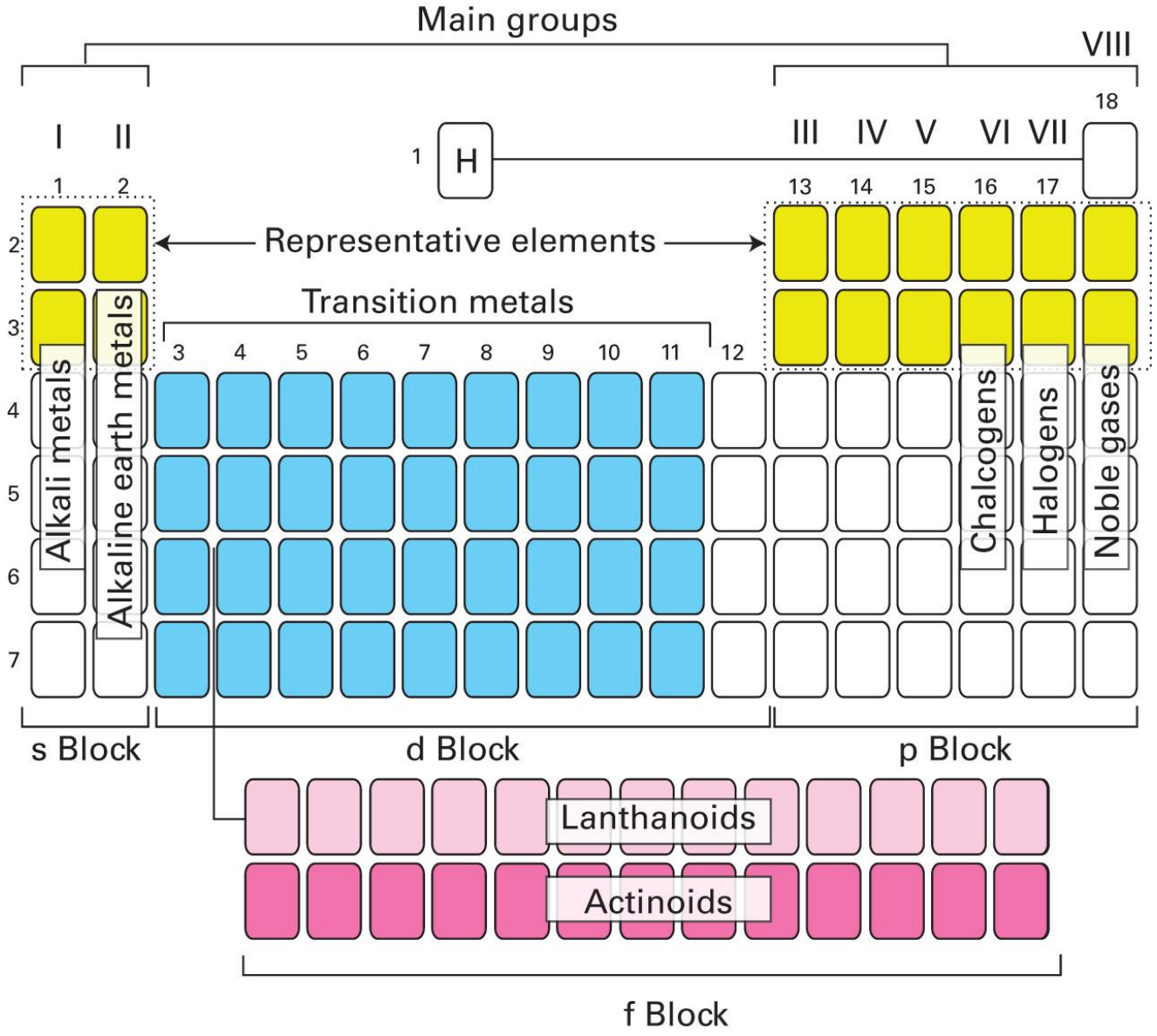
Lecture 6 January 2019

Electrons in Atoms: Z_{eff} as Determinant of Ionization Energies, and Other Properties



Trends in Atomic Properties

- Size (atomic, ionic, covalent, van der Waals radii)
- Ionization Potential ($A^0_{(g)} + I.E. \longrightarrow A^+ + e^-$)
- Electron Affinity Energies ($A^0_{(g)} + e^- \rightarrow A^- + E.A.E.$)
- Electronegativity: Ability of an atom, within a molecule to attract electrons to itself.

