Crystal Binding

Kittel Chapter 3
(1rst part)

Some basics

"Hydrogenic" atom nucleus of charge Z + $1e^-$ → $E_n \propto -\frac{Z^2}{n^2}$

Eigenstates → quantum numbers

- $n = 1, 2, \ldots$
- $\ell = 0, 1, 2, 3 \ldots n-1$ ⟹ s, p, d, f ... shells
- $\ell_z = -\ell \ldots \ell$
- $\sigma_z = +\frac{1}{2}, -\frac{1}{2}$

↓ ↓ ↓

2 6 10 ... eigenvalues

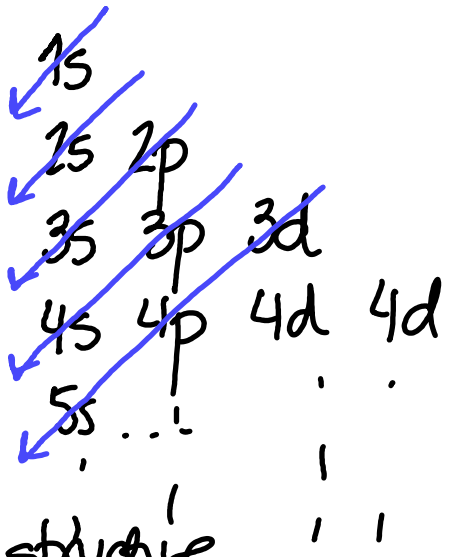
