

CEE 680: Water Chemistry

Lecture #33

Coordination Chemistry: Practice

(Stumm & Morgan, Chapt.6: pg.317-319)

Benjamin; Chapter 8.1-8.6

Which ligands for which metals?

- Benjamin 2nd ed., pg 532

Table 10.1 Some important inorganic ligands and some metals to which they bind.

Ligand	Metals	Environment/Application
H ₂ O	All	Any aquatic system
OH ⁻	Virtually all	Any aquatic system
F ⁻	Fe ³⁺ , Al ³⁺	Some natural systems; industrial systems where HF is used to treat metal surfaces
Cl ⁻	Cu ²⁺ , Cu ⁺ , Pb ²⁺ , Cd ²⁺	Estuaries, seawater; corrosion of metals
CN ⁻	Fe ³⁺ , Fe ²⁺ , Cu ⁺ , Cu ²⁺ , Ni ²⁺ , Ag ⁺	Metal plating
NH ₃	Cu ⁺ , Cu ²⁺ , Cd ²⁺ , Ni ²⁺	Metal finishing
S ₂ O ₃ ²⁻	Ag ⁺	Photofinishing
P ₂ O ₇ ⁴⁻ , P ₃ O ₁₀ ⁵⁻	Ca ²⁺ , Mn ²⁺ , Fe ³⁺	Detergents, corrosion inhibitors

Classification of Metals

- A and B type cations

A-Type Metal Cations	Transition-Metal Cations	B-Type Metal Cations
Electron configuration of inert gas; low polarizability; “hard spheres”; (H^+) , Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Al^{3+} , Sc^{3+} , La^{3+} , Si^{4+} , Ti^{4+} , Zr^{4+} , Th^{4+}	One to nine outer shell electrons; not spherically symmetric; V^{2+} , Cr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ti^{3+} , V^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+}	Electron number corresponds to Ni^0 , Pd^0 , and Pt^0 (10 or 12 outer shell electrons); low electronegativity; high polarizability; “soft spheres”; Cu^+ , Ag^+ , Au^+ , Tl^+ , Ga^+ , Zn^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+} , Sn^{2+} , Tl^{3+} , Au^{3+} , In^{3+} , Bi^{3+}

From: Stumm & Morgan,
Table 6.3, pg 284

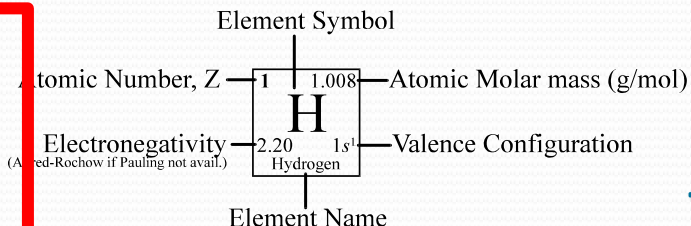
Pearson's Hard & Soft Acids

Hard Acids	Borderline	Soft Acids
<p>All A-type metal cations plus Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, UO^{2+}, VO^{2+}</p> <p>Also species such as BF_3, BCl_3, SO_3, RSO_2^+, RPO_2^+, CO_2, RCO^+, R_3C^+</p> <p><i>Preference for ligand atom:</i></p> <p>$\text{N} \gg \text{P}$ $\text{O} \gg \text{S}$ $\text{F} \gg \text{Cl}$</p> <p><i>Qualitative generalizations on stability sequence:</i></p> <p>Cations: Stability \propto (charge/radius)</p> <p>Ligands: $\text{F} > \text{O} > \text{N} = \text{Cl} > \text{Br} > \text{I} > \text{S}$ $\text{OH}^- > \text{RO}^- > \text{RCO}_2^-$ $\text{CO}_3^{2-} \gg \text{NO}_3^-$ $\text{PO}_4^{3-} \gg \text{SO}_4^{2-} \gg \text{ClO}_4^-$</p>	<p>All bivalent transition-metal cations plus Zn^{2+}, Pb^{2+}, Bi^{3+}, SO_2, NO^+, $\text{B}(\text{CH}_3)_3$</p> <p>Cations: Irving-Williams order: $\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$</p>	<p>All B-type metal cations minus Zn^{2+}, Pb^{2+}, Bi^{3+}</p> <p>All metal atoms, bulk metals I_2, Br_2, ICN, I^+, Br^+</p> <p>$\text{P} \gg \text{N}$ $\text{S} \gg \text{O}$ $\text{I} \gg \text{F}$</p> <p>Ligands: $\text{S} > \text{I} > \text{Br} > \text{Cl} = \text{N} > \text{O} > \text{F}$</p>