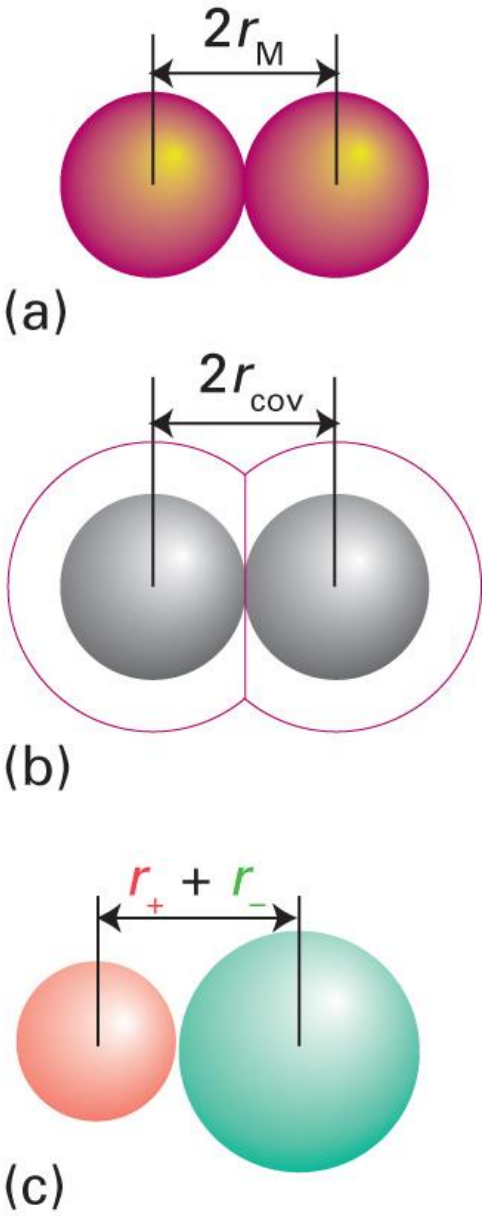
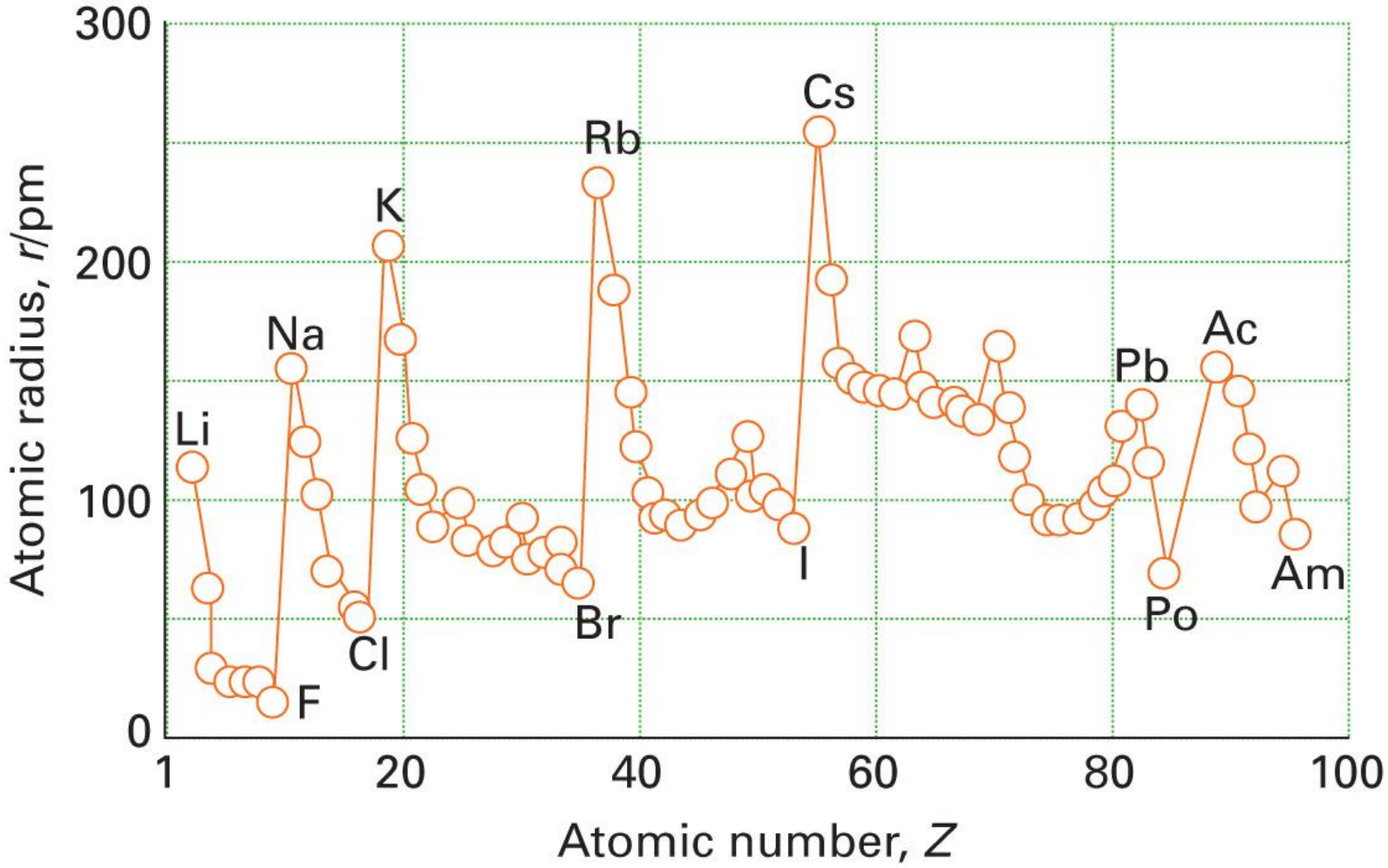


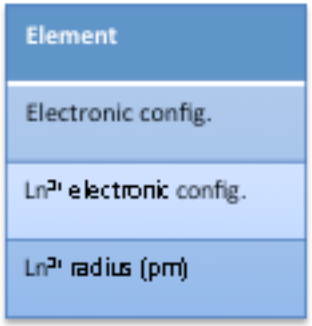
Table 1.3 Atomic radii, *r*/pm*

Li	Be											B	C	N	O	F
157	112											88	77	74	73	71
Na	Mg											Al	Si	P	S	Cl
191	160											143	118	110	104	99
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
235	197	164	147	135	129	137	126	125	125	128	137	140	122	122	117	114
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
250	215	182	160	147	140	135	134	134	137	144	152	150	140	141	135	133
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		
272	224	188	159	147	141	137	135	136	139	144	155	155	154	152		

* The values refer to coordination number 12 for metallic radii (see Section 3.2).



Lanthanide Contraction: particulary large decrease in ionic radii size due to Particularly poor shielding by electrons in f orbitals.



t	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
ation with	$5d^1 6s^2$	$4f^1 5d^1 6s^2$	$4f^3 6s^2$	$4f^4 6s^2$	$4f^5 6s^2$	$4f^6 6s^2$	$4f^7 6s^2$	$4f^7 5d^1 6s^2$	$4f^9 6s^2$	$4f^{10} 6s^2$	$4f^{11} 6s^2$	$4f^{12} 6s^2$	$4f^{13} 6s^2$	$4f^{14} 6s^2$	$4f^{14} 5d^1 6$
ctron ation	$4f^0$	$4f^1$	$4f^2$	$4f^3$	$4f^4$	$4f^5$	$4f^6$	$4f^7$	$4f^8$	$4f^9$	$4f^{10}$	$4f^{11}$	$4f^{12}$	$4f^{13}$	$4f^{14}$
ius ite)	103	102	99	98.3	97	95.8	94.7	93.8	92.3	91.2	90.1	89	88	86.8	86.1

