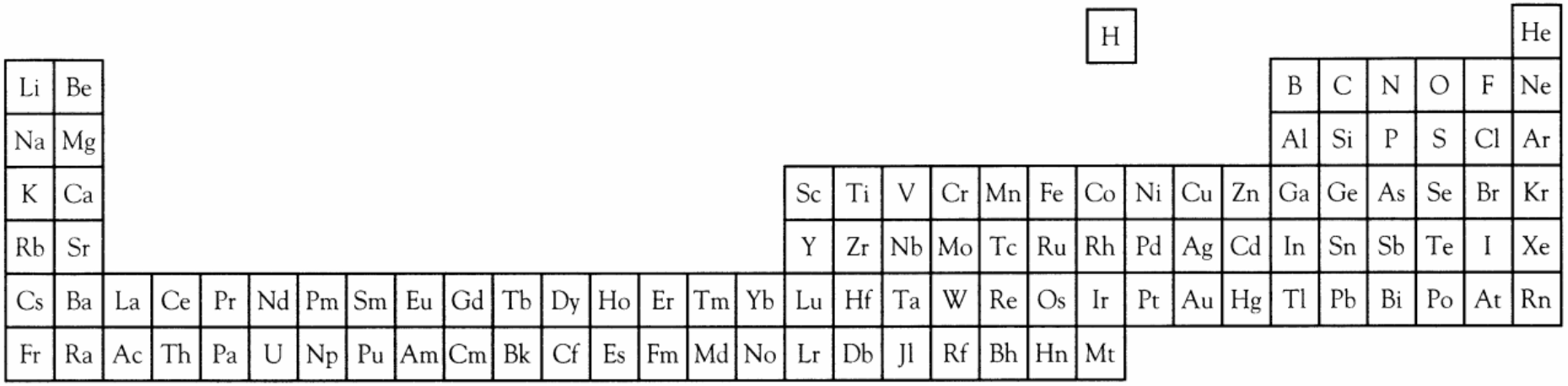
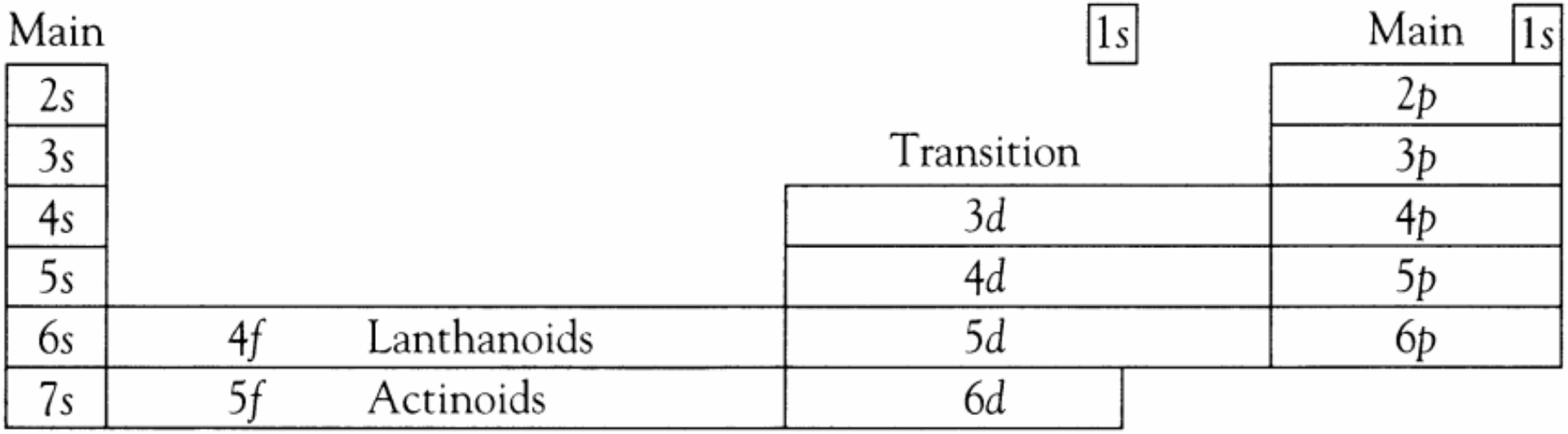
Chemistry 3830

