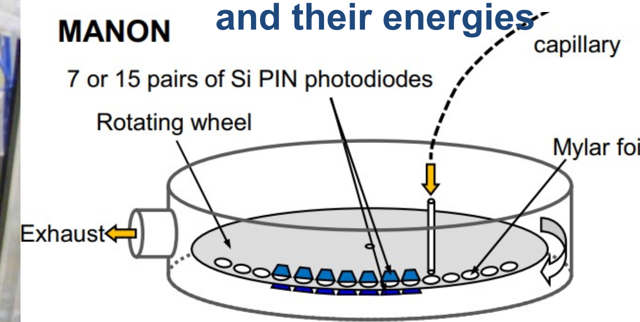
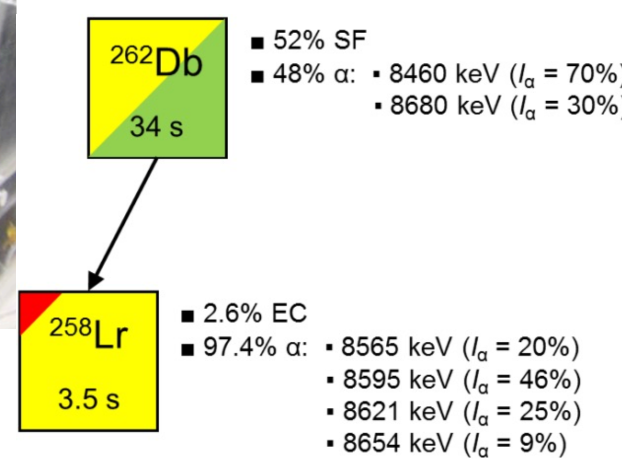
Experiment set-up



Detector: measure α particles and their energies





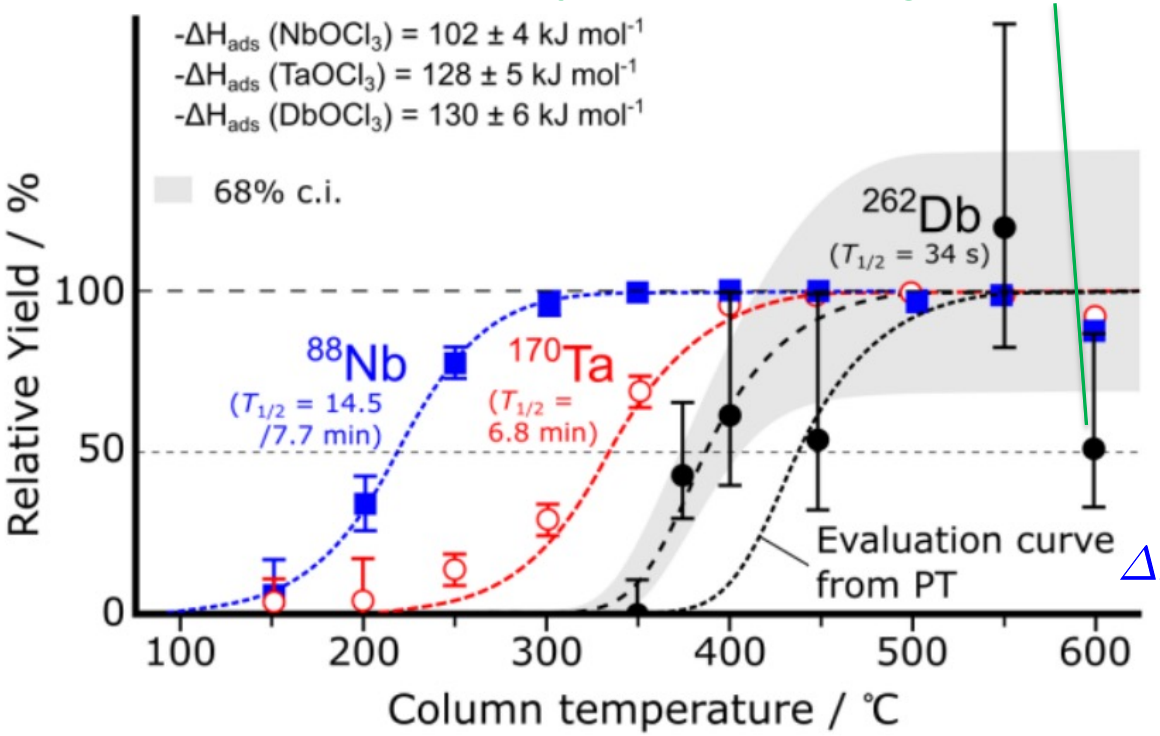
24 events (≒24 Db atoms) were detected.

