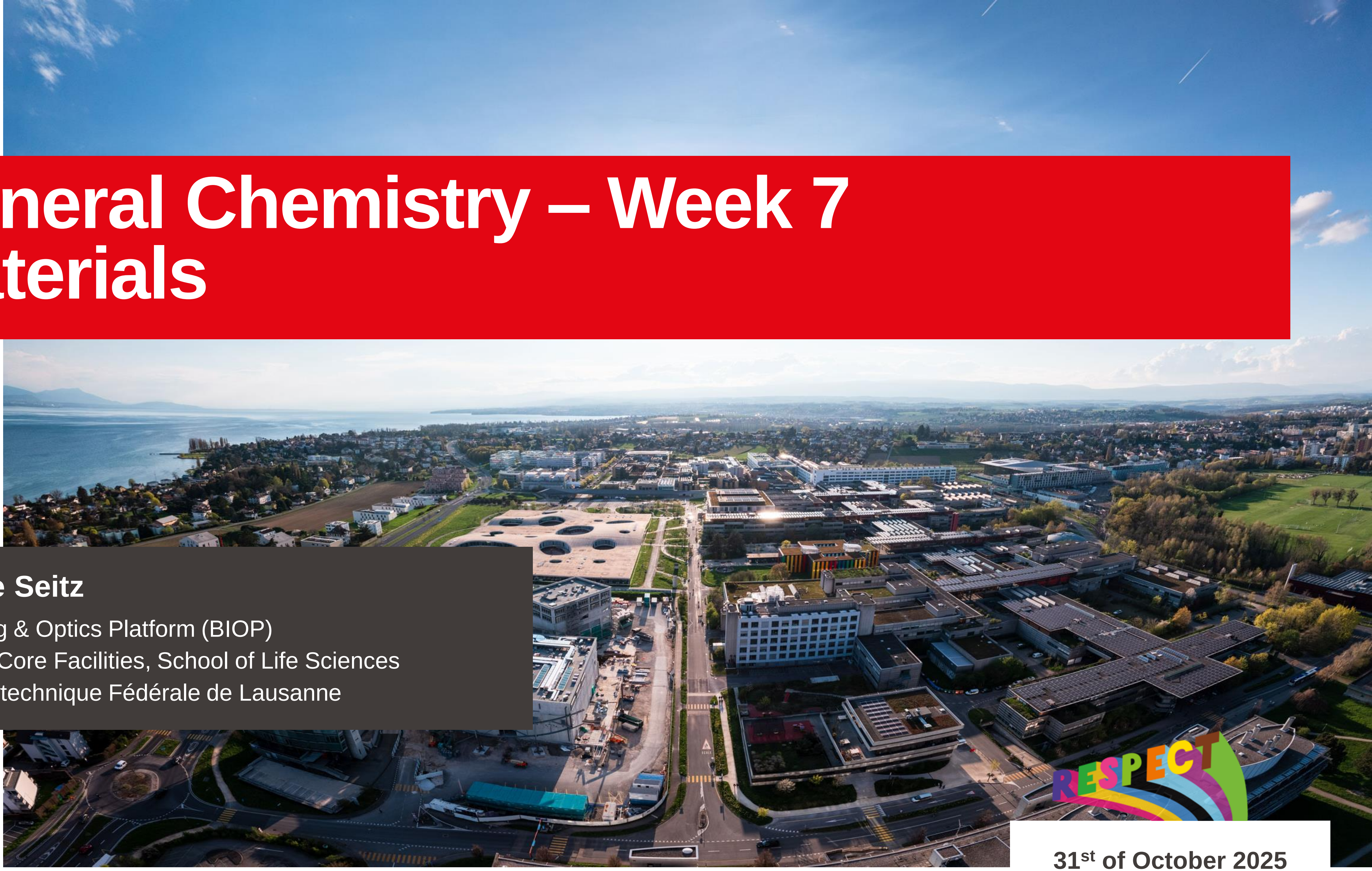

General Chemistry – Week 7
Materials

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Recap

Theromodynamics

- Entropy
  - Measure of disorder of a system
  - The entropy of the system and the surroundings needs to be considered
- Gibbs free Energy
  - $\Delta G = \Delta H - T\Delta S$

Gibbs Free Energy and Nonexpansion Work: Applied

- How much nonexpansion work is done in our body in the oxidation of glucose, $C_6H_{12}O_6$(s, glucose) + 6 O_2(g) → 6 CO_2(g) + 6 H_2O(l) to make peptide links (a link between amino acids) in a protein?
- We calculated the Gibbs free energy of reaction to be −2879 kJ per mol or 180.0 g of glucose.
- It takes 17 kJ of work to build 1 mol of peptide links in a protein.
- So 1 mole of glucose or 180. g of glucose can build about (2879 kJ)/(17 kJ) = 170 moles of peptide links.
- A typical protein has several hundred peptide links, and so several glucose molecules must be sacrificed to build one protein molecule.

Free Energy and Life

- Many biological reactions, such as the construction of a protein from amino acids or the construction of a DNA molecule, are not spontaneous and are driven by an external source of energy.

- That energy comes from sunlight and the chemicals in food that have stored solar energy.

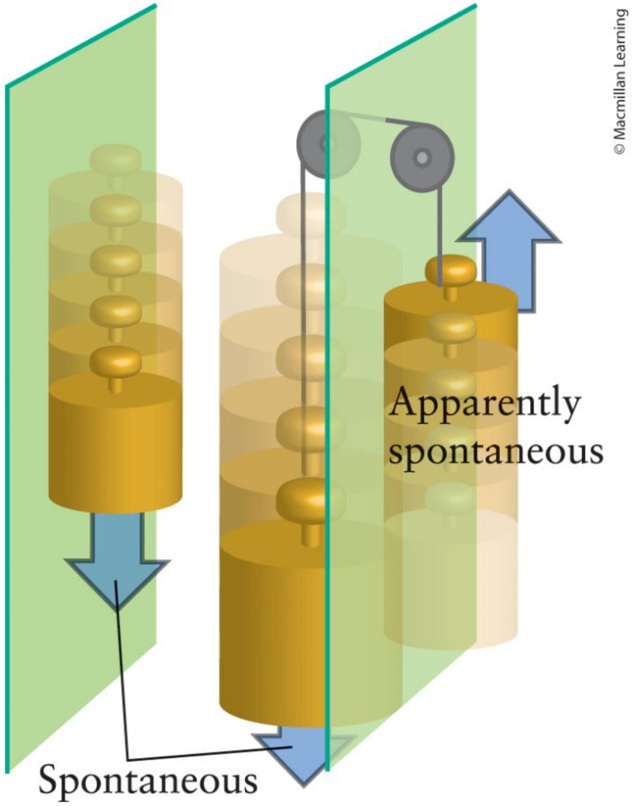
- Many biological chemical reactions are nonspontaneous reactions. To make these reactions work, we must use entropy to drive a reaction forward.

Free Energy and Life

- Staying alive is very much like using weights tied to each other over a pulley.