From: Stumm & Morgan,
Table 6.3, pg 284

Periodic Table

1 1.008 H 1s ¹ Hydrogen	3 6.941 Li 2s ¹ Lithium	4 9.012 Be 2s ² Beryllium
11 22.990 Na 3s ¹ Sodium	12 24.305 Mg 3s ² Magnesium	
19 39.098 K 4s ¹ Potassium	20 40.078 Ca 4s ² Calcium	
37 85.468 Rb 5s ¹ Rubidium	38 87.62 Sr 5s ² Strontium	
55 132.91 Cs 6s ¹ Cesium	56 137.33 Ba 6s ² Barium	
87 (223) Fr 7s ¹ Francium	88 226.03 Ra 7s ² Radium	



B

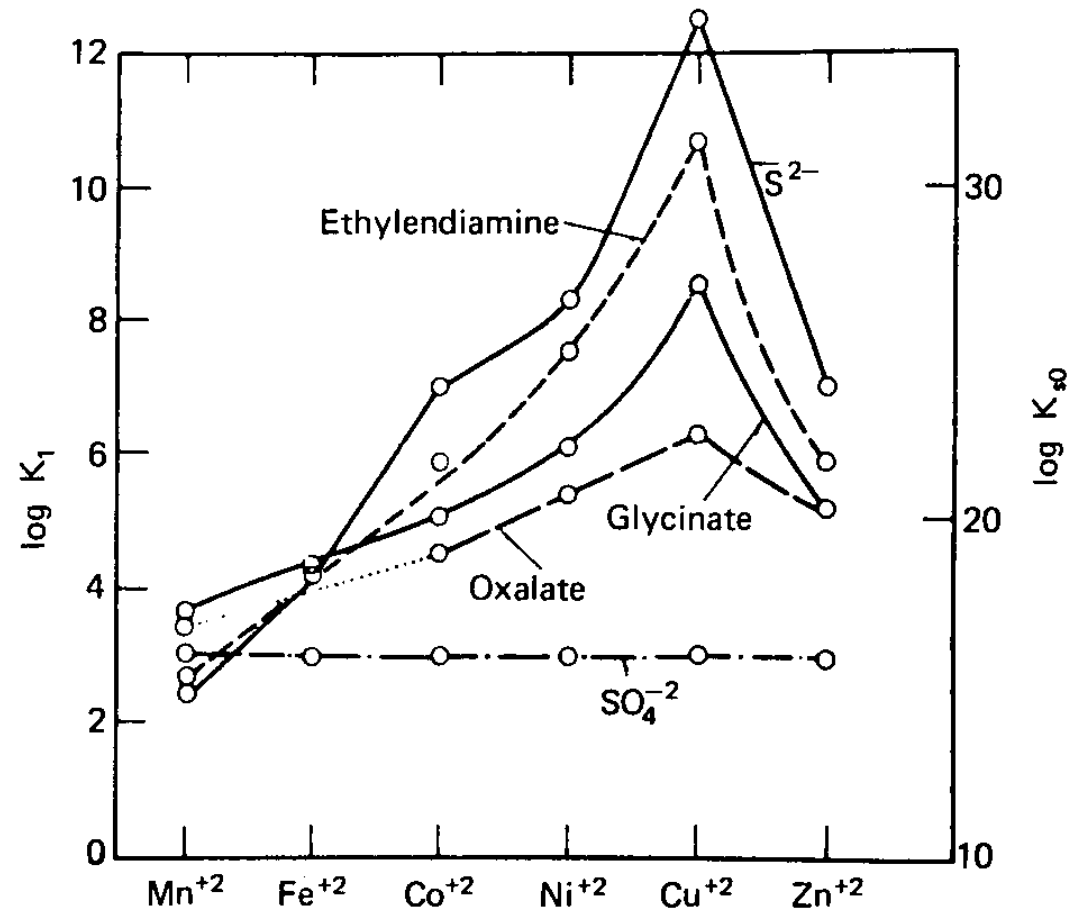
5 10.811 B 2s ² 2p ¹ Boron	6 12.011 C 2s ² 2p ² Carbon	7 14.007 N 2s ² 2p ³ Nitrogen	8 15.999 O 2s ² 2p ⁴ Oxygen	9 18.998 F 2s ² 2p ⁵ Fluorine	10 21.180 Ne n.a. 2s ² 2p ⁶ Neon
13 26.982 Al 3s ² 3p ¹ Aluminum	14 28.086 Si 3s ² 3p ² Silicon	15 30.974 P 3s ² 3p ³ Phosphorus	16 32.066 S 3s ² 3p ⁴ Sulfur	17 35.453 Cl 3s ² 3p ⁵ Chlorine	18 39.948 Ar n.a. 3s ² 3p ⁶ Argon
31 69.723 Ga 4s ² 4p ¹ Gallium	32 72.01 Ge 4s ² 4p ² Germanium	33 74.922 As 4s ² 4p ³ Arsenic	34 78.96 Se 4s ² 4p ⁴ Selenium	35 79.904 Br 4s ² 4p ⁵ Bromine	36 83.80 Kr n.a. 4s ² 4p ⁶ Krypton
49 114.82 In 5s ² 5p ¹ Indium	50 118.71 Sn 5s ² 5p ² Tin	51 121.75 Sb 5s ² 5p ³ Antimony	52 127.60 Te 5s ² 5p ⁴ Tellurium	53 126.91 I 5s ² 5p ⁵ Iodine	54 131.29 Xe 2.6 5s ² 5p ⁶ Xenon
81 204.38 Tl 6s ² 6p ¹ Thallium	82 207.2 Pb 6s ² 6p ² Lead	83 208.98 Bi 6s ² 6p ³ Bismuth	84 (209) Po 6s ² 6p ⁴ Polonium	85 (210) At 6s ² 6p ⁵ Astatine	86 (222) Rn n.a. 6s ² 6p ⁶ Radon