Counted only coupled two α-particles detected within 3.5*5 seconds (to exclude background noises)

1) Chiera, N., M.; Sato, T., K.; Eichler, R.; Tomitsuka, T.; Asai, M.; Adachi, S.; Dressler, R.; Hirose, K.; Inoue, H.; Ito, Y.; Kashihara, A.; Makii, H.; Nishio, K.; Sakama, M.; Shirai, K.; Suzuki, H.; Tokoi, K.; Tsukada, K.; Watanabe, E.; Nagame, Y. *Angew. Chem. Int. Ed.* **2021**, *60*, 17871.
2) Haba, H. *EPJ Web Conf.* **2016**, *131*, 07006.

Volatility of $DbOCl_3$

Clustering (for detection) efficiency may decrease when higher temp.



$$\Delta H^0_{subl} \approx -(1.590 \pm 0.01)\Delta H_{ads} - (34.68 \pm 2.06)\ [\mathrm{kJ/mol}]$$

$$\Delta H^0_{subl}\ (\mathrm{DbOCl_3}) = 172 \pm 10\ [\mathrm{kJ/mol}]$$

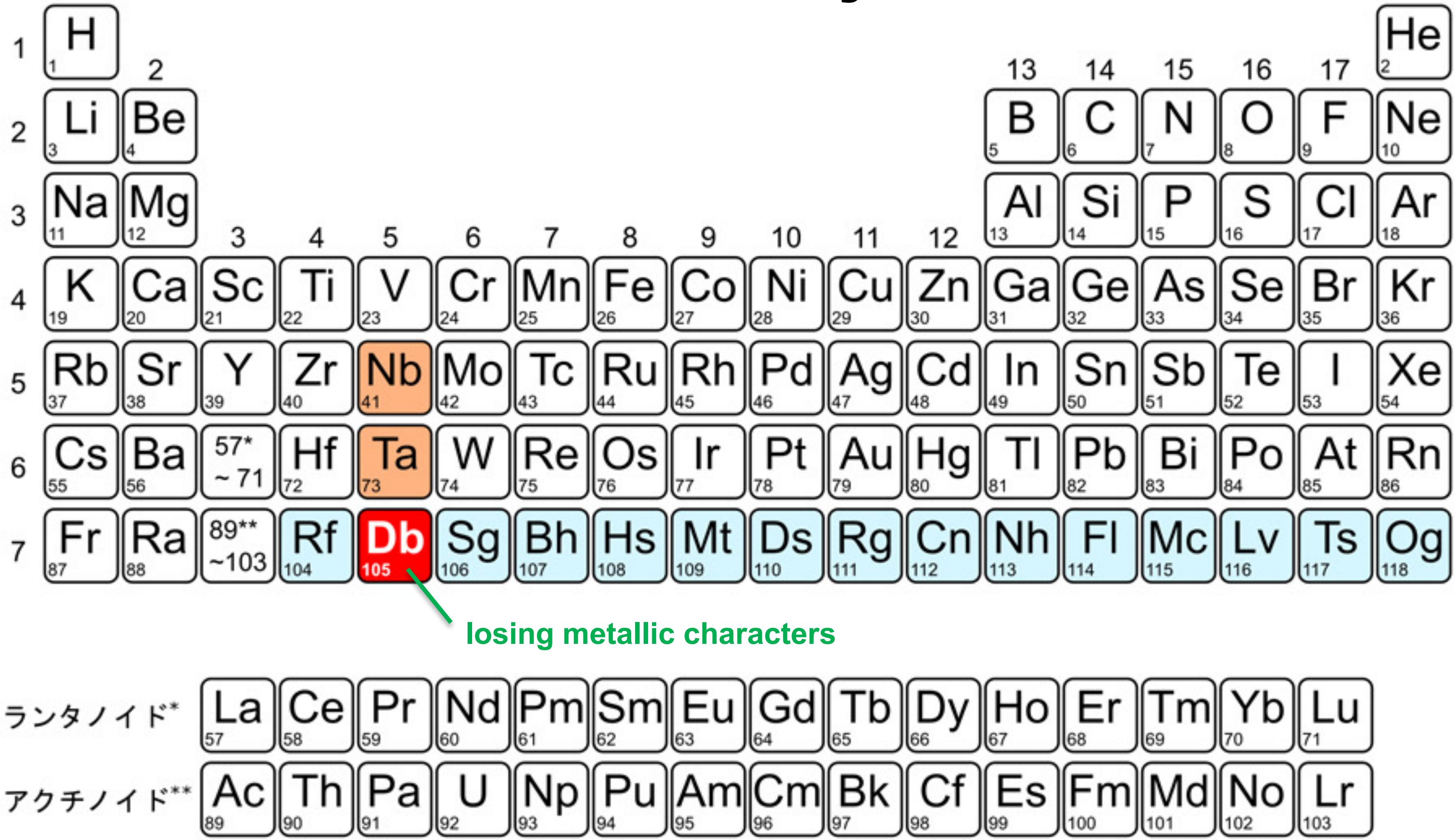
volatility: $NbOCl_3$ > $TaOCl_3$ ≧ $DbOCl_3$