If several e⁻ in the atom,

Filling order

1) Aufbau Principle "Fill by shell"
2) Madelung's rule

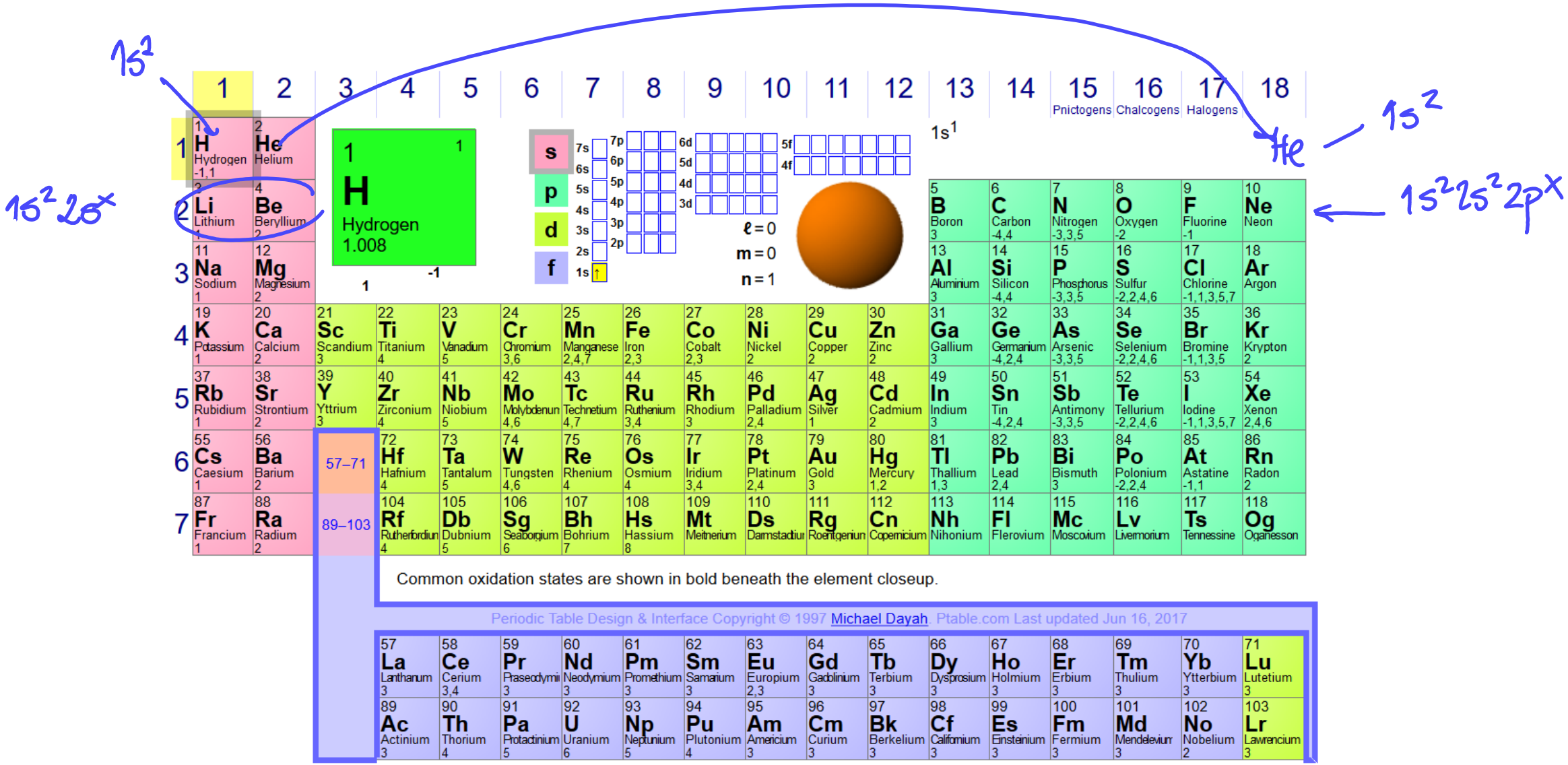
Ex. Nitrogen 7 e⁻

$1s^2\ 2s^2\ 2p^3$



the shell filling structure defines the periodic table structure

Periodic table of the elements



https://www.ptable.com/#Orbital

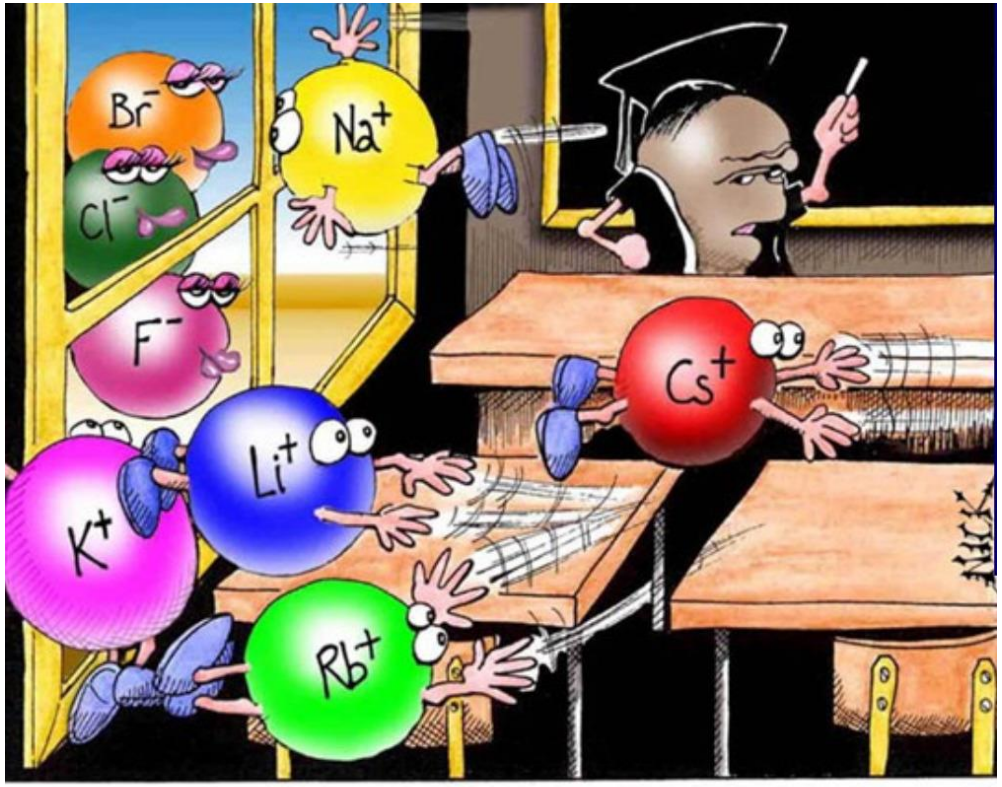
What holds a crystal together?