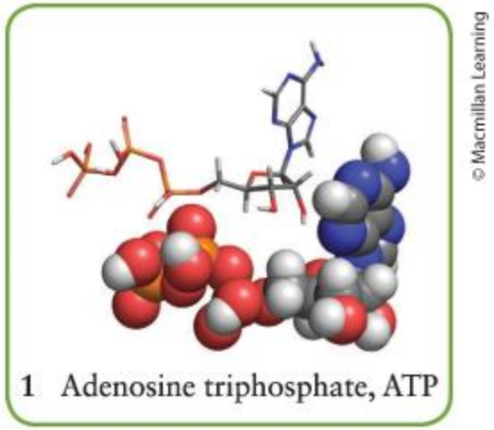
- The lighter weight can not move on its own.

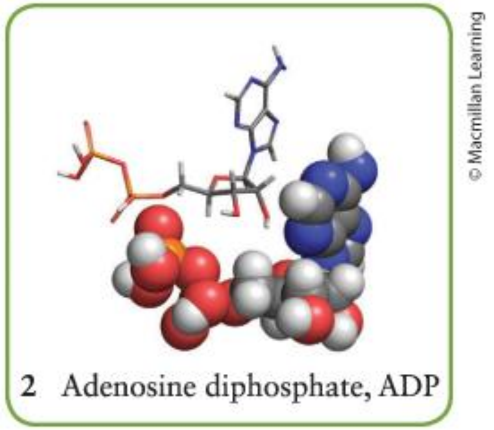
- However, by connecting a lighter weight to a heavier weight falling, then dropping the heavy weight, the light weight can soar upward.



Free Energy and Life

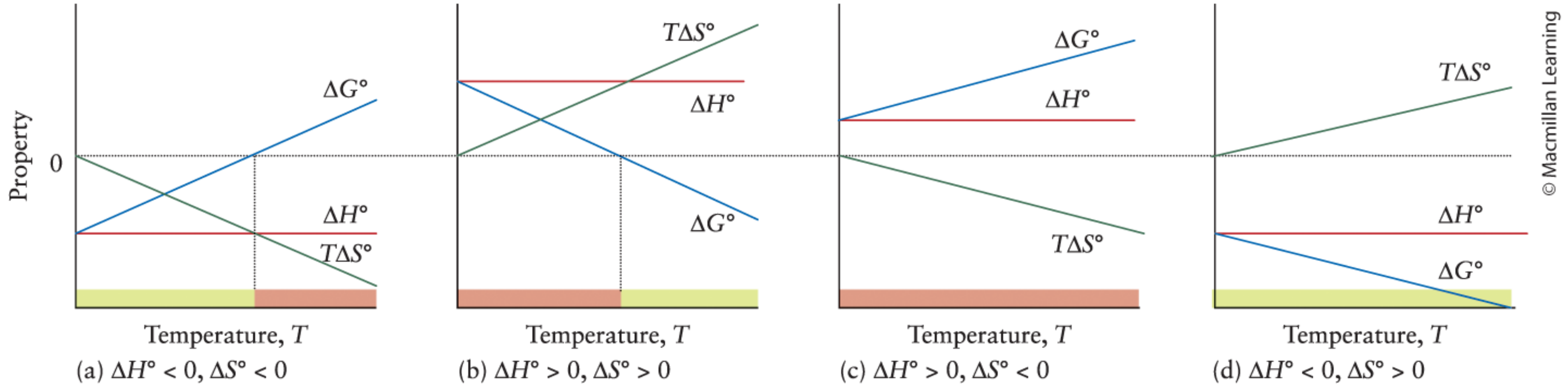
- The hydrolysis of adenosine triphosphate, ATP, to adenosine diphosphate, ADP, is frequently how biological organisms couple and drive nonspontaneous reactions.
- To restore ADP with 2 phosphates to ATP with 3 takes   +30 kJ of energy.
- We eat food in a combustion reaction that releases 2500 kJ per mole of energy per mole of glucose. Eating glucose is our heavy weight, enough to “recharge” 80 moles of ADP.
- Once we stop eating, decay begins; entropy continues forward.





The Effect of Temperature

- $\Delta G°$ does depend on temperature: $\Delta G° = \Delta H° - T\Delta S°$



Spontaneous if:

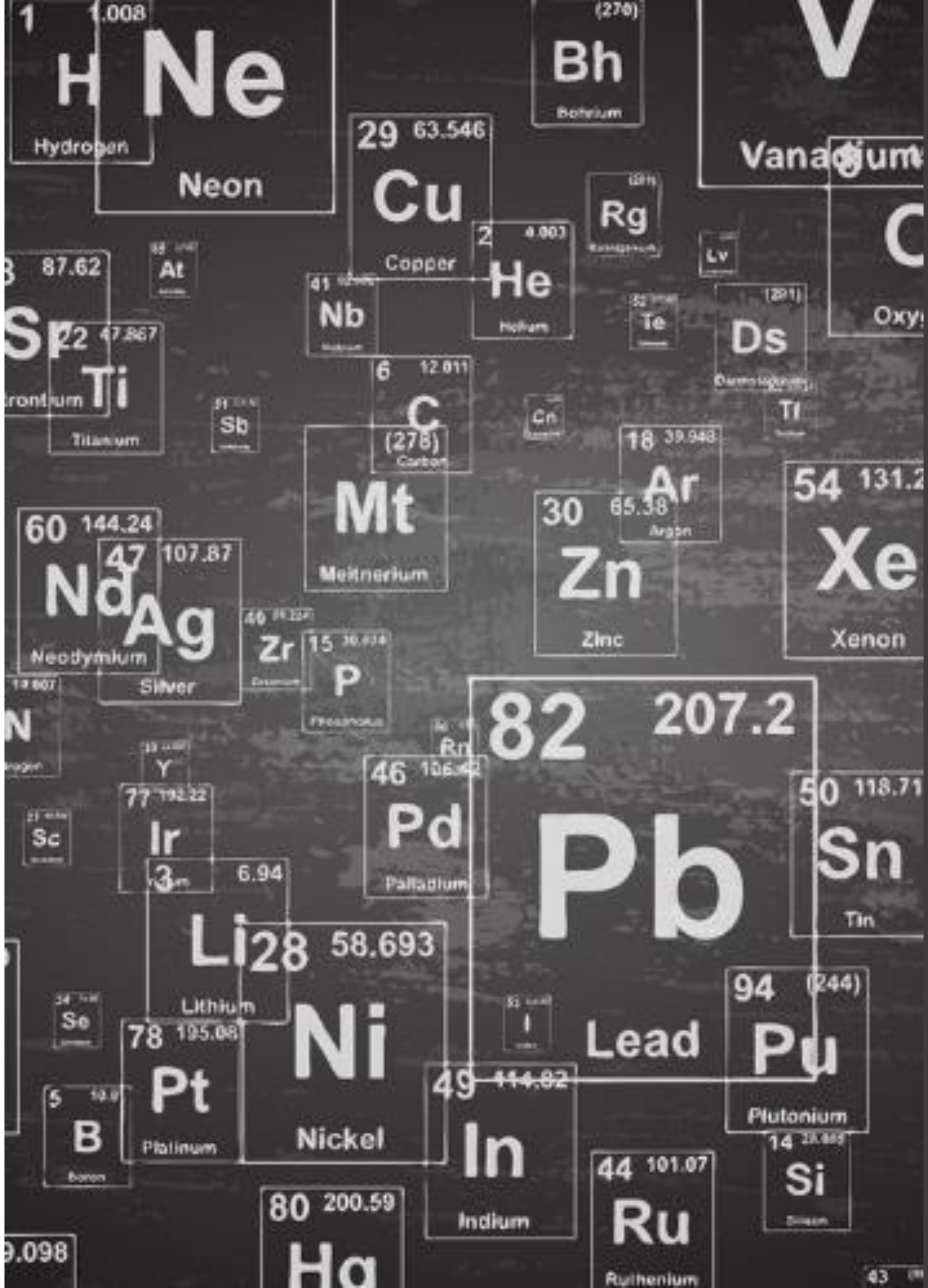
- (a) T is low (b) T is high (c) never (d) always

- Exothermic, $\Delta H° < 0$ and $\Delta S° < 0$, as long as T remains low, $\Delta G°$ is "–"
- Endothermic, $\Delta H° > 0$ and $\Delta S° > 0$, if T is high enough, $\Delta G°$ will be "–"
- Endothermic, $\Delta H° > 0$ and $\Delta S° < 0$, this is never spontaneous at any T
- Exothermic, $\Delta H° < 0$ and $\Delta S° > 0$, spontaneous at any T

The Pressure-Dependence of Gibbs Free Energy

- The Gibbs free energy of a solid or a liquid changes very little with pressure.

