

Crystal Binding

Kittel Chapter 3
(1st part)

Some basics

"Hydrogenic" atom nucleus of charge $Z + 1e^-$

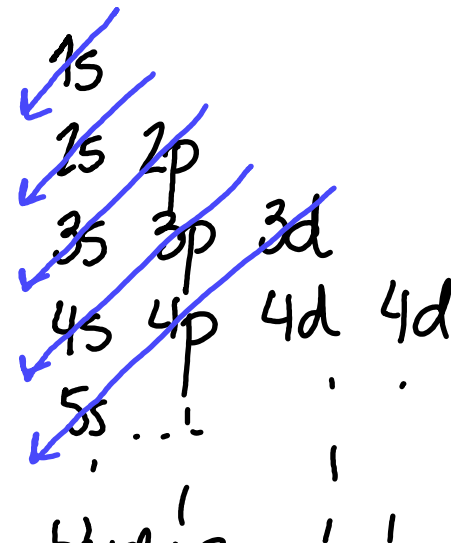
Eigenstates \rightarrow quantum numbers

{	$n = 1, 2, \dots$	}	\Rightarrow	$s, p, d, f \dots$	shells		
	$l = 0, 1, 2, 3 \dots n-1$			\downarrow	\downarrow	\downarrow	
	$l_z = -l \dots l$			2	6	10	\dots
	$\sigma_z = +\frac{1}{2}, -\frac{1}{2}$			eigenvalues			

$E_n \propto -\frac{Z^2}{n^2}$

If several e^- in the atom,
Filling order

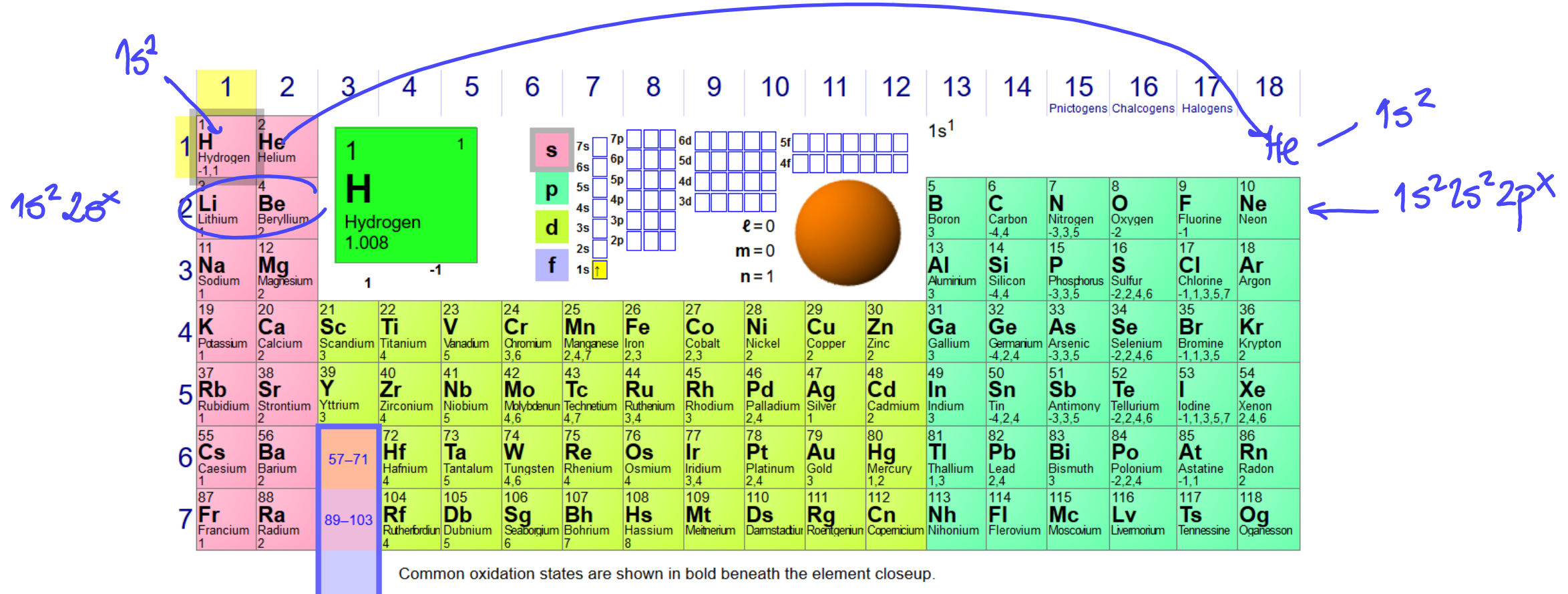
- 1) Aufbau Principle "Fill by shell"
- 2) Madelung's rule