Mainly

→ Electrostatic interaction

(induced dipoles too)

(magnetic & gravitational forces : negligible)

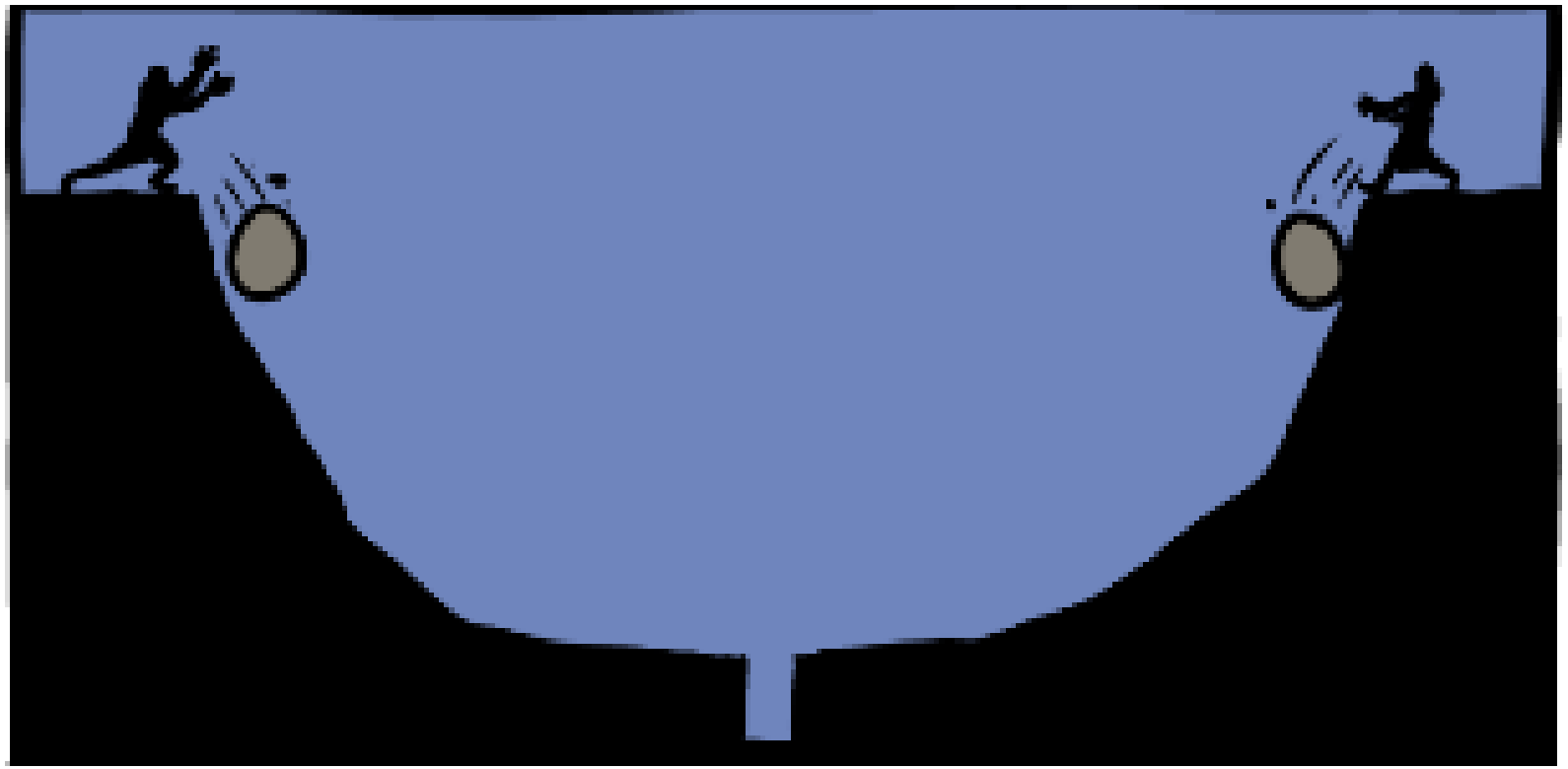


"Perhaps one of you gentlemen would mind telling me just what it is outside the window that you find so attractive..?"