more volatile than expected

decreasing the ionic character

1) Chiera, N. et al. *Angew. Chem. Int. Ed.* **2021**, *60*, 17871.
2) Eichler, B.; Türler, A.; Gäggeler, H. W. *PSI Condensed Matter Research and Material Sciences Annual Report 1994/Annex FIIIA*, **1995**, 77

Summary



- observing relativistic effects on chemical character
- obtaining experimental physicochemical parameters

→

- considering relativistic effects when calculating
- utilizing relativistic effects

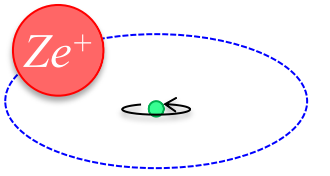
1) https://www.jaea.go.jp/02/press2021/p21070701/

Appendix

Spin-Orbit splitting (classical model)

On the electron's side, the nucleus orbits.
→A magnetic field is generated.

$$H_{\mathrm{SO}} = \frac{Ze^2}{{m_e}^2 c^2 r^2}\boldsymbol{sl}$$



$\boldsymbol{l}$**: orbital angular momentum (s, p, d, f…)**
$\boldsymbol{s}$**: spin angular momentum (↑or↓)**
$\boldsymbol{j} \equiv \boldsymbol{l} + \boldsymbol{s}$

The energies depend on not only *l* but also *s*.

1) http://cphys.s.kanazawa-u.ac.jp/20090303press/soi.html.

Pershina's calculation (1)
- introduction of relativistic effects -

Dirac equation

$$\widehat{\boldsymbol{H}}\psi = E\psi, \qquad \widehat{\boldsymbol{H}} = c\boldsymbol{\alpha}\hat{\boldsymbol{p}} + \beta mc^2 + V(\boldsymbol{r})$$

$$\begin{cases} c\sigma\hat{\boldsymbol{p}}\varphi - (2mc^2 - V(r) + \epsilon)\overline{\varphi} = 0 \\ c\sigma\hat{\boldsymbol{p}}\overline{\varphi} - (\epsilon - V(r))\varphi = 0 \end{cases}$$

in a spherical potential

$$\psi_{n\kappa m} = \begin{bmatrix} \varphi \\ \overline{\varphi} \end{bmatrix} = \begin{bmatrix} \dfrac{P_{n\kappa}(r)}{r} \mathcal{Y}_{\kappa m}(\theta,\ \phi,\ s) \\ -i\dfrac{Q_{n\kappa}(r)}{r} \mathcal{Y}_{-\kappa m}(\theta,\ \phi,\ s) \end{bmatrix}, \kappa = \begin{cases} -l-1\ (j = l+\dfrac{1}{2}) \\ l\ \ (j = l-\dfrac{1}{2}) \end{cases}$$