21 44.956 Sc 3d ¹ 4s ² Scandium	22 47.88 Ti 3d ² 4s ² Titanium	23 50.942 V 3d ³ 4s ² Vanadium	24 51.996 Cr 3d ⁵ 4s ¹ Chromium	25 54.938 Mn 3d ⁵ 4s ² Manganese	26 55.847 Fe 3d ⁶ 4s ² Iron	27 58.933 Co 3d ⁷ 4s ² Cobalt	28 58.69 Ni 3d ⁸ 4s ² Nickel	29 63.546 Cu 3d ¹⁰ 4s ¹ Copper	30 63.59 Zn 3d ¹⁰ 4s ² Zinc
39 88.906 Y 4d ¹ 5s ² Yttrium	40 91.224 Zr 4d ² 5s ² Zirconium	41 92.906 Nb 4d ⁴ 5s ¹ Niobium	42 95.94 Mo 4d ⁵ 5s ¹ Molybdenum	43 (98) Tc 4d ⁵ 5s ² Technetium	44 101.07 Ru 4d ⁷ 5s ¹ Ruthenium	45 102.91 Rh 4d ⁸ 5s ¹ Rhodium	46 106.42 Pd 4d ¹⁰ Palladium	47 107.87 Ag 4d ¹⁰ 5s ¹ Silver	48 112.41 Cd 4d ¹⁰ 5s ² Cadmium
71 174.97 Lu 4f ¹⁴ 5d ¹ 6s ² Lutetium	72 178.49 Hf 4f ¹⁴ 5d ² 6s ² Hafnium	73 180.95 Ta 4f ¹⁴ 5d ³ 6s ² Tantalum	74 183.85 W 4f ¹⁴ 5d ⁴ 6s ² Tungsten	75 186.21 Re 4f ¹⁴ 5d ⁵ 6s ² Rhenium	76 190.2 Os 4f ¹⁴ 5d ⁶ 6s ² Osmium	77 192.22 Ir 4f ¹⁴ 5d ⁷ 6s ² Iridium	78 195.08 Pt 4f ¹⁴ 5d ⁹ 6s ¹ Platinum	79 196.97 Au 4f ¹⁴ 5d ¹⁰ 6s ¹ Gold	80 200.59 Hg 4f ¹⁴ 5d ¹⁰ 6s ² Mercury
105 (262) Unp 7s ² 6d ³ Unnilpentium	106 (263) Unh 7s ² 6d ⁴ Unnilhexium	107 (264) Uns 7s ² 6d ⁵ Unnilseptium	108 (265) Uno 7s ² 6d ⁶ Unniloctium	109 (266) Une 7s ² 6d ⁷ Unnilennium					