Ex. Nitrogen $7e^-$
 $1s^2 2s^2 2p^3$

the shell filling structure defines the periodic table structure

Periodic table of the elements



Periodic Table Design & Interface Copyright © 1997 Michael Dayah Ptable.com Last updated Jun 16, 2017

57 La Lanthanum 3	58 Ce Cerium 3,4	59 Pr Praseodymi 3	60 Nd Neodymium 3	61 Pm Promethium 3	62 Sm Samarium 3	63 Eu Europium 2,3	64 Gd Gadolinium 3	65 Tb Terbium 3	66 Dy Dysprosium 3	67 Ho Holmium 3	68 Er Erbium 3	69 Tm Thulium 3	70 Yb Ytterbium 3	71 Lu Lutetium 3
89 Ac Actinium 3	90 Th Thorium 4	91 Pa Protactinium 5	92 U Uranium 6	93 Np Neptunium 5	94 Pu Plutonium 4	95 Am Americium 3	96 Cm Curium 3	97 Bk Berkelium 3	98 Cf Californium 3	99 Es Einsteinium 3	100 Fm Fermium 3	101 Md Mendelevium 3	102 No Nobelium 2	103 Lr Lawrencium 3

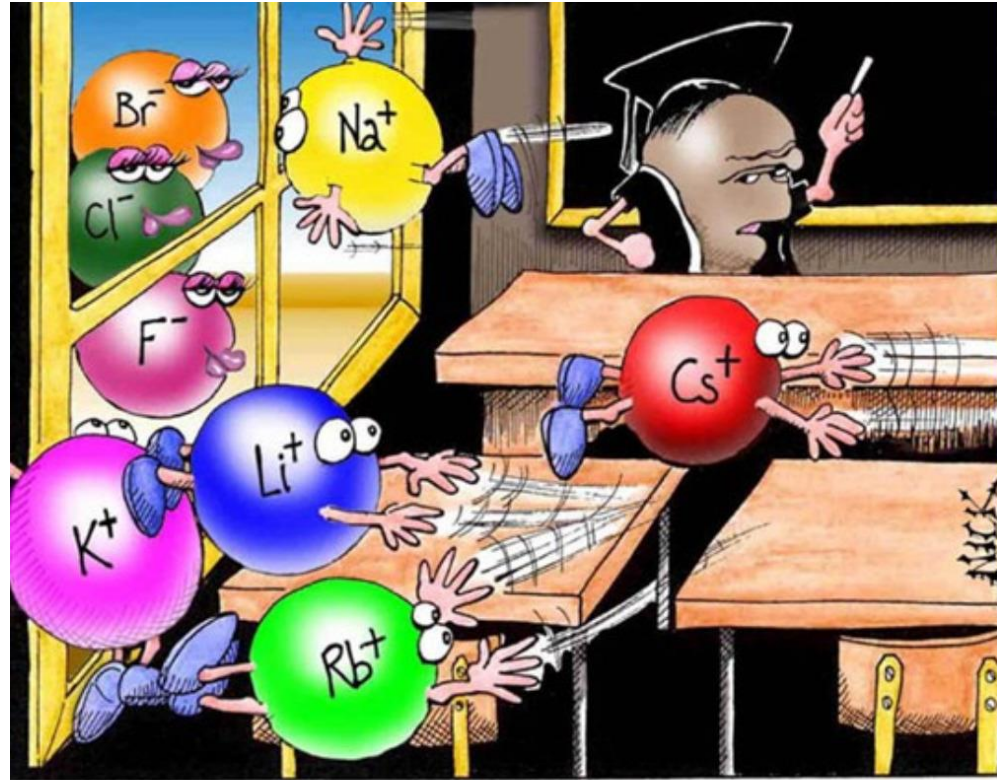
What holds a crystal together?

mainly

→ Electrostatic interaction

(induced dipoles too)

(magnetic & gravitational forces : negligible)