Electronic Configuration - 2

Aufbau (Building-up) Principle





Shielding of Nuclear Charge

Effective nuclear charge = Z_{eff} = Z – S; S = shielding constant

Z_{eff} (also called Z*) values have been calculated: available in tables

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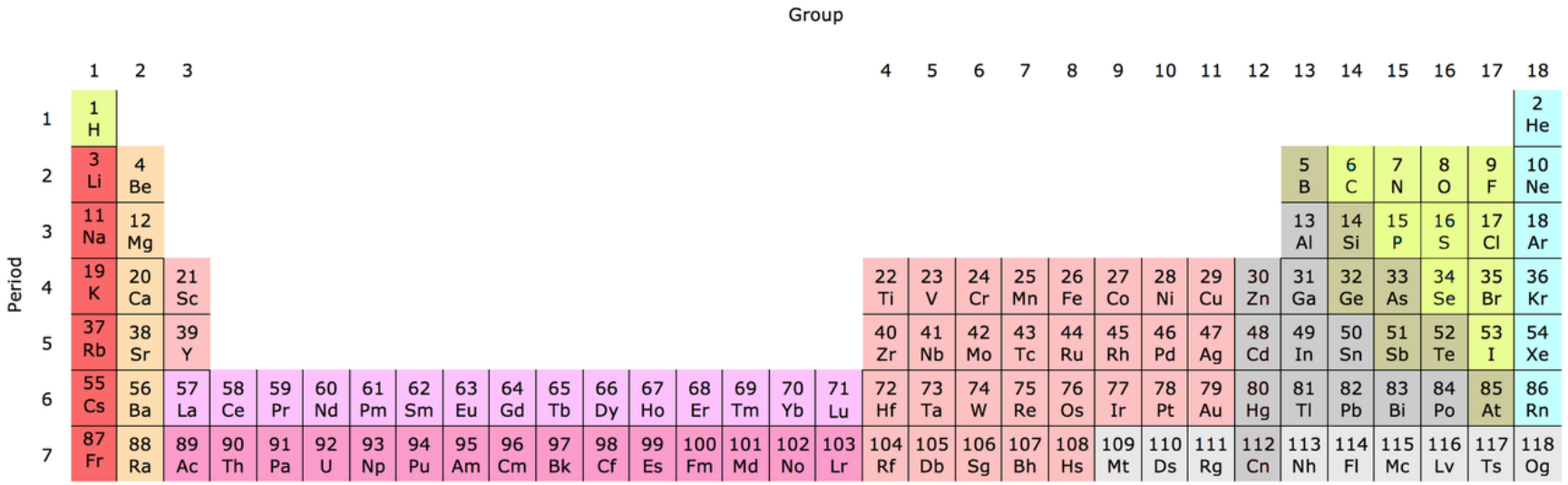
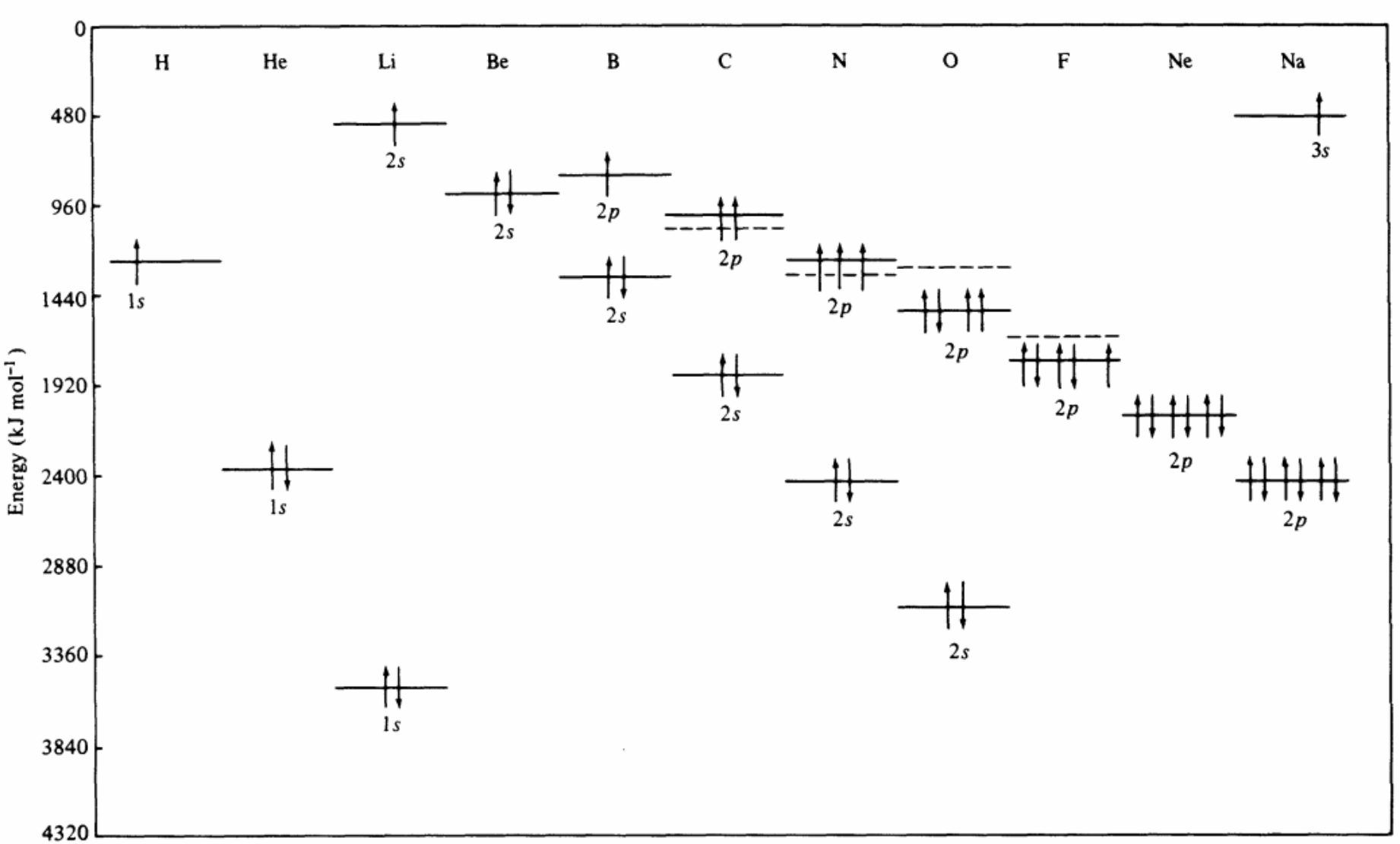