Cartoon courtesy of NearingZero.net

What causes bonding?

→ Energy minimization

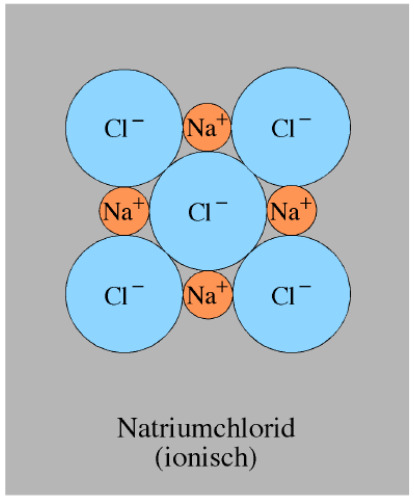


http://www.smbc-comics.com/?id=355

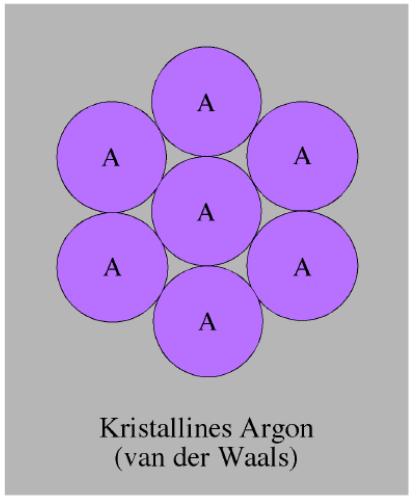
Basic types of binding

Crystals are classified with respect to their binding type

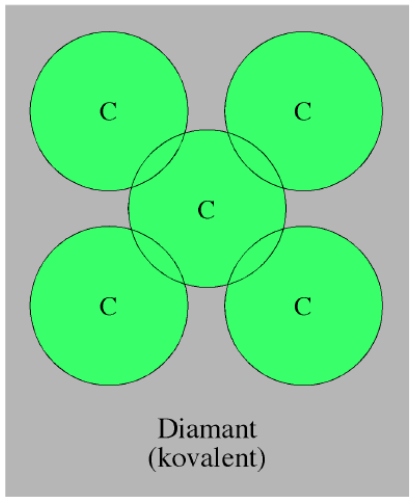
- Van der Waals
- Ionic
- Covalent
- Metal
- Hydrogen



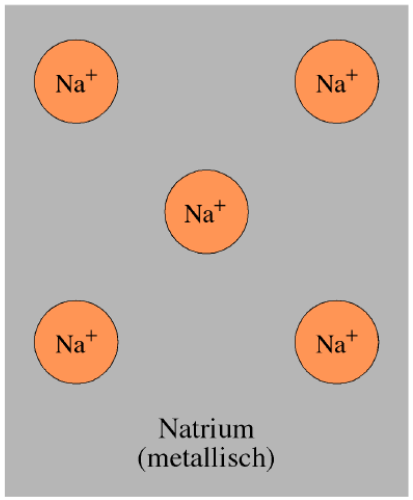
Natriumchlorid
(ionisch)



Kristallines Argon
(van der Waals)



Diamant
(kovalent)



Natrium
(metallisch)

→ the different types of bonding are due to the different distributions of valence electrons

For stability, relative energies are important:

Cohesive energy: energy that must be added to a crystal to separate its components into neutral free atoms at rest, at infinite separation, with the same electronic configuration

$$E(\text{crystal}) - E(\text{atoms})$$

Lattice energy (ionic crystals): energy that must be added to a crystal to separate its components into free ions at rest at infinite separation.