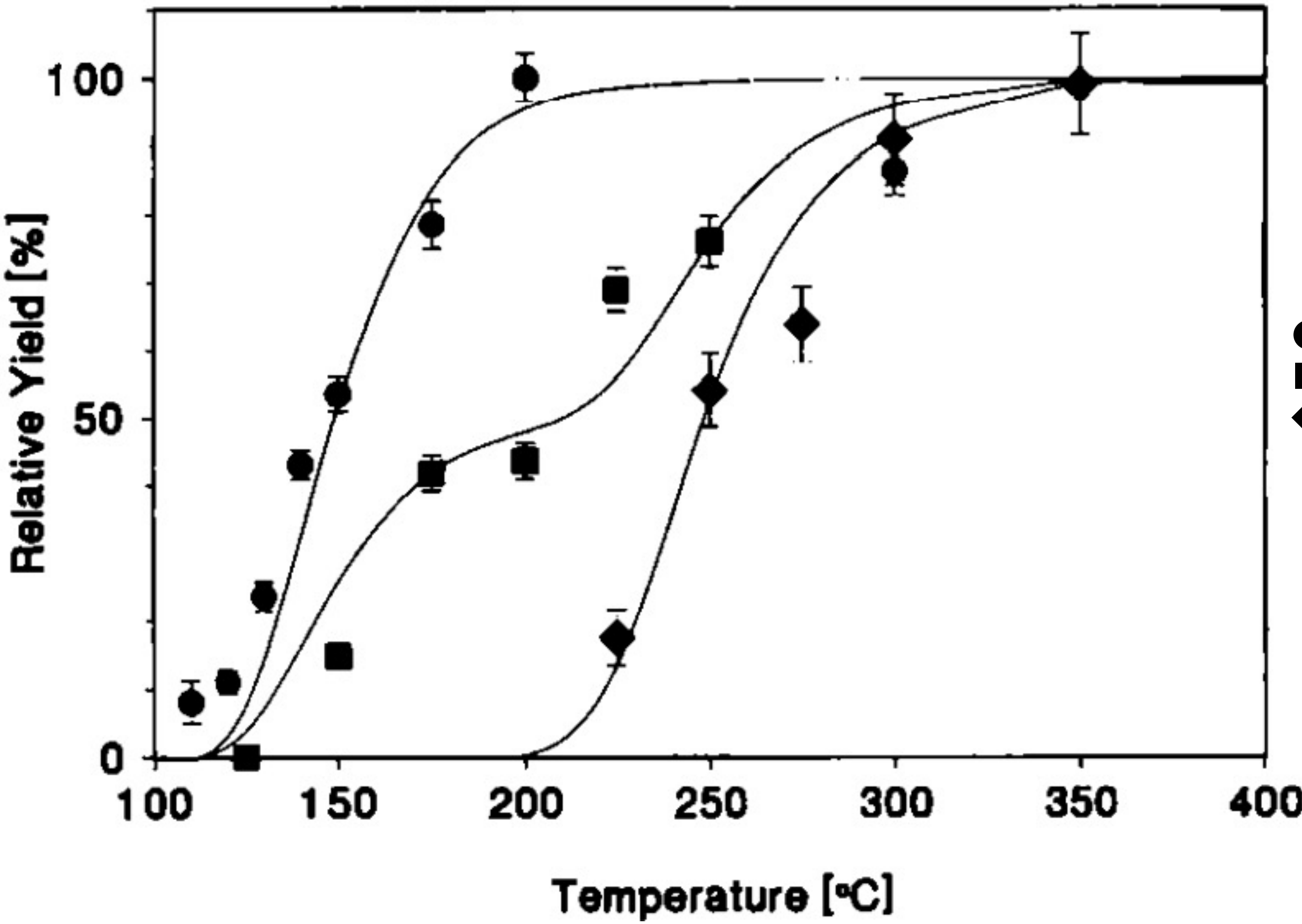
$$\mathcal{Y}_{\kappa m}(\theta,\ \phi,\ s) = \sum_{\nu} \langle s\nu lm-\nu | jm \rangle Y_{lm-\nu}(\theta,\phi)\xi_{\nu}(s)$$