Multi-Electron Atoms



Valence orbitals: Ionization energy of orbitals are between 480 and 2400 kJ/mol

Shielding of Nuclear Charge

Table of effective nuclear charges for elements 1 to 36

Element	1*s*	2*s*	2*p*	3*s*	3*p*	4s	3*d*	4*p*
H	1.000							
He	1.688							
Li	2.691	1.279						
Be	3.685	1.912						
B	4.680	2.576	2.421					
C	5.673	3.217	3.136					
N	6.665	3.847	3.834					
O	7.658	4.492	4.453					
F	8.650	5.128	5.100					
Ne	9.642	5.758	5.758					
Na	10.626	6.571	6.802	2.507				
Mg	11.619	7.392	7.826	3.308				
Al	12.591	8.214	8.963	4.117	4.066			
Si	13.575	9.020	9.945	4.903	4.285			
P	14.558	9.825	10.961	5.642	4.886			
S	15.541	10.629	11.977	6.367	5.482			
Cl	16.524	11.430	12.993	7.068	6.116			
Ar	17.508	12.230	14.008	7.757	6.764			
K	18.490	13.006	15-027	8.680	7.726	3.495		
Ca	19.473	13.776	16.041	9.602	8.658	4.398		
Sc	20.457	14.574	17.055	10.340	9.406	4.632	7.120	
Ti	21.441	15.377	18.065	11.033	10.104	4.817	8.141	
V	22.426	16.181	19.073	11.709	10.785	4.981	8.983	
Cr	23.414	16.984	20.075	12.368	11.466	5.133	9.757	
Mn	24.396	17.794	21.084	13.018	12.109	5.283	10.528	
Fe	25.381	18.599	22.089	13.676	12.778	5.434	11.180	
Co	26.367	19.405	23.092	14.322	13.435	5.576	11.855	
Ni	27.353	20.213	24.095	14.961	14.085	5.711	12.530	
Cu	28.339	21.020	25.097	15.594	14-731	5.858	13.201	
Zn	29.325	21.828	26.098	16.219	15.369	5.965	13.878	
Ga	30.309	22.599	27.091	16.996	16.204	7.067	15.093	6.222
Ge	31.294	23.365	28.082	17.760	17.014	8.044	16.251	6.780
As	32.278	24.127	29.074	18.596	17.850	8.944	17.378	7.449
Se	33.262	24.888	30.065	19.403	18.705	9.758	18.477	8.287
Br	34.247	25.643	31.056	20.218	19-571	10.553	19.559	9.028
Kr	35.232	26.398	32.047	21.033	20.434	11.316	20.626	9.769