Cations are smaller than Neutral atom

Anions are Larger than Neutral atom

Table 1.4 Ionic radii, *r*/pm*

Li^+	Be^{2+}	B^{3+}			N^{3-}	O^{2-}	F^-
59(4)	27(4)	11(4)			146	135(2)	128(2)
76(6)						138(4)	131(4)
						140(6)	133(6)
						142(8)	
Na^+	Mg^{2+}	Al^{3+}			P^{3-}	S^{2-}	Cl^-
99(4)	49(4)	39(4)			212	184(6)	181(6)
102(6)	72(6)	53(6)					
132(8)	103(8)						
K^+	Ca^{2+}	Ga^{3+}			As^{3-}	Se^{2-}	Br^-
138(6)	100(6)	62(6)			222	198(6)	196(6)
151(8)	112(8)						
159(10)	123(10)						
160(12)	134(12)						
Rb^+	Sr^{2+}	In^{3+}	Sn^{2+}	Sn^{4+}		Te^{2-}	I^-
148(6)	118(6)	80(6)	83(6)	69(6)		221(6)	220(6)
160(8)	125(8)	92(8)	93(8)				
173(12)	144(12)						
Cs^+	Ba^{2+}	Tl^{3+}					
167(6)	135(6)	89(6)					
174(8)	142(8)	Tl^+					
188(12)	175(12)	150(6)					

* Numbers in parentheses are the coordination number of the ion. For more values, see *Resource section 1*.

Trends in Atomic Properties

- Size (atomic, ionic, covalent, van der Waals radii)
- Ionization Potential energy

  $(A^0_{(g)} + \text{I.E.} \longrightarrow A^+ + e^-)$
- Electron Affinity Energy $(A^0_{(g)} + e^- \longrightarrow A^- + \text{E.A.E.})$
- Electronegativity: Ability of an atom, within a molecule to attract electrons to itself.

Ionization Energies (eV) of Atoms and Ions

Hydrogen	H	1	13.5984				
Helium	He	2	24.5874	54.417760			
Lithium	Li	3	5.3917	75.6400	122.45429		
Beryllium	Be	4	9.3227	18.21114	153.89661	217.71865	
Boron	B	5	8.2980	25.1548	37.93064	259.37521	340.22580
Carbon	C	6	11.2603	24.3833	47.8878	64.4939	392.087
Nitrogen	N	7	14.5341	29.6013	47.44924	77.4735	97.8902
Oxygen	O	8	13.6181	35.1211	54.9355	77.41353	113.8990
Fluorine	F	9	17.4228	34.9708	62.7084	87.1398	114.2428
Neon	Ne	10	21.5646	40.96296	63.45	97.12	126.21
Sodium	Na	11	5.1391	47.2864	71.6200	98.91	138.40
Magnesium	Mg	12	7.6462	15.03527	80.1437	109.2655	141.27
Aluminum	Al	13	5.9858	18.82855	28.44765	119.992	153.825
Silicon	Si	14	8.1517	16.34584	33.49302	45.14181	166.767
Phosphorus	P	15	10.4867	19.7695	30.2027	51.4439	65.0251
Sulfur	S	16	10.3600	23.33788	34.79	47.222	72.5945
Chlorine	Cl	17	12.9676	23.8136	39.61	53.4652	67.8
Argon	Ar	18	15.7596	27.62965	40.74	59.81	75.02
Potassium	K	19	4.3407	31.63	45.806	60.91	82.66
Calcium	Ca	20	6.1132	11.87172	50.9131	67.27	84.50
Scandium	Sc	21	6.5615	12.79977	24.75666	73.4894	91.65
Titanium	Ti	22	6.8281	13.5755	27.4917	43.2672	99.30
Vanadium	V	23	6.7462	14.618	29.311	46.709	65.2817
Chromium	Cr	24	6.7665	16.4857	30.96	49.16	69.46
Manganese	Mn	25	7.4340	15.6400	33.668	51.2	72.4
Iron	Fe	26	7.9024	16.1877	30.652	54.8	75.0
Cobalt	CO	27	7.8810	17.084	33.50	51.3	79.5
Nickel	Ni	28	7.6398	18.16884	35.19	54.9	76.06
Copper	Cu	29	7.7264	20.2924	36.841	57.38	79.8
Zinc	Zn	30	9.3942	17.96439	39.723	59.4	82.6
Gallium	Ga	31	5.9993	20.51514	30.71	64	87
Germanium	Ge	32	7.8994	15.93461	34.2241	45.7131	93.5
Arsenic	As	33	9.7886	18.5892	28.351	50.13	62.63
Selenium	Se	34	9.7524	21.19	30.8204	42.9450	68.3
Bromine	Br	35	11.8138	21.591	36.	47.3	59.7
Krypton	Kr	36	13.9996	24.35984	36.950	52.5	64.7
Rubidium	Rb	37	4.1771	27.2895	40	52.6	71.0
Strontium	Sr	38	5.6949	11.0301	42.89	57	71.6
Yttrium	Y	39	6.2171	12.22	20.52	60.597	77.0