$Y_{lm-\nu}(\theta,\phi)$: spherical harmonic function

$$\begin{cases} c\left(\dfrac{d}{dr} - \dfrac{\kappa}{r}\right) Q_i(r) + V(r)P_i(r) = \epsilon_i P_i(r) \\ c\left(-\dfrac{d}{dr} - \dfrac{\kappa}{r}\right) P_i(r) - 2c^2 Q_i(r) + V(r)Q_i(r) = \epsilon_i Q_i(r) \end{cases}$$

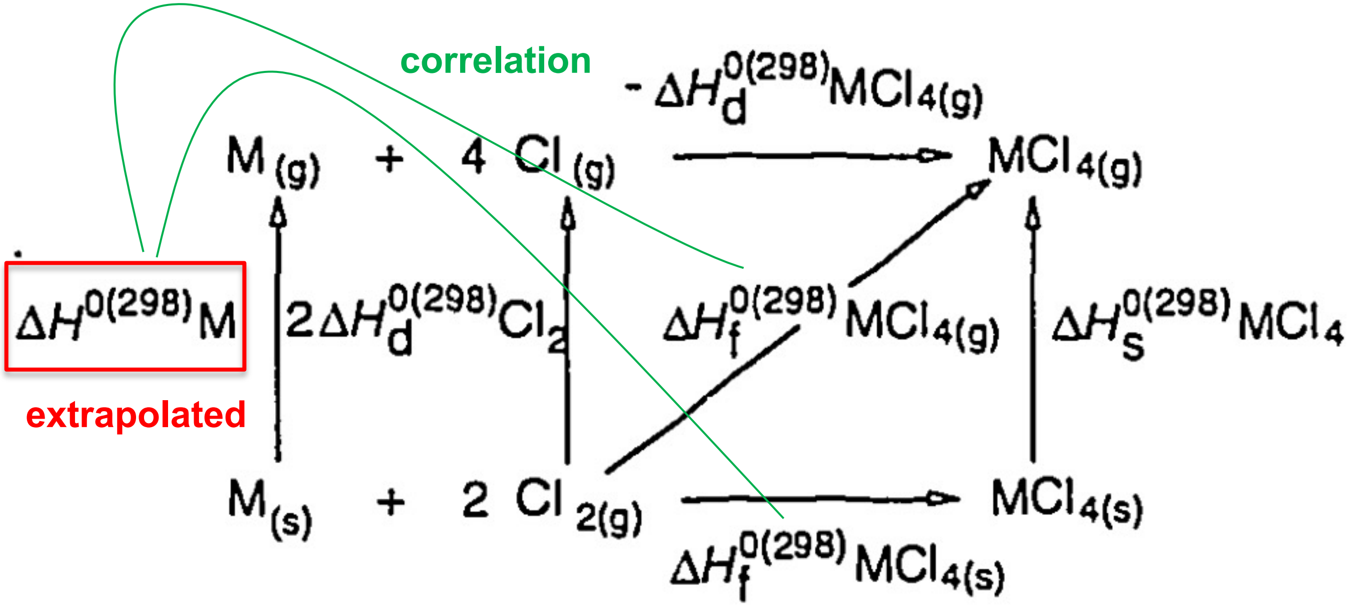
1) Rosen, A.; Ellis, D., E. *J. Chem. Phys.* **1975**, *62*, 3039.
2) 永 目 諭 一 郎（編著）『超重元素化学の最前線』、日本放射化学会、**2019**.