Effective nuclear charge = $Z_{eff} = Z - S$

S = shielding constant

K versus Cu

Shielding of Nuclear Charge

Summary:

1. *s* orbitals are less shielded than other orbitals, and simultaneously more effective at shielding other orbitals/electrons
2. *p* orbitals are quite similar to *s* orbitals, but are slightly more shielded and less effective at shielding other orbitals/electrons
3. *d* or *f* orbitals are much less penetrating (toward the nucleus); hence, they are very well shielded by intervening *s* or *p* orbitals. They themselves are very poor at shielding higher lying orbitals.

Slater's Rules

$$Z_{eff} = Z - S$$

Slater's Rules for calculating the shielding constant S

1. Write out the electron configuration of the elements in the following order and observe Slater's groupings!:

   (1*s*)(2*s*, 2*p*)(3*s*, 3*p*)(3*d*)(4*s*,4*p*)(4*d*)(4f)(5*s*, 5*p*)(5*d*) etc.
2. Electrons in any grouping to the right (higher-lying oribtals) of the group being considered contribute nothing to the shielding constant.
3. All of the electrons in the same grouping shield each other by **0.35** (except 1*s* where 0.30 works better.)
4. All electrons in *s*,*p* groupings are shielded by **0.85** by all electrons in the (*n* – 1) shell, while *d* or *f* electrons are completely shielded by any electrons in groups to the left, i.e. **1.0**.
5. All electrons in (*n*-2) and lower shells shield completely, **1.0**.