- However, the pressure dependence of the Gibbs free energy of a gas is significant.

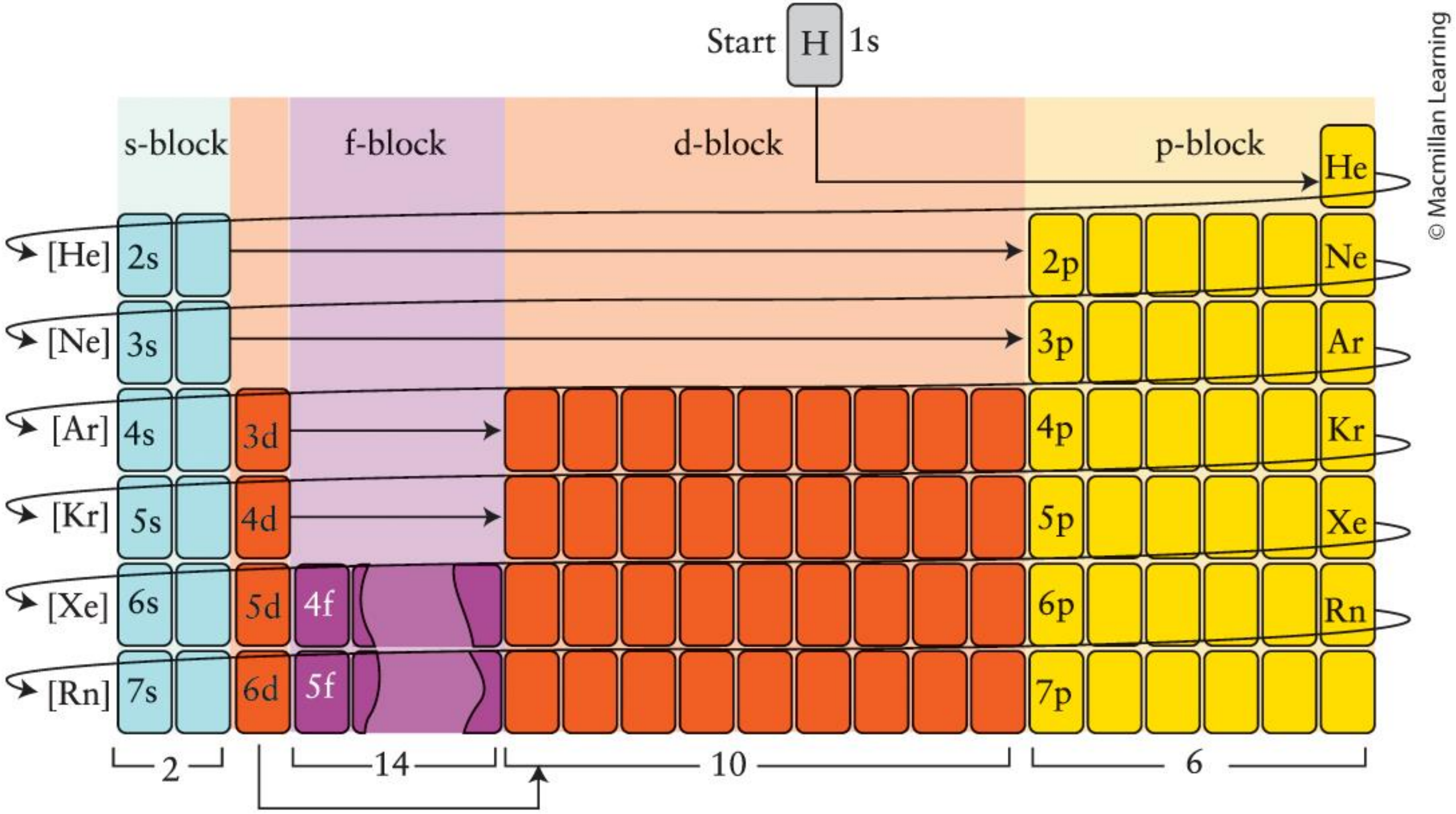


Periodic Table of Elements

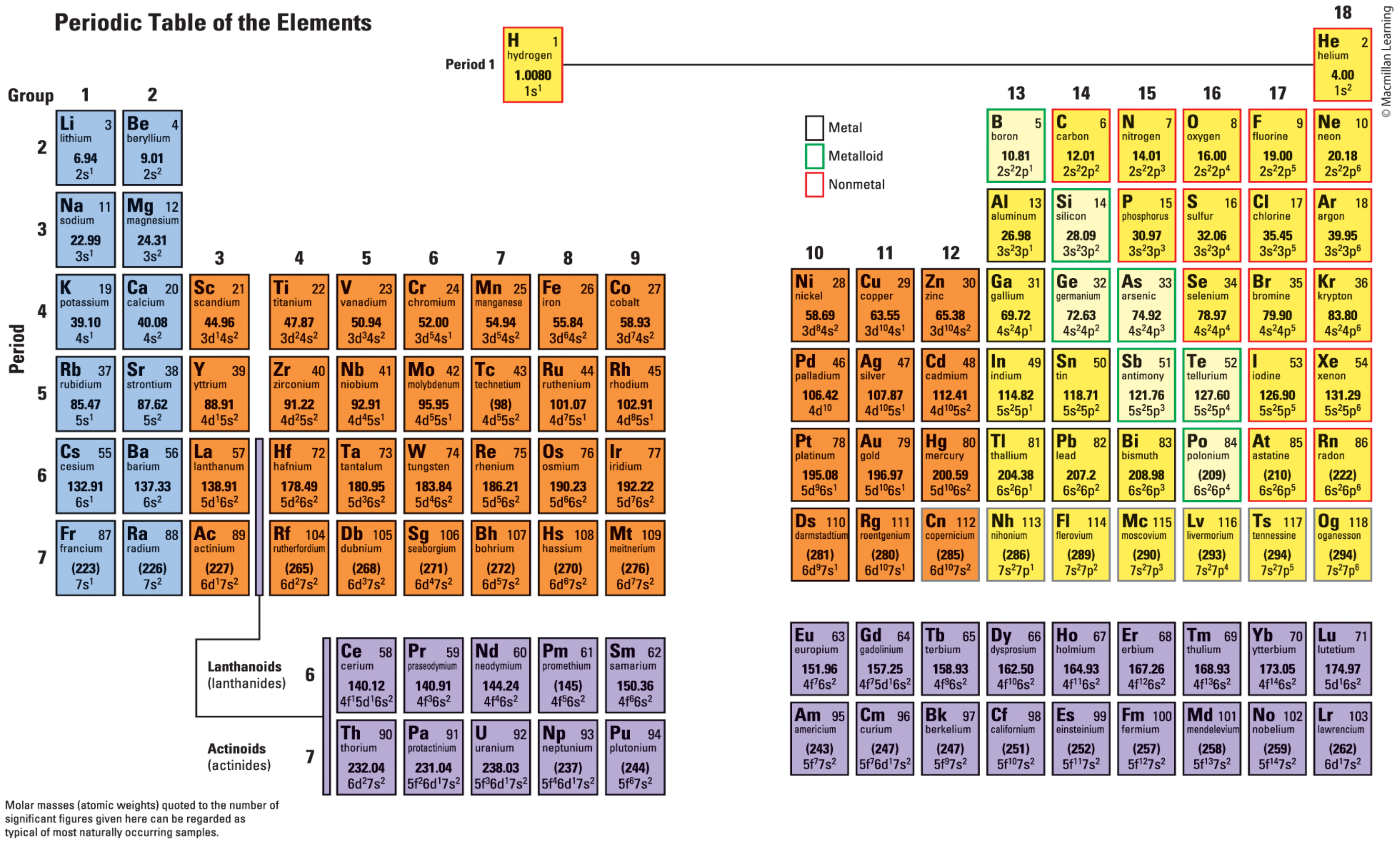
Learning objectives

- The following lectures survey the properties of the elements.
- We recall the principles of the periodic table of the Elements
  - Building principle of atoms
  - Electronic configuration
  - Periodicity
- We understand that an atom’s property is related to its location in the periodic table.
- We explore descriptive chemistry: how to prepare and the properties and applications of elements and their compounds.