$$E(\text{crystal}) - E(\text{ions})$$

Cohesive energies

Table 1 Cohesive energies

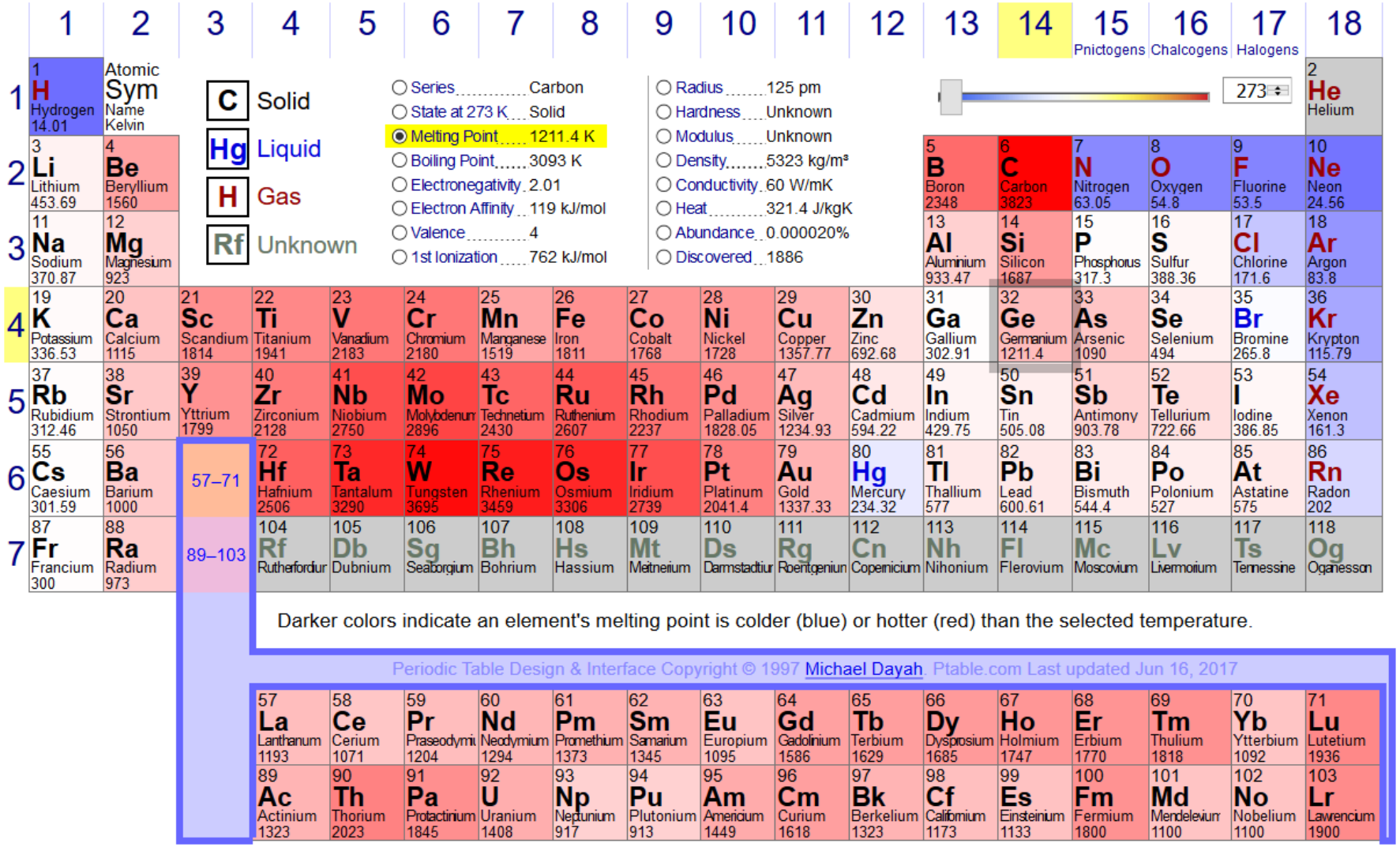
Energy required to form separated neutral atoms in their ground electronic state from the solid at 0 K at 1 atm. The data were supplied by Prof. Leo Brewer.