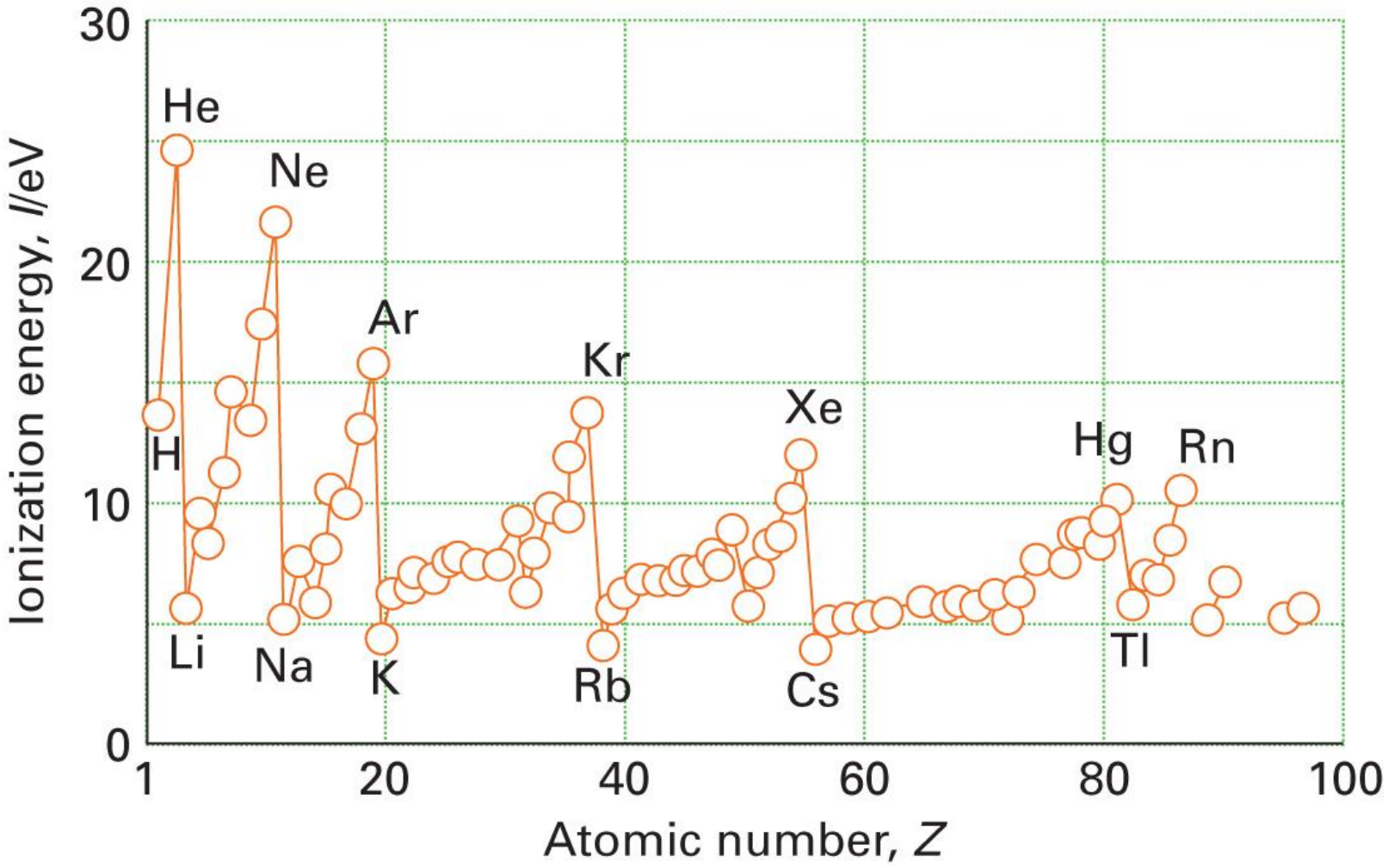
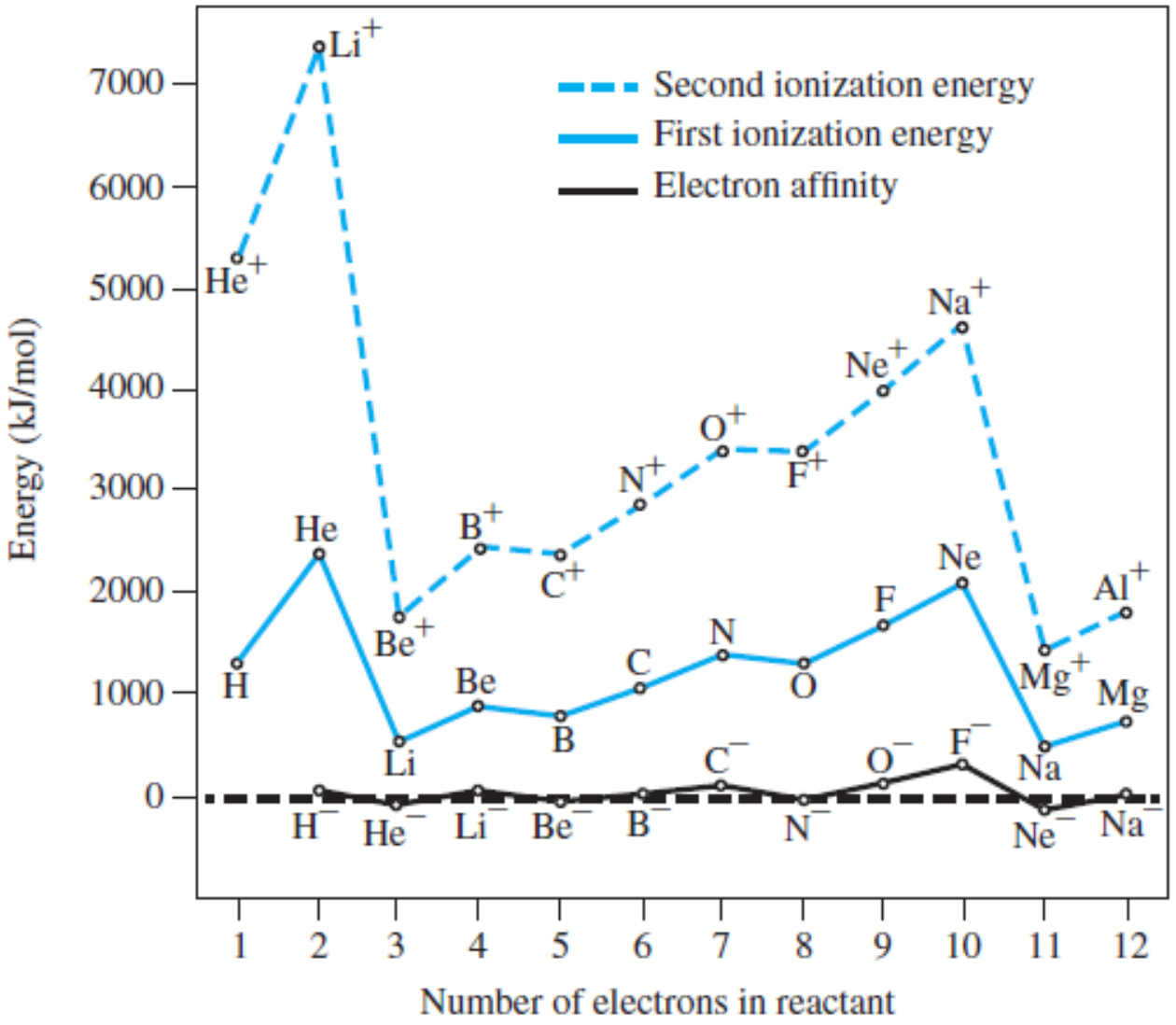


Table 1.5 First, second, and third (and some fourth) ionization energies of the elements, I/(kJ mol^{-1})