7 138.91 La 5d ¹ 6s ² Lanthanum	58 140.11 Ce 5d ¹ 4f ¹ Cerium	59 140.91 Pr 5d ⁰ 4f ³ Praseodymium	60 144.24 Nd 5d ⁰ 4f ⁴ Neodymium	61 (145) Pm 5d ⁰ 4f ⁵ Promethium	62 150.36 Sm 5d ⁰ 4f ⁶ Samarium	63 151.96 Eu 5d ⁰ 4f ⁷ Europium	64 157.25 Gd 5d ¹ 4f ⁷ Gadolinium	65 158.93 Tb 5d ⁰ 4f ⁹ Terbium	66 162.50 Dy 5d ⁰ 4f ¹⁰ Dysprosium	67 164.93 Ho 5d ⁰ 4f ¹¹ Holmium	68 167.26 Er 5d ⁰ 4f ¹² Erbium	69 168.93 Tm 5d ⁰ 4f ¹³ Thulium	70 173.04 Yb 5d ⁰ 4f ¹⁴ Ytterbium
89 227.03 Ac 6d ¹ 7s ² Actinium	90 232.04 Th 6d ² 7s ² Thorium	91 231.04 Pa 5f ² 6d ¹ 7s ² Protactinium	92 238.03 U 5f ³ 6d ¹ 7s ² Uranium	93 237.05 Np 5f ⁴ 6d ¹ 7s ² Neptunium	94 (244) Pu 5f ⁶ 7s ² Plutonium	95 (243) Am 5f ⁷ 7s ² Americium	96 (247) Cm 5f ⁷ 6d ¹ 7s ² Curium	97 (247) Bk 5f ⁹ 7s ² Berkelium	98 (251) Cf 5f ¹⁰ 7s ² Californium	99 (252) Es 5f ¹¹ 7s ² Einsteinium	100 (257) Fm 5f ¹² 7s ² Fermium	101 (258) Md 5f ¹³ 7s ² Mendelevium	102 (259) No 5f ¹⁴ 7s ² Nobelium