Filling Order for Orbitals



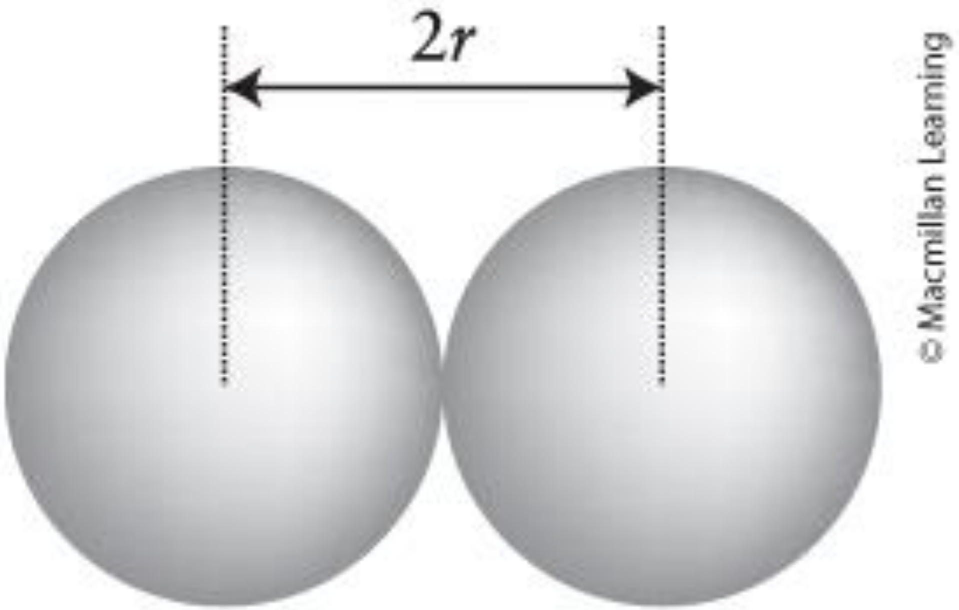
The periodic table



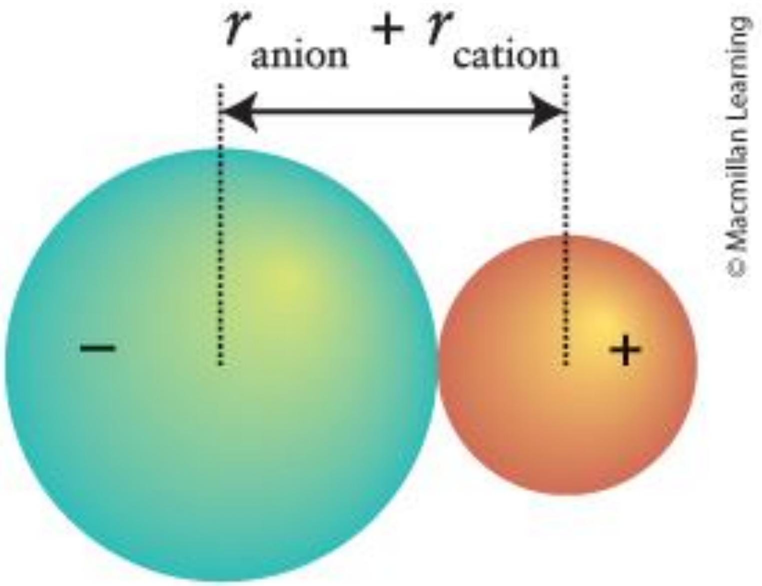
Periodic Trends in Atomic Properties

- Valence electrons experience increasing effective nuclear charge going across a period from left to right. Valence electrons experience decreasing effective nuclear charge going down a group because the valence electrons in those shells are farther from the nucleus.
- Five atomic properties are related to effective nuclear charge.
  - atomic radius,
  - ionization energy,
  - electron affinity,
  - electronegativity, and
  - polarizability.