H							He
1312							2373
							5259
Li	Be	B	C	N	O	F	Ne
513	899	801	1086	1402	1314	1681	2080
7297	1757	2426	2352	2855	3386	3375	3952
11809	14844	3660	4619	4577	5300	6050	6122
		25018					
Na	Mg	Al	Si	P	S	Cl	Ar
495	737	577	786	1011	1000	1251	1520
4562	1476	1816	1577	1903	2251	2296	2665
6911	7732	2744	3231	2911	3361	3826	3928
		11574					
K	Ca	Ga	Ge	As	Se	Br	Kr
419	589	579	762	947	941	1139	1351
3051	1145	1979	1537	1798	2044	2103	3314
4410	4910	2963	3302	2734	2974	3500	3565
Rb	Sr	In	Sn	Sb	Te	I	Xe
403	549	558	708	834	869	1008	1170
2632	1064	1821	1412	1794	1795	1846	2045
3900	4210	2704	2943	2443	2698	3197	3097
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
375	502	590	716	704	812	926	1036
2420	965	1971	1450	1610	1800	1600	
3400	3619	2878	3080	2466	2700	2900	



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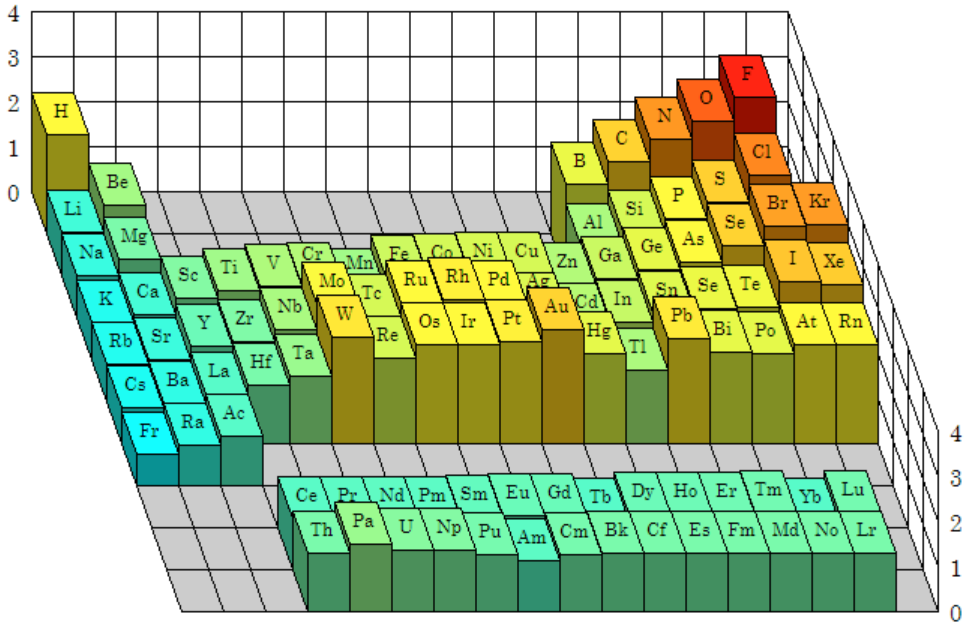
375	502	590	716	704	812	926	1036
2420	965	1971	1450	1610	1800	1600	
3400	3619	2878	3080	2466	2700	2900	

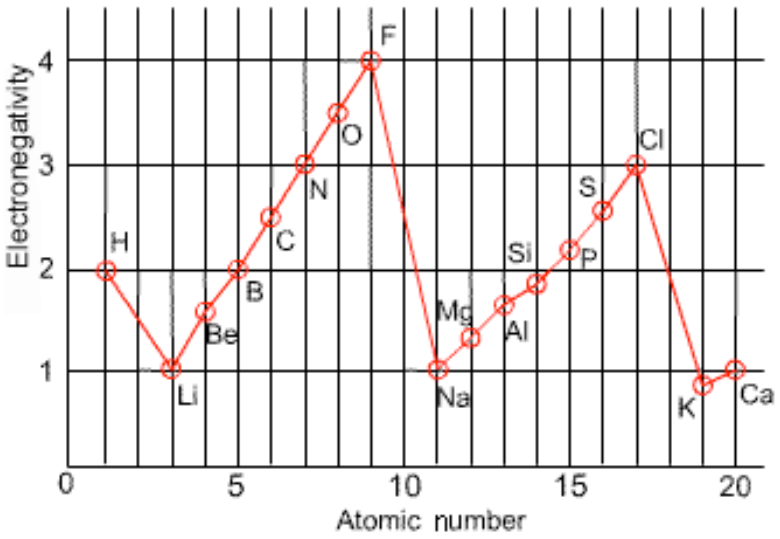
Table 1.6 First electron affinities of the main-group elements, E_a/(kJ mol^{-1})*

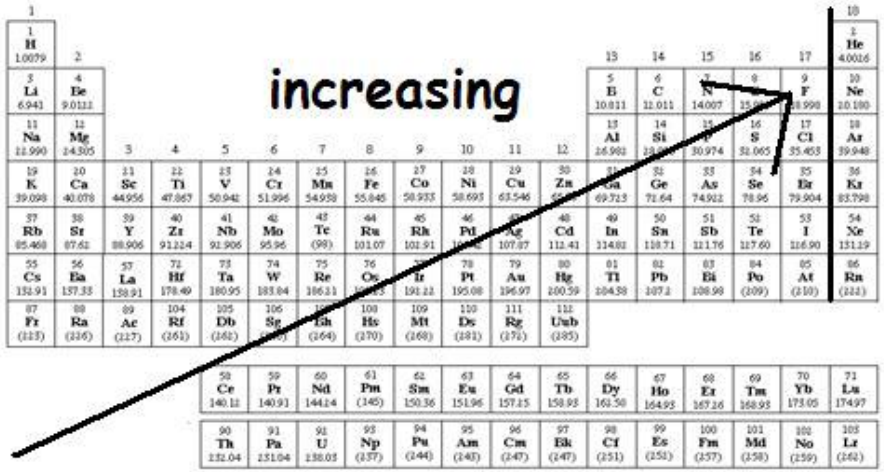
H							He
72							−48
Li	Be	B	C	N	O	F	Ne
60	≤ 0	27	122	−8	141	328	−116
					−780		
Na	Mg	Al	Si	P	S	Cl	Ar
53	≤ 0	43	134	72	200	349	−96
					−492		
K	Ca	Ga	Ge	As	Se	Br	Kr
48	2	29	116	78	195	325	−96
Rb	Sr	In	Sn	Sb	Te	I	Xe
47	5	29	116	103	190	295	−77

* The first values refer to the formation of the ion X^- from the neutral atom; the second value to the formation of X^{2-} from X^-.