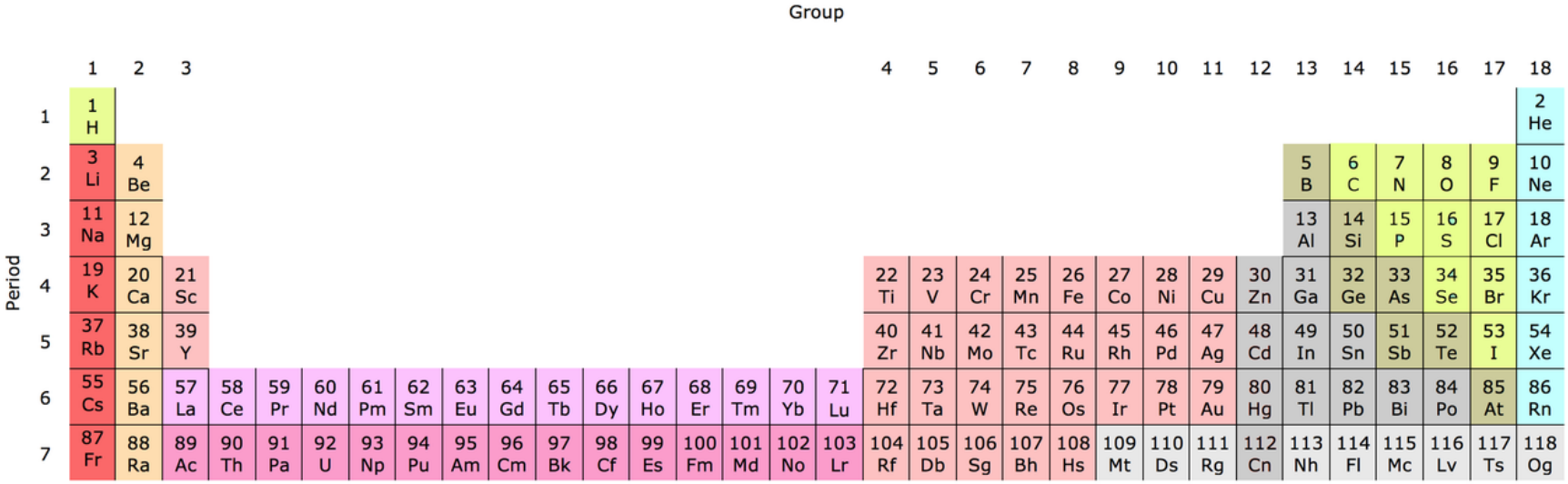
N: $(1s)^2\ (2s, 2p)^5$

Z_{eff} for a 2*p* electron

Thus $Z_{eff} = 7 - [(2 \times 0.85) + (4 \times 0.35)] = 3.9$