Atomic Radius and Ionic Radius

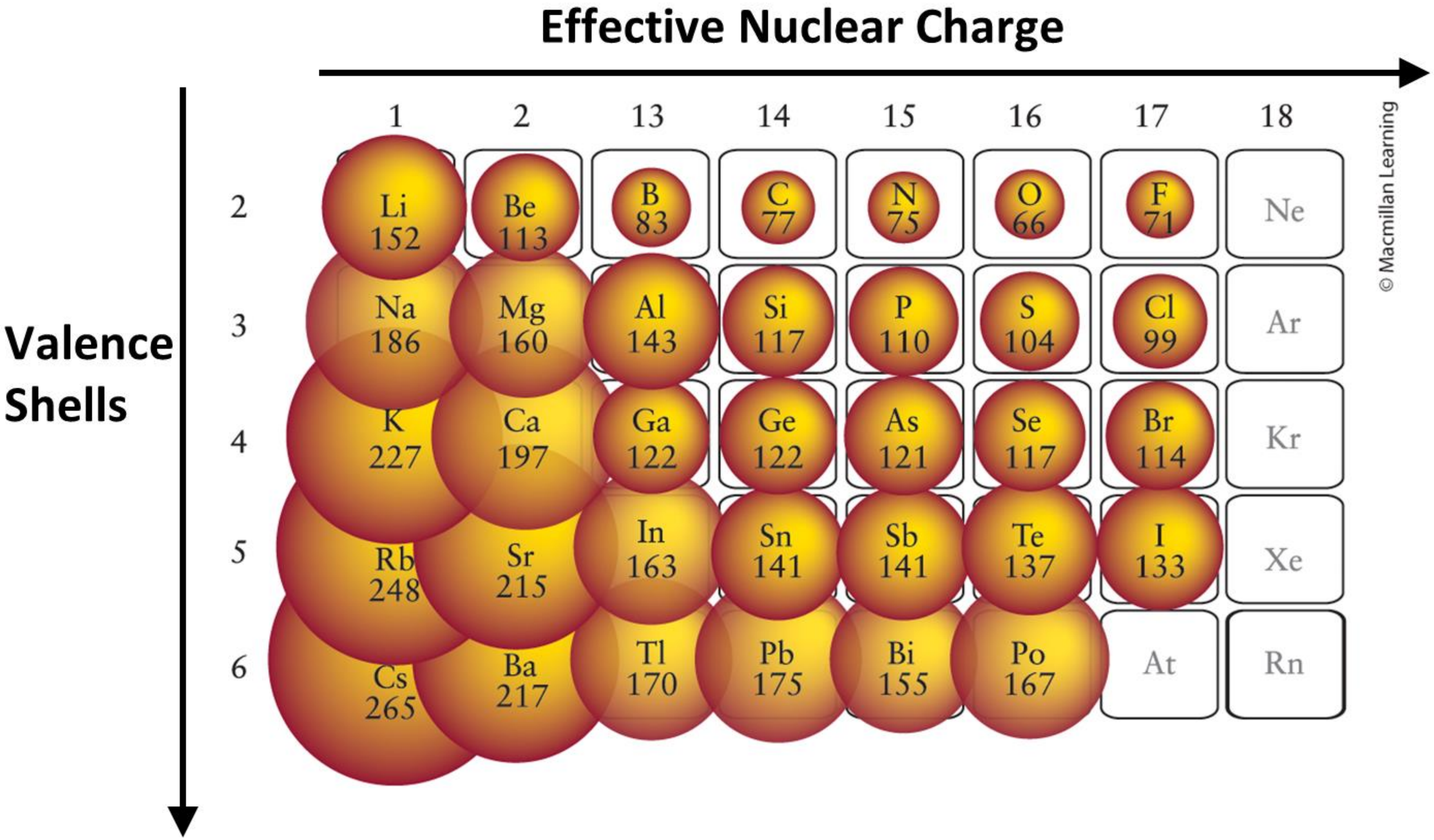


1 Atomic radius

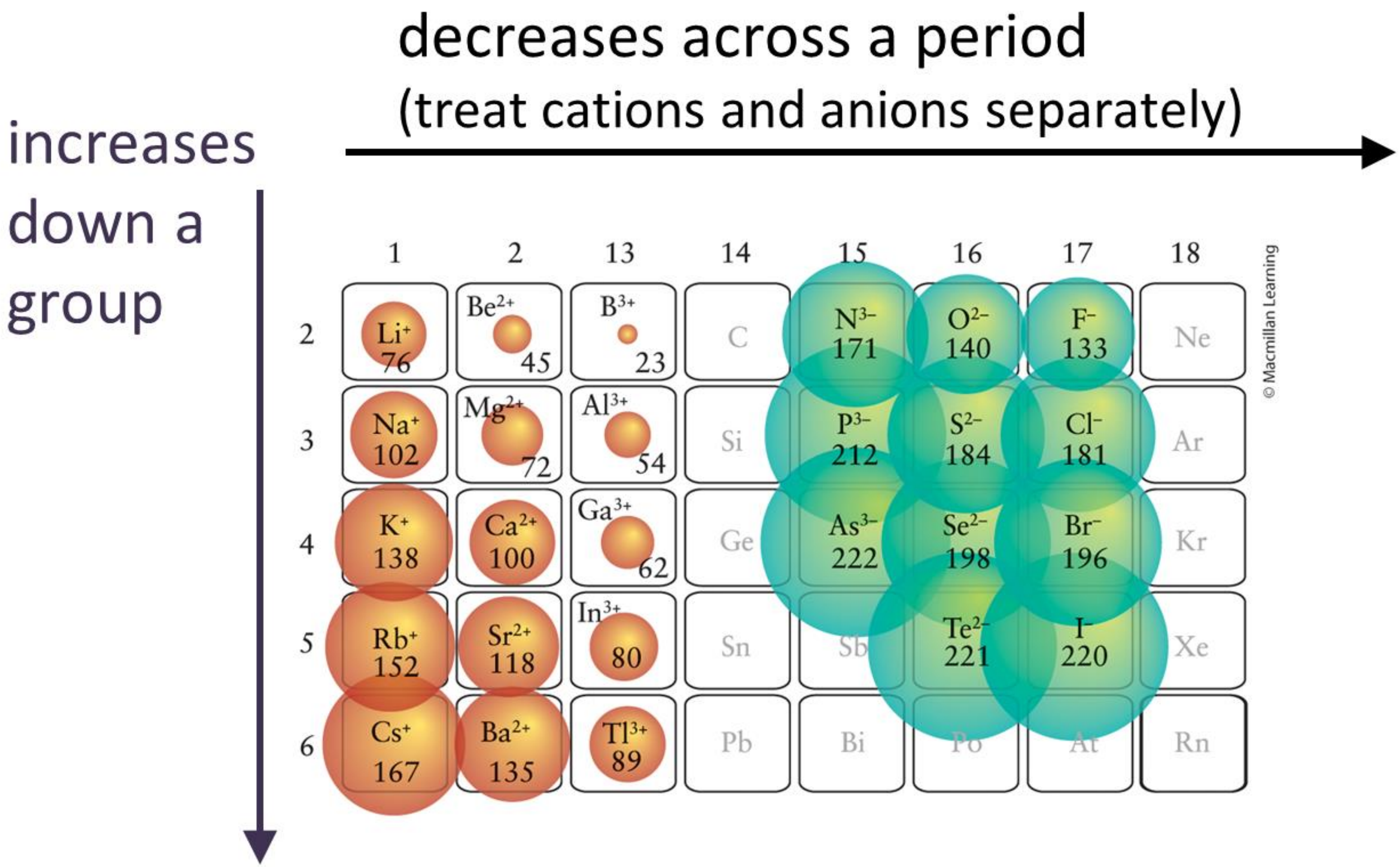


2 Ionic radius

Periodic Trend of Atomic Radius



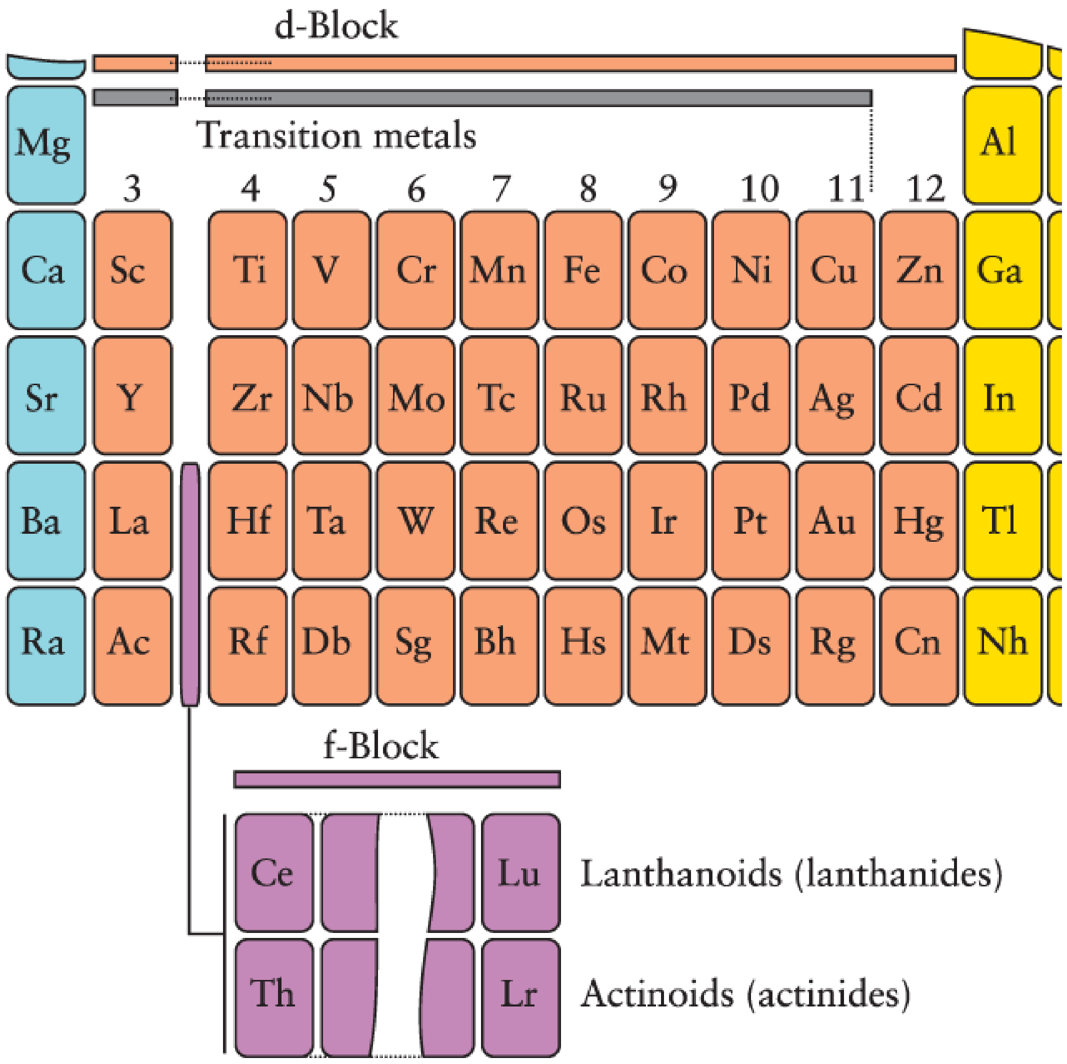
Periodic Trend of Ionic Radius



Blocks on the Periodic Table

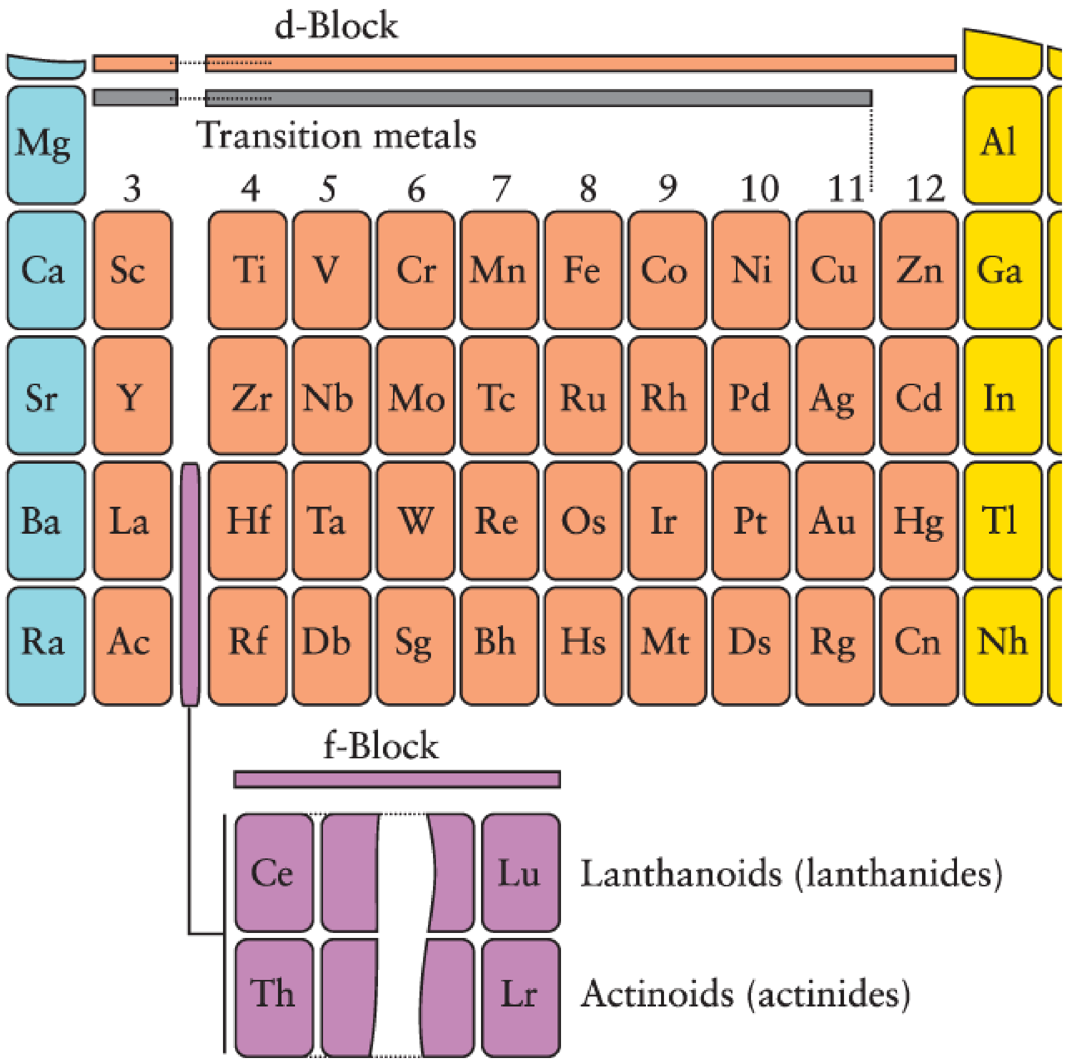
Blocks on the Periodic Table

- Groups 1-2 are the s-block, and groups 13-18 are the p-block. The s-block and the p-block are called main group elements.
- Groups 3-12 are the d-block.
- Within the d-block, groups 3-11 are called the transition metals representing a transition from the highly reactive s-block metals to the p-block metals.