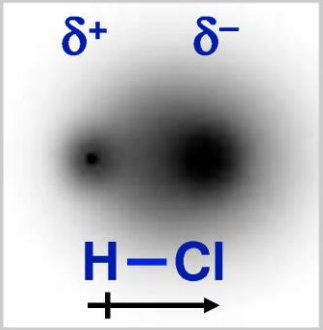


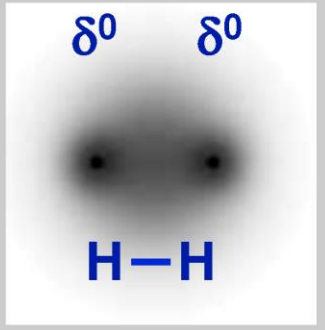
Electronegativity





Electronegativity





BDE: 427 436 kJ/mol

Electronegativity-

- Pauling

$$|\chi_A - \chi_B| = 0.208 \sqrt{E_{A\text{-}B} - \underbrace{1/2(E_{A\text{-}A} + E_{B\text{-}B})}_{\text{arithmetic mean}}}$$

$$|\chi_A - \chi_B| = 0.208 \sqrt{E_{A\text{-}B} - \underbrace{(E_{A\text{-}A}.E_{B\text{-}B})^{1/2}}_{\text{geometric mean}}}$$

- Mulliken

$$\chi_m = \frac{1}{2}(I + E_{ea})$$

- Rochow

Allred and Rochow Scale

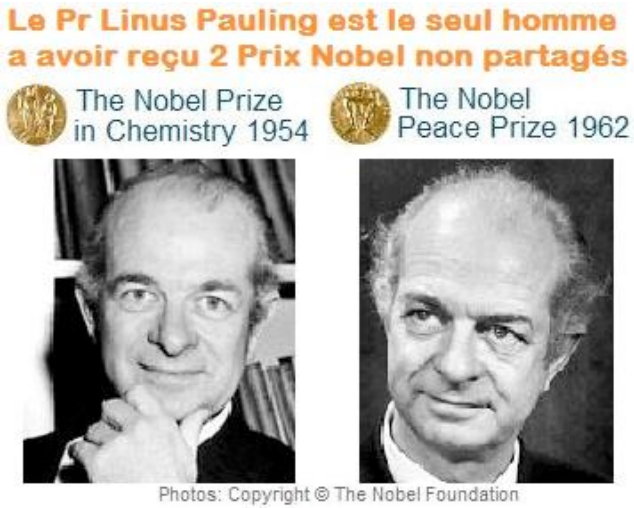
This scale considers electronegativity as the force acting on electrons at a distance of the covalent radius.

$$\chi = 0.744 + \frac{0.359\, Z_{eff}}{r_{cov}^2}$$

Z_{eff} = Effective nuclear charge

r_{cov} = Covalent radius of the atom in Angstroms.

Linus Pauling



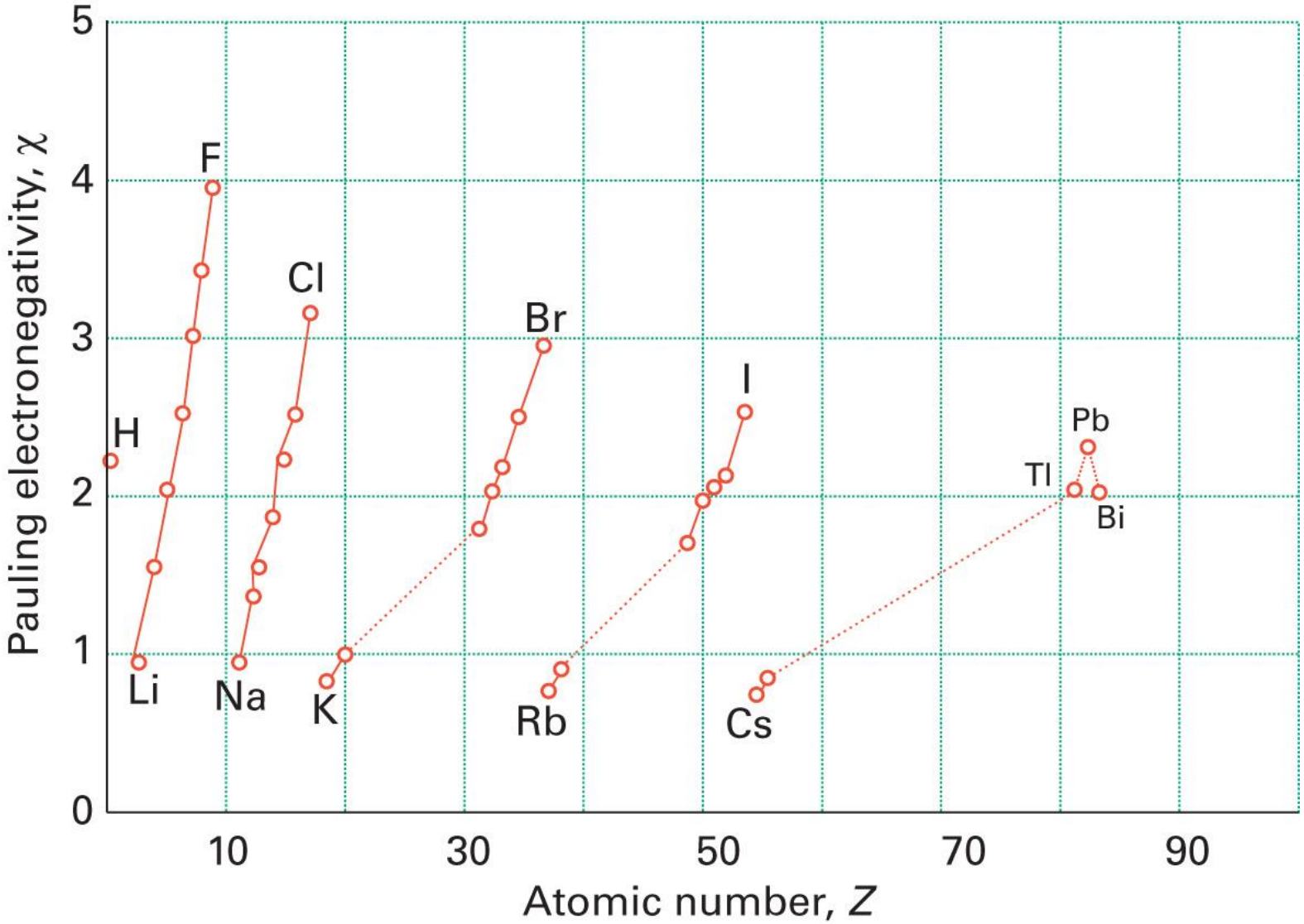
BDE H_2 = 436 kJ/mol
BDE Cl_2 = 239
BDE HCl = 427