Contamination of $NbOCl_3$

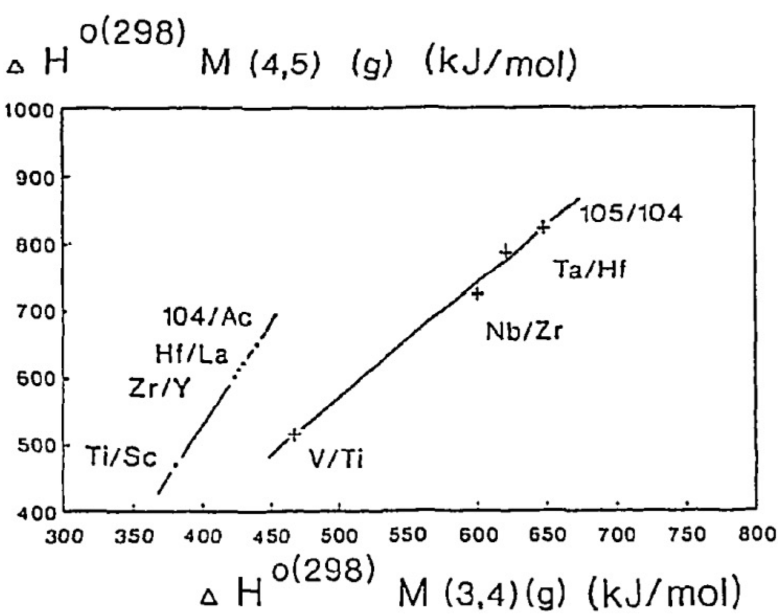


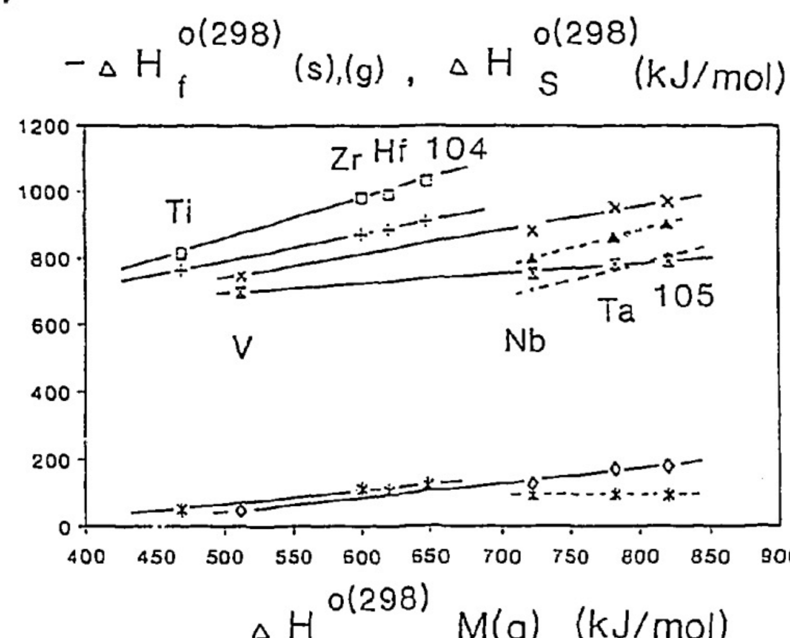
1) Türler, A.; Eichler, B.; Jost, D., T.; Piguet, D.; Gäggeler, H. W.; Gregorich, K., E.; Kadkhodayan, B.; Kreek, S., A.; Lee, D., M.; Mohar, M.; Sylwester, E.; Hoffman, D., C.; Hübener, S. *Radiochim. Acta* **1996**, *73*, 55.

Extrapolation of ΔH_{subl}



$\Delta H_f MOCl_3(g) - \Delta H_f MOCl_3(s)$
$= \Delta H_{subl} MOCl_3$





1) Eichler, B.; Türler, A.; Gäggeler, H. W. *PSI Condensed Matter Research and Material Sciences Annual Report 1994/Annex FIIIA*, **1995**, 77