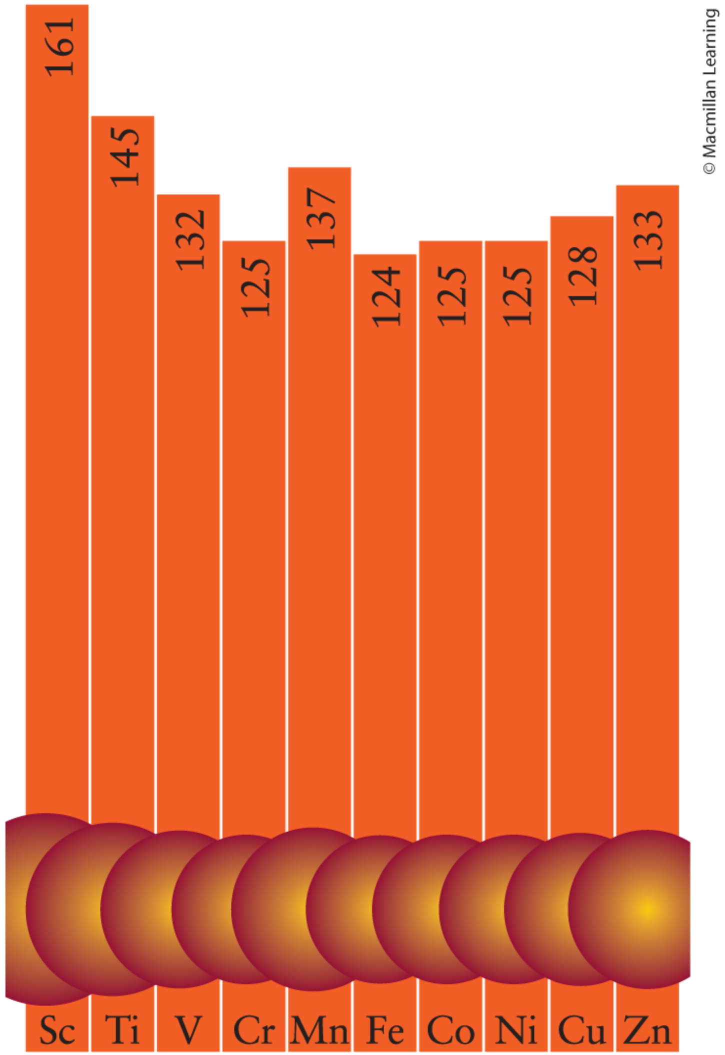
Blocks on the Periodic Table

- The f-block consists of inner transition metals that located within the d-block. Lanthanoids occur in period 6, and actinoids occur in period 7.



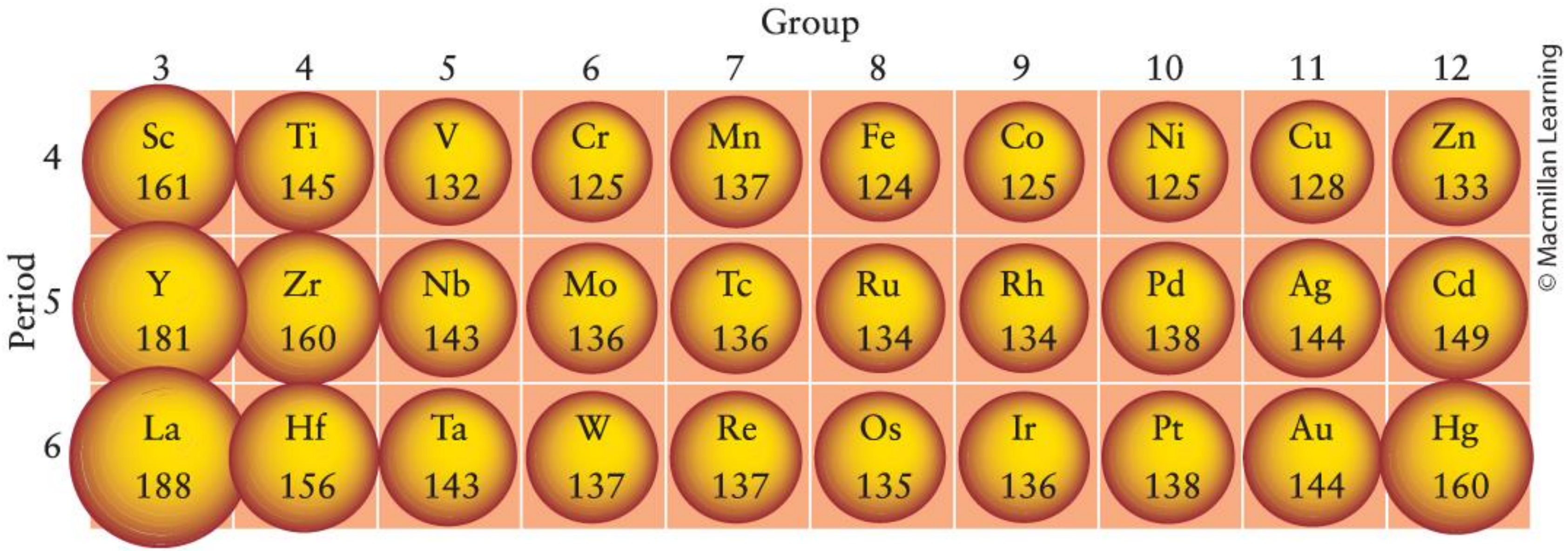
Trends in Atomic Radii of d-Block Elements

- Additional d-electrons increase electron-electron repulsions more rapidly, than nuclear charge increases, so the radii increase
- Moving across a period from left to right, atomic radii of d-block elements *decrease*, then *increase* due to lack of shielding from d-orbitals.



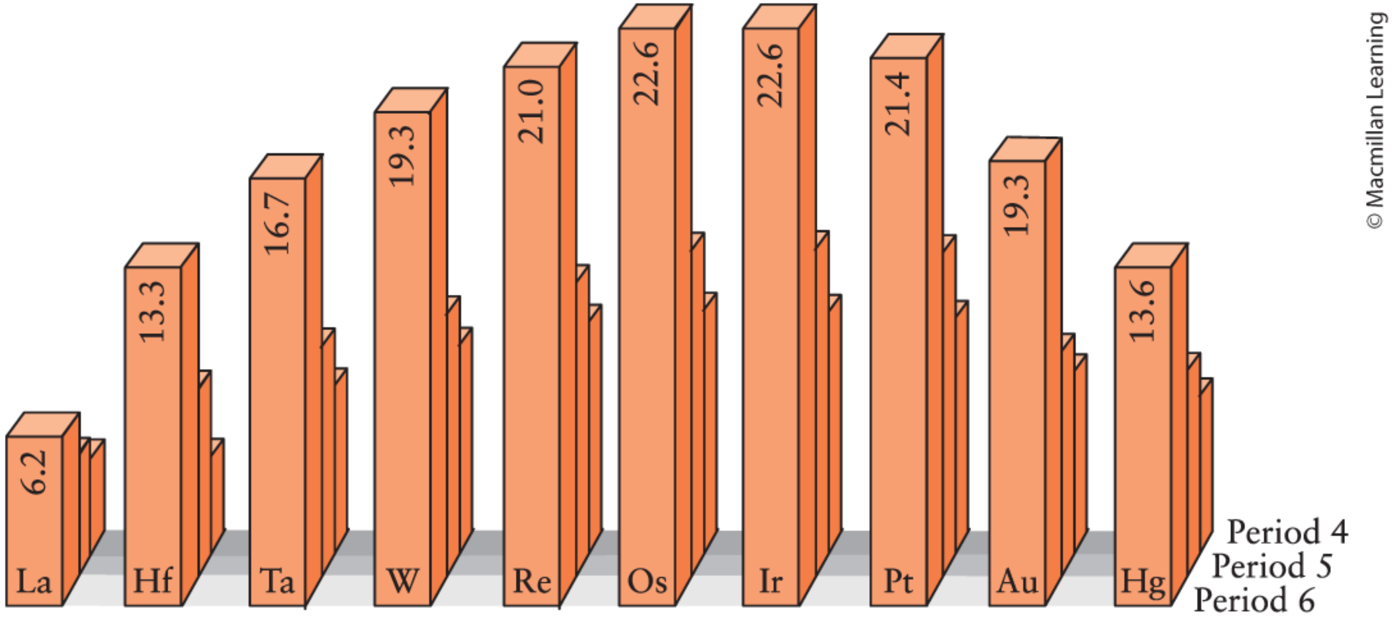
Trends in Atomic Radii of d-Block Elements

- The trends in atomic radii of d-block elements are slightly different from main-group elements.