Me-ligand affinities

- Irving-Williams series



From: Stumm & Morgan,
Figure 6.11, pg 286

Periodic Table

1 1.008 H 2.20 1s ¹ Hydrogen	2 4.003 He n.a. 1s ² Helium	<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center; margin-right: 10px;"> <p>Element Symbol</p> <p>Atomic Number, Z</p> <p>Electronegativity (Allred-Rochow if Pauling not avail.)</p> </div> <div style="border: 1px solid black; padding: 5px; text-align: center;"> <p>1 1.008</p> <p>H</p> <p>2.20 1s¹</p> <p>Hydrogen</p> </div> <div style="text-align: center; margin-left: 10px;"> <p>Atomic Molar mass (g/mol)</p> <p>Valence Configuration</p> <p>Element Name</p> </div> </div>																3 6.941 Li 0.98 2s ¹ Lithium	4 9.012 Be 1.57 2s ² Beryllium	5 10.811 B 2.04 2s ² 2p ¹ Boron	6 12.011 C 2.55 2s ² 2p ² Carbon	7 14.007 N 3.04 2s ² 2p ³ Nitrogen	8 15.999 O 3.44 2s ² 2p ⁴ Oxygen	9 18.998 F 3.98 2s ² 2p ⁵ Fluorine	10 21.180 Ne n.a. 2s ² 2p ⁶ Neon	11 22.990 Na 0.93 3s ¹ Sodium	12 24.305 Mg 1.31 3s ² Magnesium	13 26.982 Al 1.61 3s ² 3p ¹ Aluminum	14 28.086 Si 1.90 3s ² 3p ² Silicon	15 30.974 P 2.19 3s ² 3p ³ Phosphorus	16 32.066 S 2.58 3s ² 3p ⁴ Sulfur	17 35.453 Cl 3.16 3s ² 3p ⁵ Chlorine	18 39.948 Ar n.a. 3s ² 3p ⁶ Argon	19 39.098 K 0.82 4s ¹ Potassium	20 40.078 Ca 1.00 4s ² Calcium	21 44.956 Sc 1.36 4s ² 3d ¹ Scandium	22 47.88 Ti 1.54 4s ² 3d ² Titanium	23 50.942 V 1.63 4s ² 3d ³ Vanadium	24 51.996 Cr 1.66 4s ¹ 3d ⁵ Chromium	25 54.938 Mn 1.55 4s ² 3d ⁵ Manganese	26 55.847 Fe 1.83 4s ² 3d ⁶ Iron	27 58.933 Co 1.88 4s ² 3d ⁷ Cobalt	28 58.69 Ni 1.91 4s ² 3d ⁸ Nickel	29 63.546 Cu 1.90 4s ¹ 3d ¹⁰ Copper	30 65.39 Zn 1.65 4s ² 3d ¹⁰ Zinc	31 69.723 Ga 1.81 4s ² 4p ¹ Gallium	32 72.61 Ge 2.01 4s ² 4p ² Germanium	33 74.922 As 2.18 4s ² 4p ³ Arsenic	34 78.96 Se 2.55 4s ² 4p ⁴ Selenium	35 79.904 Br 2.96 4s ² 4p ⁵ Bromine	36 83.80 Kr n.a. 4s ² 4p ⁶ Krypton	37 85.468 Rb 0.82 5s ¹ Rubidium	38 87.62 Sr 0.95 5s ² Strontium	39 88.906 Y 1.22 5s ² 4d ¹ Yttrium	40 91.224 Zr 1.33 5s ² 4d ² Zirconium	41 92.906 Nb 1.6 5s ¹ 4d ⁴ Niobium	42 95.94 Mo 2.16 5s ¹ 4d ⁵ Molybdenum	43 (98) Tc 1.9 5s ² 4d ⁵ Technetium	44 101.07 Ru 2.2 5s ¹ 4d ⁷ Ruthenium	45 102.91 Rh 2.28 5s ¹ 4d ⁸ Rhodium	46 106.42 Pd 2.20 4d ¹⁰ Palladium	47 107.87 Ag 1.93 5s ¹ 4d ¹⁰ Silver	48 112.41 Cd 1.69 5s ² 4d ¹⁰ Cadmium	49 114.82 In 1.78 5s ² 5p ¹ Indium	50 118.71 Sn 1.96 5s ² 5p ² Tin	51 121.75 Sb 2.05 5s ² 5p ³ Antimony	52 127.60 Te 2.1 5s ² 5p ⁴ Tellurium	53 126.91 I 2.66 5s ² 5p ⁵ Iodine	54 131.29 Xe 2.6 5s ² 5p ⁶ Xenon	55 132.91 Cs 0.79 6s ¹ Cesium	56 137.33 Ba 0.89 6s ² Barium	71 174.97 Lu 1.27 6s ² 5d ¹ Lutetium	72 178.49 Hf 1.3 6s ² 5d ² Hafnium	73 180.95 Ta 1.5 6s ¹ 5d ⁴ Tantalum	74 183.85 W 2.36 6s ² 5d ⁴ Tungsten	75 186.21 Re 1.9 6s ² 5d ⁵ Rhenium	76 190.2 Os 2.2 6s ¹ 5d ⁶ Osmium	77 192.22 Ir 2.20 6s ² 5d ⁷ Iridium	78 195.08 Pt 2.28 6s ¹ 5d ⁹ Platinum	79 196.97 Au 2.54 6s ¹ 5d ¹⁰ Gold	80 200.59 Hg 2.00 6s ² 5d ¹⁰ Mercury	81 204.38 Tl 1.62 6s ² 6p ¹ Thallium	82 207.2 Pb 2.33 6s ² 6p ² Lead	83 208.98 Bi 2.02 6s ² 6p ³ Bismuth	84 (209) Po 2.0 6s ² 6p ⁴ Polonium	85 (210) At 2.2 6s ² 6p ⁵ Astatine	86 (222) Rn n.a. 6s ² 6p ⁶ Radon	87 (223) Fr 0.7 7s ¹ Francium	88 226.03 Ra 0.89 7s ² Radium	103 (260) Lr 1.3 7s ² 6d ¹ Lawrencium	104 (261) Unq n.a. 7s ² 6d ² Unnilquadium	105 (262) Unp n.a. 7s ² 6d ³ Unnilpentium	106 (263) Unh n.a. 7s ² 6d ⁴ Unnilhexium	107 (264) Uns n.a. 7s ² 6d ⁵ Unnilseptium	108 (265) Uno n.a. 7s ² 6d ⁶ Unniloctium	109 (266) Une n.a. 7s ² 6d ⁷ Unnilennium										
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55 132.91 Cs 0.79 6s ¹ Cesium	56 137.33 Ba 0.89 6s ² Barium	71 174.97 Lu 1.27 6s ² 5d ¹ Lutetium	72 178.49 Hf 1.3 6s ² 5d ² Hafnium	73 180.95 Ta 1.5 6s ¹ 5d ⁴ Tantalum	74 183.85 W 2.36 6s ² 5d ⁴ Tungsten	75 186.21 Re 1.9 6s ² 5d ⁵ Rhenium	76 190.2 Os 2.2 6s ¹ 5d ⁶ Osmium	77 192.22 Ir 2.20 6s ² 5d ⁷ Iridium	78 195.08 Pt 2.28 6s ¹ 5d ⁹ Platinum	79 196.97 Au 2.54 6s ¹ 5d ¹⁰ Gold	80 200.59 Hg 2.00 6s ² 5d ¹⁰ Mercury	81 204.38 Tl 1.62 6s ² 6p ¹ Thallium	82 207.2 Pb 2.33 6s ² 6p ² Lead	83 208.98 Bi 2.02 6s ² 6p ³ Bismuth	84 (209) Po 2.0 6s ² 6p ⁴ Polonium	85 (210) At 2.2 6s ² 6p ⁵ Astatine	86 (222) Rn n.a. 6s ² 6p ⁶ Radon	87 (223) Fr 0.7 7s ¹ Francium	88 226.03 Ra 0.89 7s ² Radium	103 (260) Lr 1.3 7s ² 6d ¹ Lawrencium	104 (261) Unq n.a. 7s ² 6d ² Unnilquadium	105 (262) Unp n.a. 7s ² 6d ³ Unnilpentium	106 (263) Unh n.a. 7s ² 6d ⁴ Unnilhexium	107 (264) Uns n.a. 7s ² 6d ⁵ Unnilseptium	108 (265) Uno n.a. 7s ² 6d ⁶ Unniloctium	109 (266) Une n.a. 7s ² 6d ⁷ Unnilennium																																																																																
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57 138.91 La 1.10 6s ² 5d ¹ Lanthanum	58 140.11 Ce 1.12 5d ¹ 4f ¹ Cerium	59 140.91 Pr 1.13 6s ² 4f ³ Praseodymium	60 144.24 Nd 1.14 6s ² 4f ⁴ Neodymium	61 (145) Pm 1.07 6s ² 4f ⁵ Promethium	62 150.36 Sm 1.17 6s ² 4f ⁶ Samarium	63 151.96 Eu 1.01 6s ² 4f ⁷ Europium	64 157.25 Gd 1.20 5d ¹ 4f ⁷ Gadolinium	65 158.93 Tb 1.10 6s ² 4f ⁹ Terbium	66 162.50 Dy 1.22 6s ² 4f ¹⁰ Dysprosium	67 164.93 Ho 1.23 6s ² 4f ¹¹ Holmium	68 167.26 Er 1.24 6s ² 4f ¹² Erbium	69 168.93 Tm 1.25 6s ² 4f ¹³ Thulium	70 173.04 Yb 1.06 6s ² 4f ¹⁴ Ytterbium
89 227.03 Ac 1.10 7s ² 6d ¹ Actinium	90 232.04 Th 1.3 7s ² 6d ² Thorium	91 231.04 Pa 1.5 6d ¹ 5f ² Protactinium	92 238.03 U 1.38 6d ¹ 5f ³ Uranium	93 237.05 Np 1.36 6d ¹ 5f ⁴ Neptunium	94 (244) Pu 1.28 7s ² 5f ⁶ Plutonium	95 (243) Am 1.3 7s ² 5f ⁷ Americium	96 (247) Cm 1.3 6d ¹ 5f ⁷ Curium	97 (247) Bk 1.3 7s ² 5f ⁹ Berkelium	98 (251) Cf 1.3 7s ² 5f ¹⁰ Californium	99 (252) Es 1.3 7s ² 5f ¹¹ Einsteinium	100 (257) Fm 1.3 7s ² 5f ¹² Fermium	101 (258) Md 1.3 7s ² 5f ¹³ Mendelevium	102 (259) No 1.3 7s ² 5f ¹⁴ Nobelium



- To next lecture