Tabulated $Z_{eff} = 3.834$

Slater's Rules



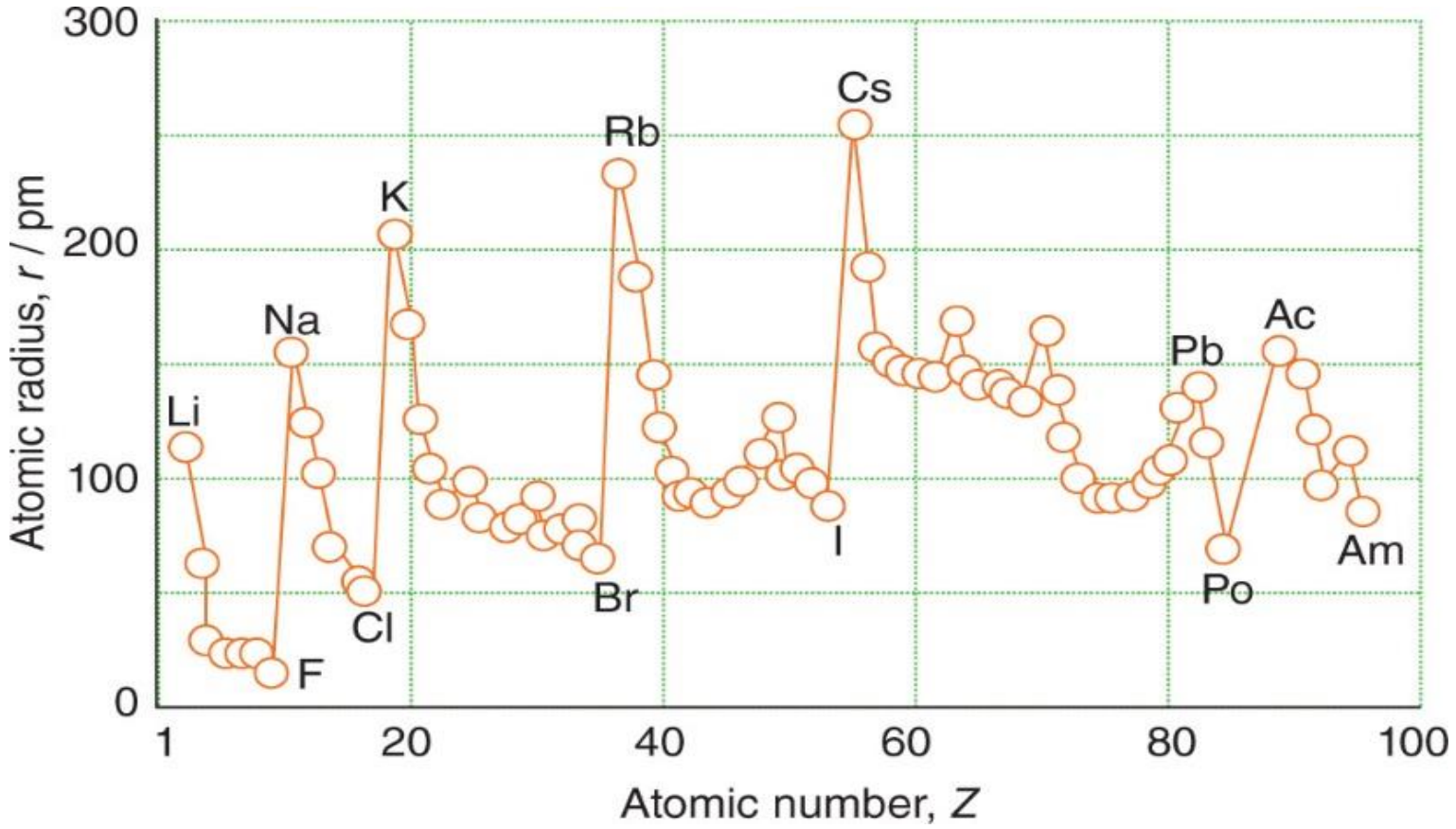
Zn: $(1s)^2(2s,2p)^8(3s,3p)^8(3d)^{10}(4s)^2$ Z_{eff} for a *4s* electron