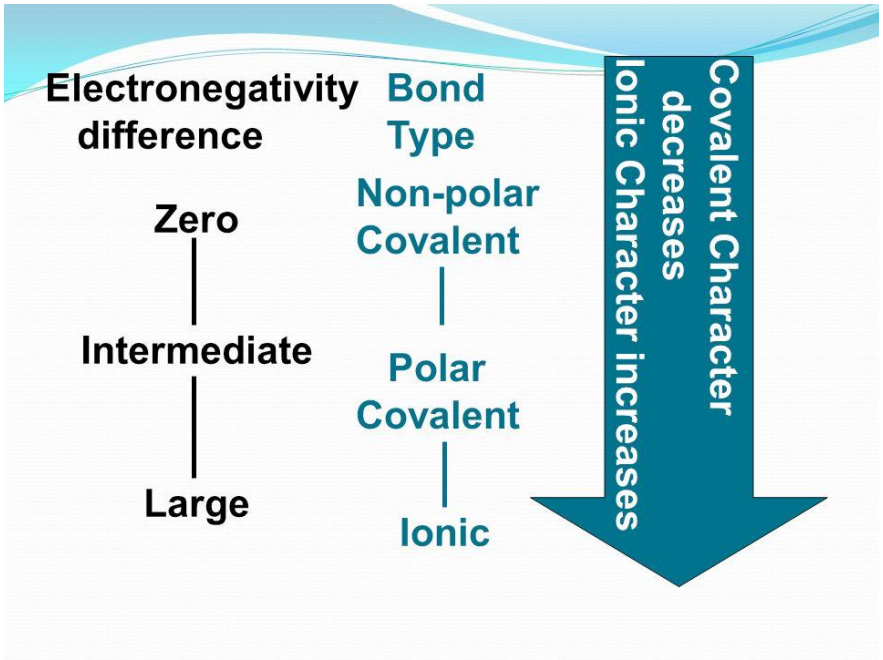
Pauling: If strictly covalent: BDE HCl should be average of H2 and Cl2

Which would be ½ (436 + 239) = 338 kJ/mol. The extra stability is Due to electronegativity difference, and electrostatic attraction.

Table 1.7 Pauling χ_P, Mulliken, χ_M, and Allred–Rochow, χ_{AR}, electronegativities

H							He
2.20							5.5
3.06							
2.20							
Li	Be	B	C	N	O	F	Ne
0.98	1.57	2.04	2.55	3.04	3.44	3.98	
1.28	1.99	1.83	2.67	3.08	3.22	4.43	4.60
0.97	1.47	2.01	2.50	3.07	3.50	4.10	5.10
Na	Mg	Al	Si	P	S	Cl	Ar
0.93	1.31	1.61	1.90	2.19	2.58	3.16	
1.21	1.63	1.37	2.03	2.39	2.65	3.54	3.36
1.01	1.23	1.47	1.74	2.06	2.44	2.83	3.30
K	Ca	Ga	Ge	As	Se	Br	Kr
0.82	1.00	1.81	2.01	2.18	2.55	2.96	3.0
1.03	1.30	1.34	1.95	2.26	2.51	3.24	2.98
0.91	1.04	1.82	2.02	2.20	2.48	2.74	3.10
Rb	Sr	In	Sn	Sb	Te	I	Xe
0.82	0.95	1.78	1.96	2.05	2.10	2.66	2.6
0.99	1.21	1.30	1.83	2.06	2.34	2.88	2.59
0.89	0.99	1.49	1.72	1.82	2.01	2.21	2.40
Cs	Ba	Tl	Pb	Bi			
0.79	0.89	2.04	2.33	2.02			
0.70	0.90	1.80	1.90	1.90			
0.86	0.97	1.44	1.55	1.67			