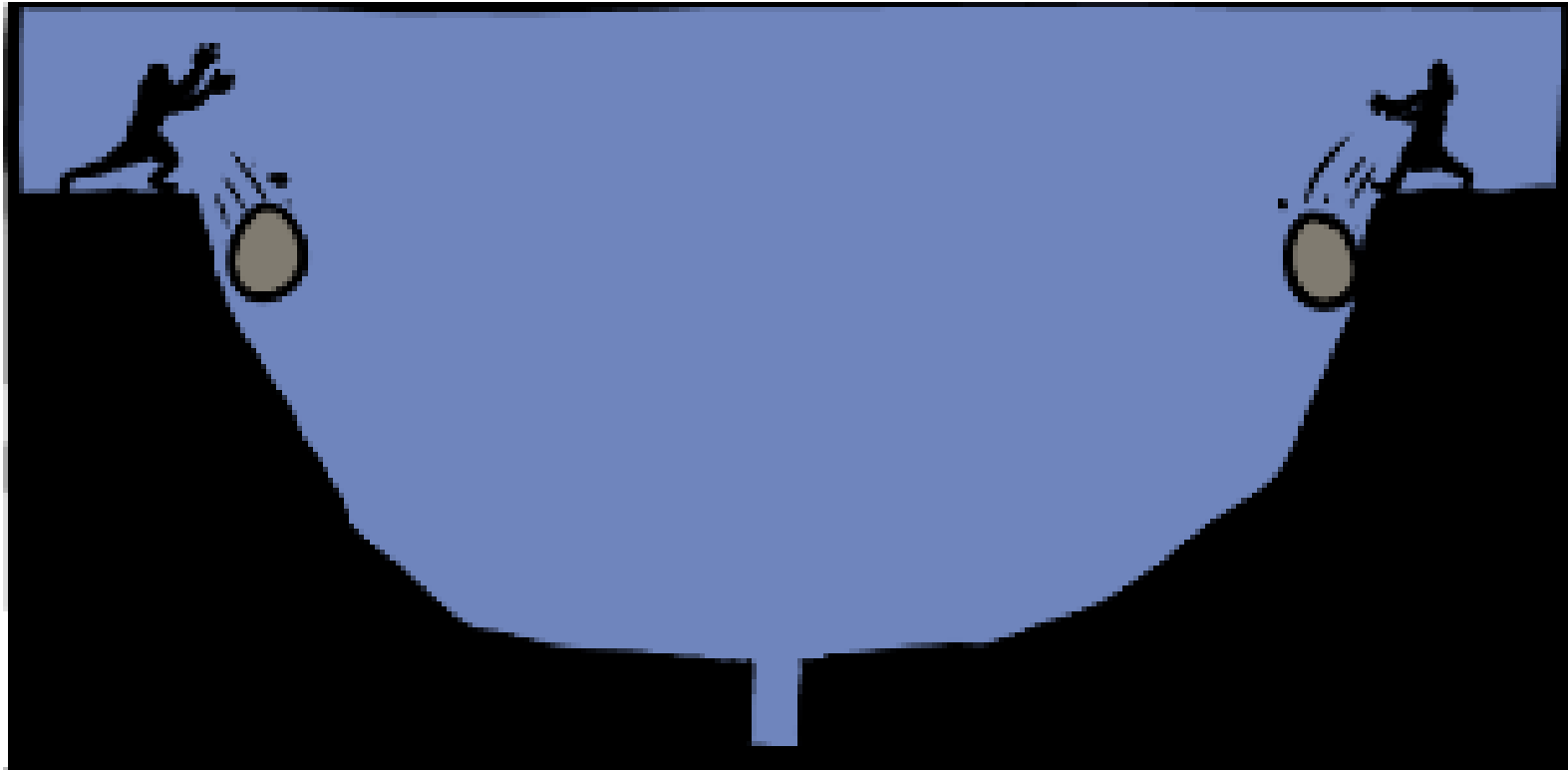


"Perhaps one of you gentlemen would mind telling me just what it is outside the window that you find so attractive..?"

Cartoon courtesy of NearingZero.net

What causes bonding?