$Z_{eff} = 30 - [(10 \times 1.00) + (18 \times 0.85) + (1 \times 0.35)] = 4.35$ Tabulated $Z_{eff} = 5.965$

Zn: $(1s)^2(2s,2p)^8(3s,3p)^8(3d)^{10}(4s)^2$ Z_{eff} for a 3*d* electron

$Z^* = 30 - [(18 \times 1.00) + (9 \times 0.35)] = 8.85$ Tabulated $Z_{eff} = 13.878$

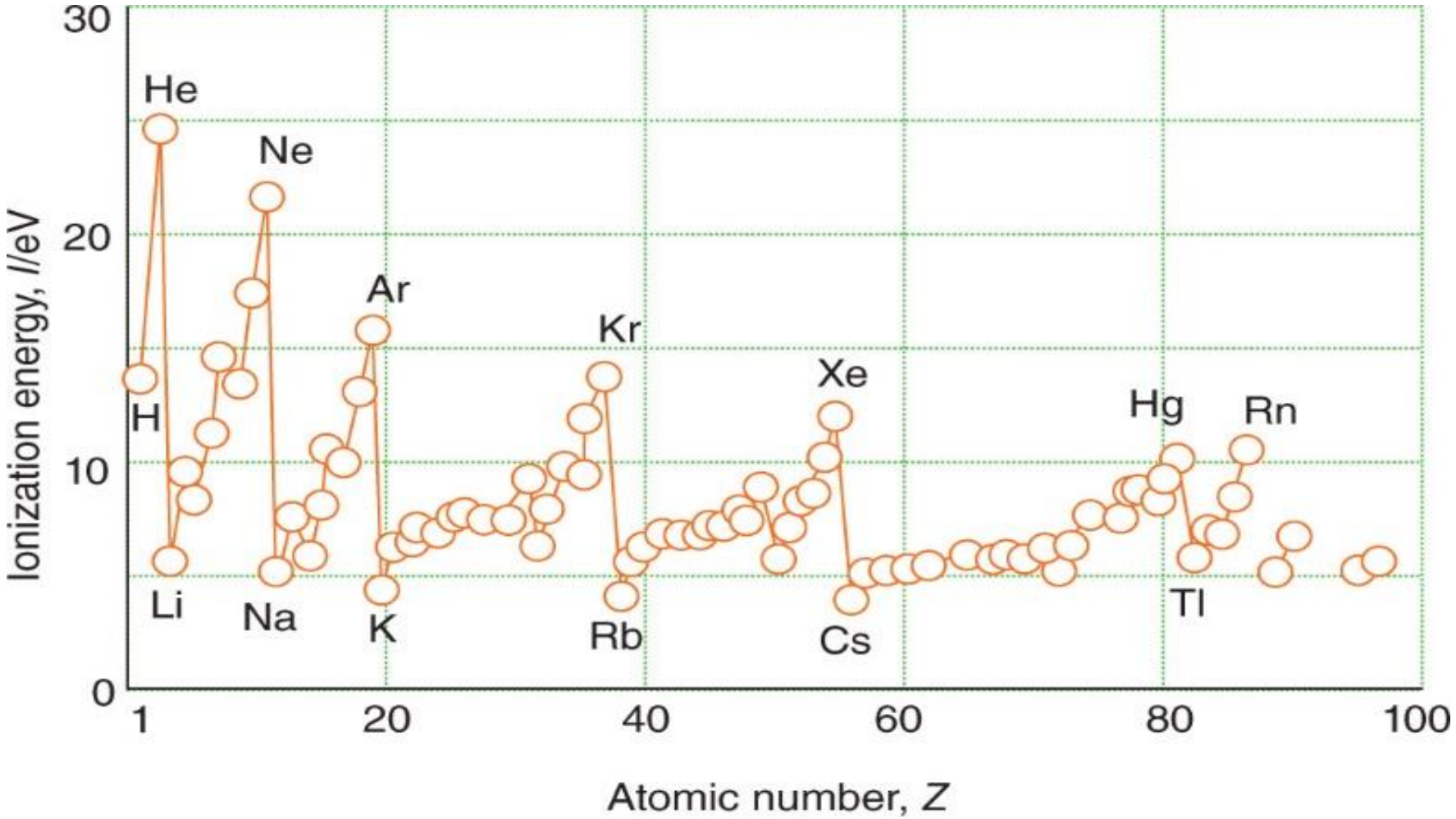
Periodic Variation in Size



B: $(1s)^2\ (2s, 2p)^3$ $Z_{eff} = 7 - [(2 \times 0.85) + (4 \times 0.35)] = 2.60$ Tabulated $Z_{eff} = 2.421$

F: $(1s)^2\ (2s, 2p)^7$ $Z_{eff} = 9 - [(2 \times 0.85) + (6 \times 0.35)] = 5.20$ Tabulated $Z_{eff} = 5.100$

Periodic Variation in Ionization Energy



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F: $(1s)^2\ (2s, 2p)^7$ $Z_{eff} = 9 - [(2 \times 0.85) + (6 \times 0.35)] = 5.20$ Tabulated $Z_{eff} = 5.100$

Electronegativity, χ

Developed by Linus Pauling in 1932

Tendency of atoms in molecules to attract electrons to themselves

1. Pauling definition:

$$\Delta H(A-B) = \frac{1}{2}[\Delta H(A-A) + \Delta H(B-B)] + 96.5\,[\chi(B) - \chi(A)]^2 \; ; where\; \chi(B) \geq \chi(A)$$

Originally: χ(F) set to 4.0

SAMPLE PROBLEM: Using the scale χ(F) = 3.98, calculate the electronegativity of Br.
Bond dissociation energies for Br–Br = 193 kJ mol^{-1}, F–F = 155 kJ mol^{-1} and Br–F in BrF =260 kJ mol^{-1}.

SOLUTION:

$$260 = \frac{1}{2}[193+155] + 96.5[3.98 - \chi(\mathrm{Br})]^2 \qquad \therefore \sqrt{86} = (3.98 - \chi(\mathrm{Br})); \therefore \chi(\mathrm{Br}) = 3.04$$