en= electronegativity

en > 1.7 = ionic bond

en < 1.7 = Polar covalent bond

en = 0
is non-polar covalent bond

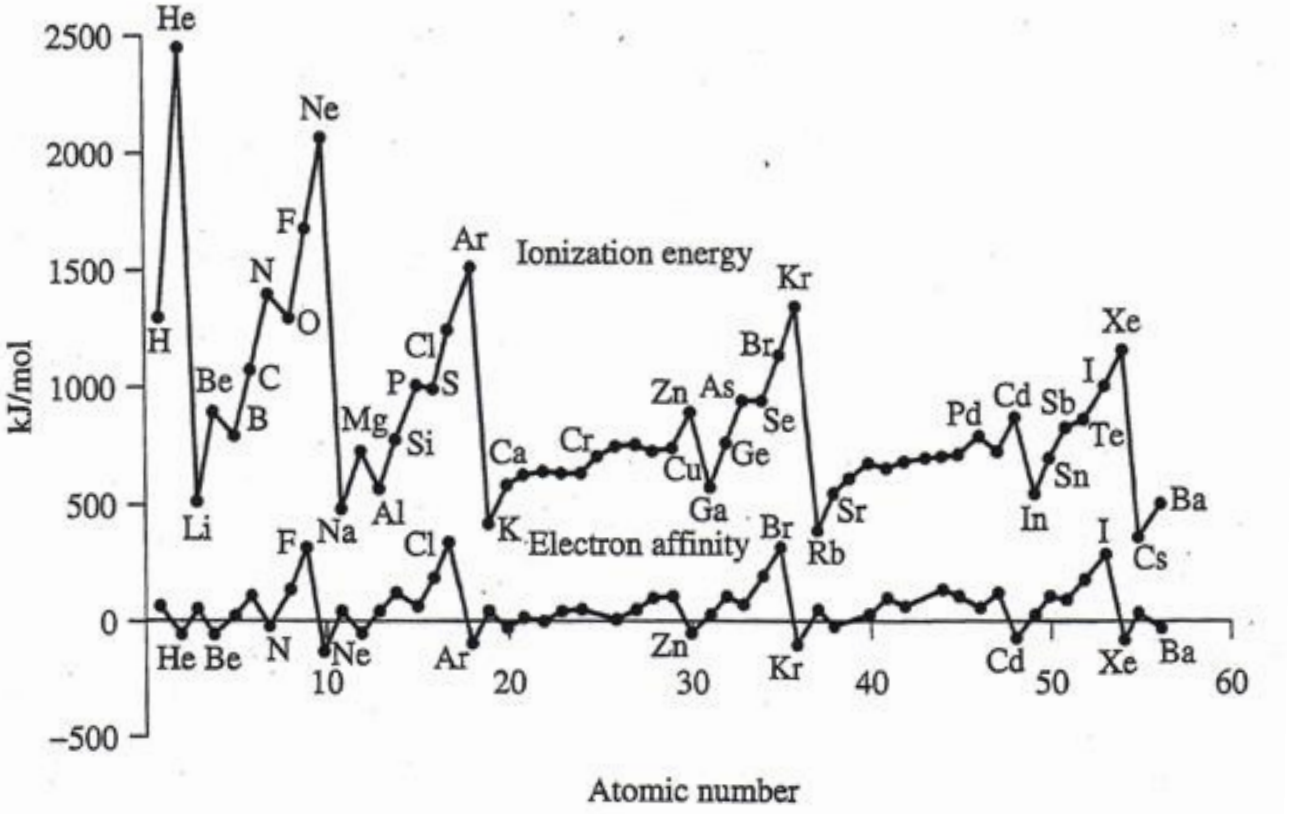
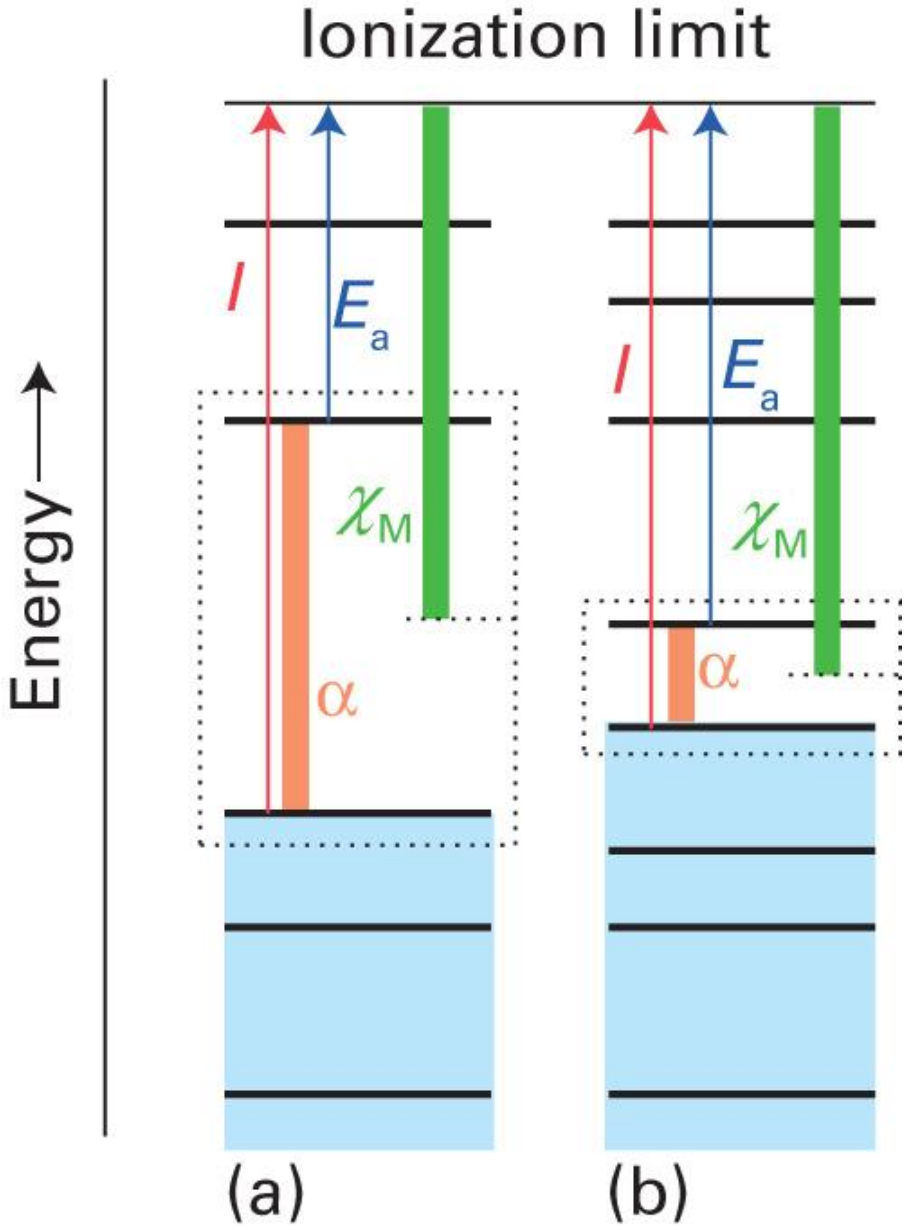


FIGURE 2-13 Ionization Energies and Electron Affinities. Ionization energy = ΔU for $M(g) \longrightarrow M^+(g) + e$ (Data from C.E. Moore, *Ionization Potentials and Ionization Limits*, National Standards Reference Data Series, U. S. National Bureau of Standards, Washington, DC, **1970**, NSRDS-NBS 34) Electron affinity = ΔU for $M^-(g) \longrightarrow M(g) + e^-$ (Data from H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data*, **1985**, *14*, 731). Numerical values are in Appendices B-2 and B-3.



Lewis Structures

See: https://www.youtube.com/watch?v=DQclmBeIKTc

OF_2 CH_4 H_2

CO_2 BH_3 O_3

NH_4^+ SO_4^{2-} PO_4^{3-}

Lecture 7 January 2019

Lewis Structures, Formal Charges, Oxidation States