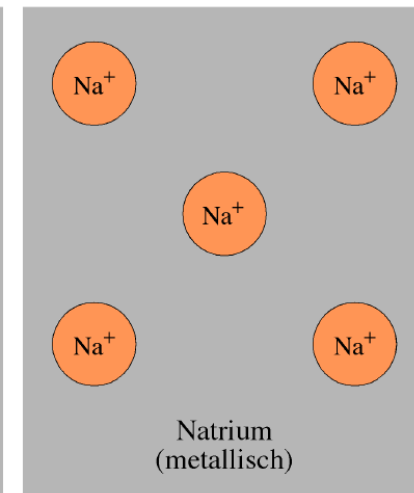
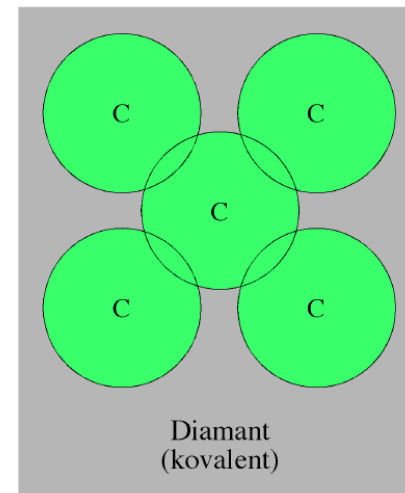
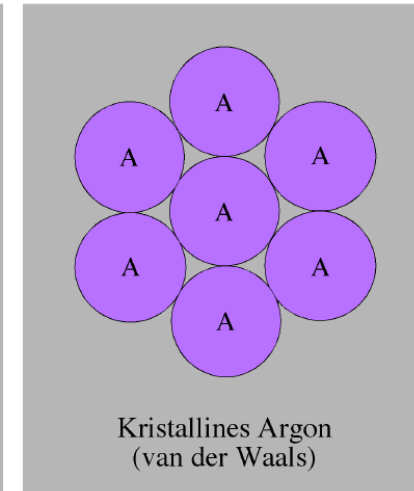
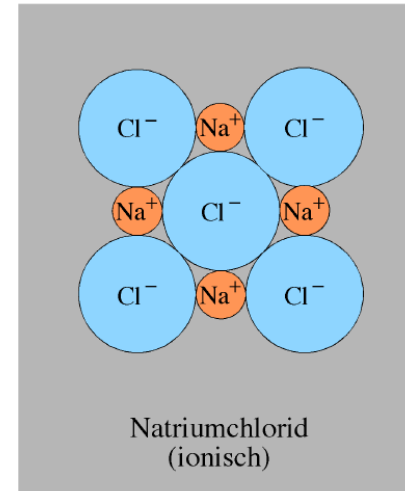
→ Energy minimization



Basic types of binding

Crystals are classified with respect to their binding type

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



→ 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

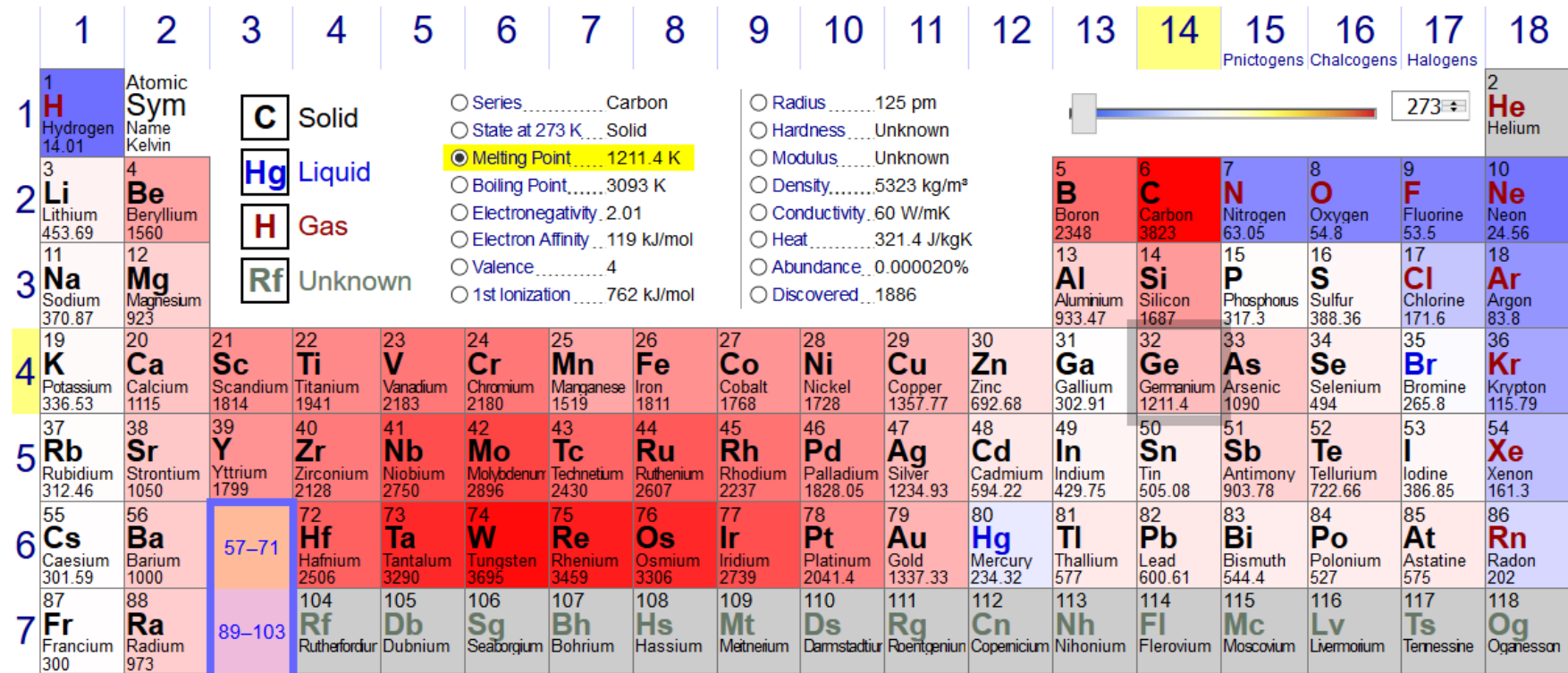
Energy required to form separated neutral atoms in their ground electronic state from the solid at 0 K at 1 atm. The data were supplied by Prof. Leo Brewer.