Li 158. 1.63 37.7	Be 320. 3.32 76.5											B 561 5.81 134	C 711 7.37 170.	N 474. 4.92 113.4	O 251. 2.60. 60.03	F 81.0 0.84 19.37	Ne 1.92 0.020 0.46
Na 107. 1.113 25.67	Mg 145. 1.51 34.7	← kJ/mol →										Al 327. 3.39 78.1	Si 446. 4.63 106.7	P 331. 3.43 79.16	S 275. 2.85 65.75	Cl 135. 1.40 32.2	Ar 7.74 0.080 1.85
		← eV/atom →															
		← kcal/mol →															
K 90.1 0.934 21.54	Ca 178. 1.84 42.5	Sc 376 3.90 89.9	Ti 468. 4.85 111.8	V 512. 5.31 122.4	Cr 395. 4.10. 94.5	Mn 282. 2.92 67.4	Fe 413. 4.28 98.7	Co 424. 4.39 101.3	Ni 428. 4.44 102.4	Cu 336. 3.49 80.4	Zn 130 1.35 31.04	Ga 271. 2.81 64.8	Ge 372. 3.85 88.8	As 285.3 2.96 68.2	Se 237 2.46 56.7	Br 118. 1.22 28.18	Kr 11.2 0.116 2.68
Rb 82.2 0.852 19.64	Sr 166. 1.72 39.7	Y 422. 4.37 100.8	Zr 603. 6.25 144.2	Nb 730. 7.57 174.5	Mo 658 6.82 157.2	Tc 661. 6.85 158.	Ru 650. 6.74 155.4	Rh 554. 5.75 132.5	Pd 376. 3.89 89.8	Ag 284. 2.95 68.0	Cd 112. 1.16 26.73	In 243. 2.52 58.1	Sn 303. 3.14 72.4	Sb 265. 2.75 63.4	Te 211 2.19 50.34	I 107. 1.11 25.62	Xe 15.9 0.16. 3.80
Cs 77.6 0.804 18.54	Ba 183. 1.90 43.7	La 431. 4.47 103.1	Hf 621 6.44 148.4	Ta 782. 8.10 186.9	W 859. 8.90 205.2	Re 775. 8.03 185.2	Os 788. 8.17 188.4	Ir 670. 6.94 160.1	Pt 564. 5.84 134.7	Au 368. 3.81 87.96	Hg 65. 0.67 15.5	Tl 182. 1.88 43.4	Pb 196. 2.03 46.78	Bi 210. 2.18 50.2	Po 144. 1.50 34.5	At	Rn 19.5 0.202 4.66
Fr	Ra 160. 1.66 38.2	Ac 410. 4.25 98.															

Ce 417. 4.32 99.7	Pr 357. 3.70 85.3	Nd 328. 3.40 78.5	Pm	Sm 206. 2.14 49.3	Eu 179. 1.86 42.8	Gd 400. 4.14 95.5	Tb 391. 4.05 93.4	Dy 294. 3.04 70.2	Ho 302. 3.14 72.3	Er 317. 3.29 75.8	Tm 233. 2.42 55.8	Yb 154. 1.60 37.1	Lu 428. 4.43 102.2
Th 598. 6.20 142.9	Pa	U 536. 5.55 128.	Np 456 4.73 109.	Pu 347. 3.60 83.0	Am 264. 2.73 63.	Cm 385 3.99 92.1	Bk	Cf	Es	Fm	Md	No	Lr

Melting point

→ Cohesive energy has a strong impact on the melting point



https://www.ptable.com/#Orbital

Van der Waals interaction

typical between inert atoms (He, Ne, Kr...) and between inert molecules (i.e. N_2)

Noble (inert) gases : electron distribution in the crystalline state = free atom

- all electronic shells are completly filled
- spherically symmetric charge distributions
- closed packed structures (fcc) [except He]
- ionization energy is high

- weakly bounded : interaction between induced dipoles
  → van der Waals interaction