Electronegativity, χ

1		Chem 3830 Periodic Table with Pauling Electronegativity															18
1.0079 H 1 (2.20)	2	Pauling–type Electronegativity (in brackets)										13	14	15	16	17	4.0026 He 2
6.941 Li 3 (0.98)	9.0122 Be 4 (1.57)											10.811 B 5 (2.04)	12.011 C 6 (2.55)	14.0067 N 7 (3.04)	15.9994 O 8 (3.44)	18.9984 F 9 (3.98)	20.1797 Ne 10
22.9898 Na 11 (0.93)	24.3050 Mg 12 (1.31)	3	4	5	6	7	8	9	10	11	12	26.9815 Al 13 (1.61)	28.0855 Si 14 (1.90)	30.9738 P 15 (2.19)	32.066 S 16 (2.58)	35.4527 Cl 17 (3.16)	39.948 Ar 18
39.0983 K 19 (0.82)	40.078 Ca 20 (1.00)	44.9559 Sc 21 (1.36)	47.88 Ti 22 (1.54)	50.9415 V 23 (1.63)	51.9961 Cr 24 (1.66)	54.9380 Mn 25 (1.55)	55.847 Fe 26 (1.83)	58.9332 Co 27 (1.88)	58.693 Ni 28 (1.91)	63.546 Cu 29 (1.90)	65.39 Zn 30 (1.65)	69.723 Ga 31 (1.81)	72.61 Ge 32 (2.01)	74.9216 As 33 (2.18)	78.96 Se 34 (2.55)	79.904 Br 35 (2.96)	83.80 Kr 36 (3.00)
85.4678 Rb 3 (0.82)7	87.62 Sr 38 (0.95)	88.9059 Y 39 (1.22)	91.224 Zr 40 (1.33)	92.9064 Nb 41 (1.60)	95.94 Mo 42 (2.16)	(98) Tc 43 (1.90)	101.07 Ru 44 (2.20)	102.906 Rh 45 (2.28)	106.42 Pd 46 (2.20)	107.868 Ag 47 (1.93)	112.411 Cd 48 (1.69)	114.82 In 49 (1.78)	118.710 Sn 50 (1.80)	121.757 Sb 51 (2.05)	127.60 Te 52 (2.10)	126.905 I 53 (2.66)	131.29 Xe 546016(2 .6)
132.905 Cs 55 (0.79)	137.327 Ba 56 (0.89)	La-Lu	178.49 Hf 72 (1.30)	180.948 Ta 73 (1.50)	183.85 W 74 (2.36)	186.207 Re 75 (1.90)	190.2 Os 76 (2.20)	192.22 Ir 77 (2.20)	195.08 Pt 78 (2.28)	196.967 Au 79 (2.54)	200.59 Hg 80 (2.00)	204.383 Tl 81 (2.04)	207.19 Pb 82 (2.33)	208.980 Bi 83 (2.02)	(210) Po 84 (2.00)	(210) At 85 (2.20)	(222) Rn 86
(223) Fr 87 (0.70)	226.025 Ra 88 (0.90)	Ac-Lr	(267) Rf 104	(268) Db 105	(271) Sg 106	(272) Bh 107	(270) Hs 108	(276) Mt 109	(281) Dt 110	(280) Rg 111	(285) Cn 112	(286) Nh 113	(289) Fl 114	(290) Mc 115	(293) Lv 116	(294) Ts 117	(294) Og 118

Developed by Prof. R. T. Boeré modified by M. Gerken (updated September, 2018)

Electronegativity, χ

2. Mulliken definition (also called: Absolute Electronegativity):

What do you expect from a very electronegative element?

1. It should hold on to its electrons; it should have a high I_1

2. It should attract electrons; it should have a high E_{ea}

$$\chi_{Mulliken} = \frac{1}{2}(I_1 + E_{ea})$$

Scaled to fit the Pauling values:

$$\chi = 1.35\sqrt{\chi_{Mulliken}} - 1.37$$

Ionization Energies (IE)

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
11 809	14 844	3660	4619	4577	5300	6050	6122
		25 018					
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
		11 574					
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	

Electron Affinities (EA)

TABLE 1.6 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 –780	328	–116
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
53	≤0	43	134	72	200 –492	349	–96
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, χ

3. Allred-Rochow definition:

Related to the electrostatic force that an incoming electron experiences

$$\chi_{AR} = \frac{e^2 Z_{eff}}{r^2}$$

$$on\ the\ Pauling\ scale\text{:}\ \chi_{AR} = \frac{0.3509\ Z_{eff}}{r^2} + 0.744; r\ in\ \text{Å}$$

Z_{eff} should be calculated *for an incoming electron*. This is best done by calculating the Z_{eff} using Slater's rules (or tables) for the **mono-anion of the element**

r in Å, approximately the covalent radius of the atom

Electronegativity, χ

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

H							**He**
2.20							
3.06							3.5
2.20							5.5
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			

Van Arkel–Ketelaar Triangle