← kJ/mol →
← eV/atom →
← kcal/mol →

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											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																												
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.	<table border="1"> <tbody> <tr> <td>Ce 417. 4.32 99.7</td> <td>Pr 357. 3.70 85.3</td> <td>Nd 328. 3.40 78.5</td> <td>Pm</td> <td>Sm 206. 2.14 49.3</td> <td>Eu 179. 1.86 42.8</td> <td>Gd 400. 4.14 95.5</td> <td>Tb 391. 4.05 93.4</td> <td>Dy 294. 3.04 70.2</td> <td>Ho 302. 3.14 72.3</td> <td>Er 317. 3.29 75.8</td> <td>Tm 233. 2.42 55.8</td> <td>Yb 154. 1.60 37.1</td> <td>Lu 428. 4.43 102.2</td> </tr> <tr> <td>Th 598. 6.20 142.9</td> <td>Pa</td> <td>U 536. 5.55 128.</td> <td>Np 456 4.73 109.</td> <td>Pu 347. 3.60 83.0</td> <td>Am 264. 2.73 63.</td> <td>Cm 385 3.99 92.1</td> <td>Bk</td> <td>Cf</td> <td>Es</td> <td>Fm</td> <td>Md</td> <td>No</td> <td>Lr</td> </tr> </tbody> </table>															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
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



Darker colors indicate an element's melting point is colder (blue) or hotter (red) than the selected temperature.

Periodic Table Design & Interface Copyright © 1997 Michael Dayah. Ptable.com Last updated Jun 16, 2017

57 La Lanthanum 1193	58 Ce Cerium 1071	59 Pr Praseodymium 1204	60 Nd Neodymium 1294	61 Pm Promethium 1373	62 Sm Samarium 1345	63 Eu Europium 1095	64 Gd Gadolinium 1586	65 Tb Terbium 1629	66 Dy Dysprosium 1685	67 Ho Holmium 1747	68 Er Erbium 1770	69 Tm Thulium 1818	70 Yb Ytterbium 1092	71 Lu Lutetium 1936
89 Ac Actinium 1323	90 Th Thorium 2023	91 Pa Protactinium 1845	92 U Uranium 1408	93 Np Neptunium 917	94 Pu Plutonium 913	95 Am Americium 1449	96 Cm Curium 1618	97 Bk Berkelium 1323	98 Cf Californium 1173	99 Es Einsteinium 1133	100 Fm Fermium 1800	101 Md Mendelevium 1100	102 No Nobelium 1100	103 Lr Lawrencium 1900

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 completely filled
- spherically symmetric charge distributions
- closed packed structures (fcc) [except He]
- ionization energy is high
- weakly bonded : interaction between induced dipoles
→ van der Waals interaction