- The atomic radii of d-block elements increase from Period 4 to Period 5. However, as a result of lanthanide contraction, d-block elements in Periods 5 and 6 have similar atomic radii.

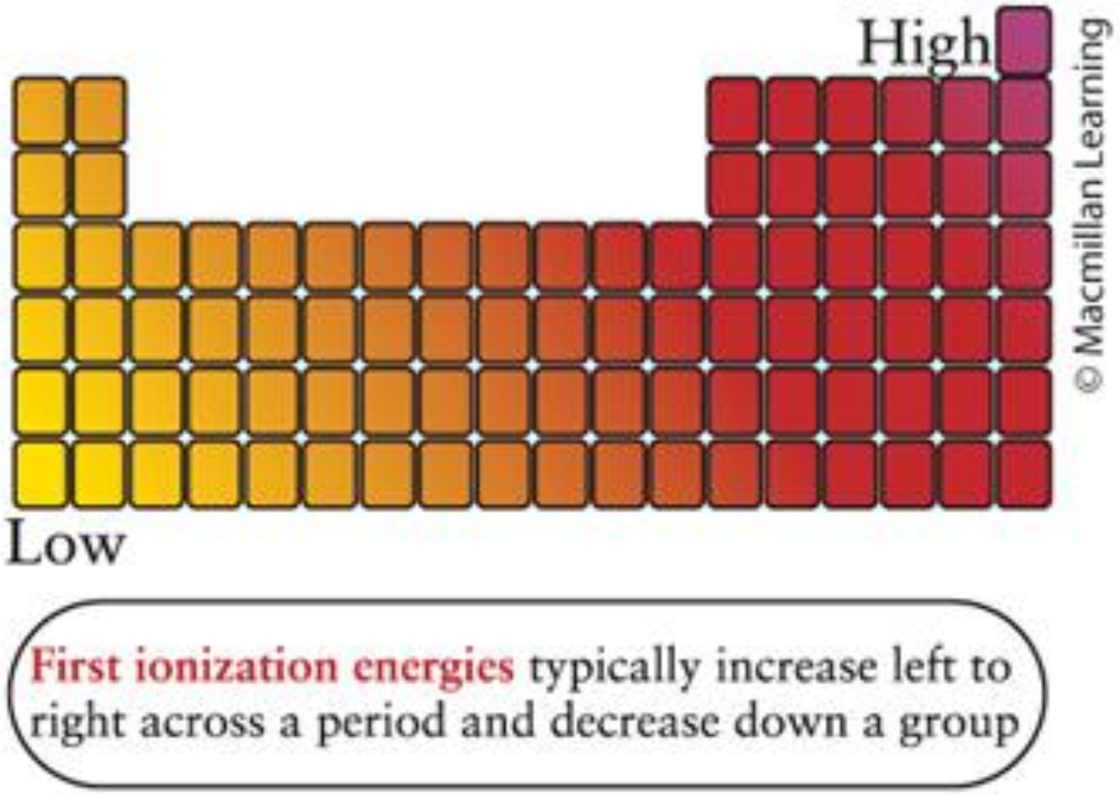
Trends in Density



- Lanthanide contraction affects the densities of Period 6 elements.
- The atomic radii of Period 6 elements are similar to Period 5, but the atomic masses of Period 6 elements are much greater, resulting in higher densities.
- Lanthanide contraction is also the reason for the low reactivity, or “nobility,” of gold and silver.

Trends in First Ionization Energy

- First ionization energies typically increase from left to right across a period and decrease down a group.
- Moving across a period, the increasing effective nuclear charge grips electrons more tightly, resulting in greater first ionization energies.
- Moving down a group, the decreasing effective nuclear charge is due to additional atomic shells. The more shells, the more core electrons shield outer electrons from the nuclear charge, making it easier to remove valence electrons.

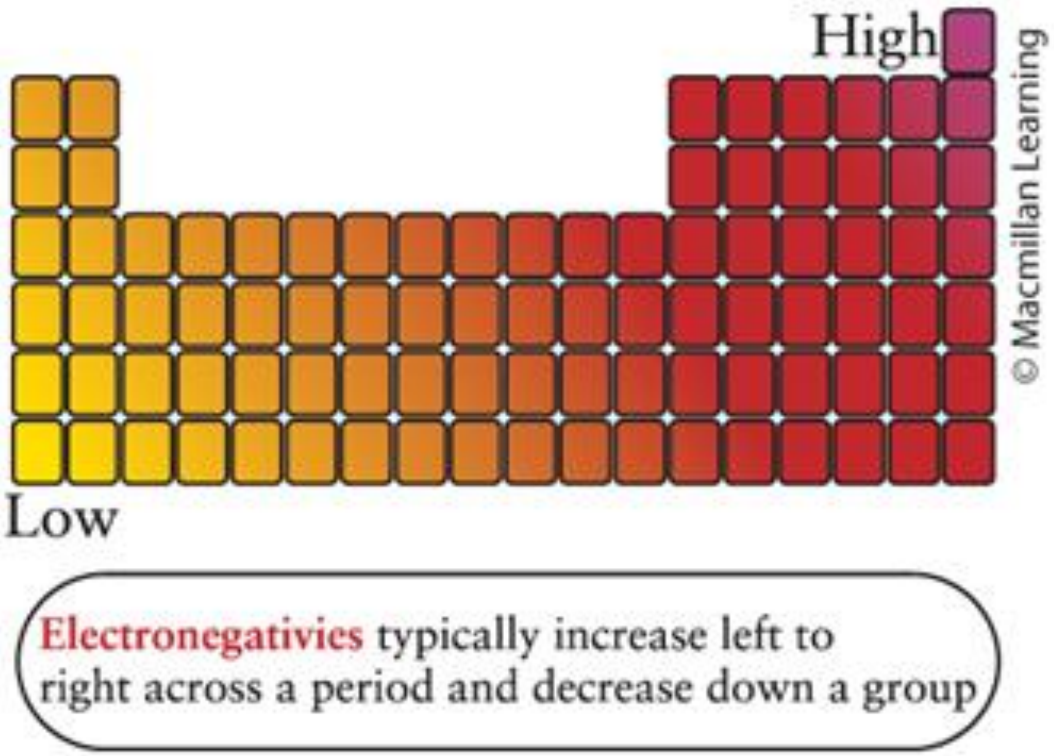


Trends in Electron Affinity

- Electron affinity is the energy released when an electron is added to a gaseous atom to form an anion.
- Periodic trends in electron affinity are not as clear as other atomic properties. However, the highest electron affinities are found at the top right of the periodic table.
- Atoms with a higher effective nuclear charge release more energy.

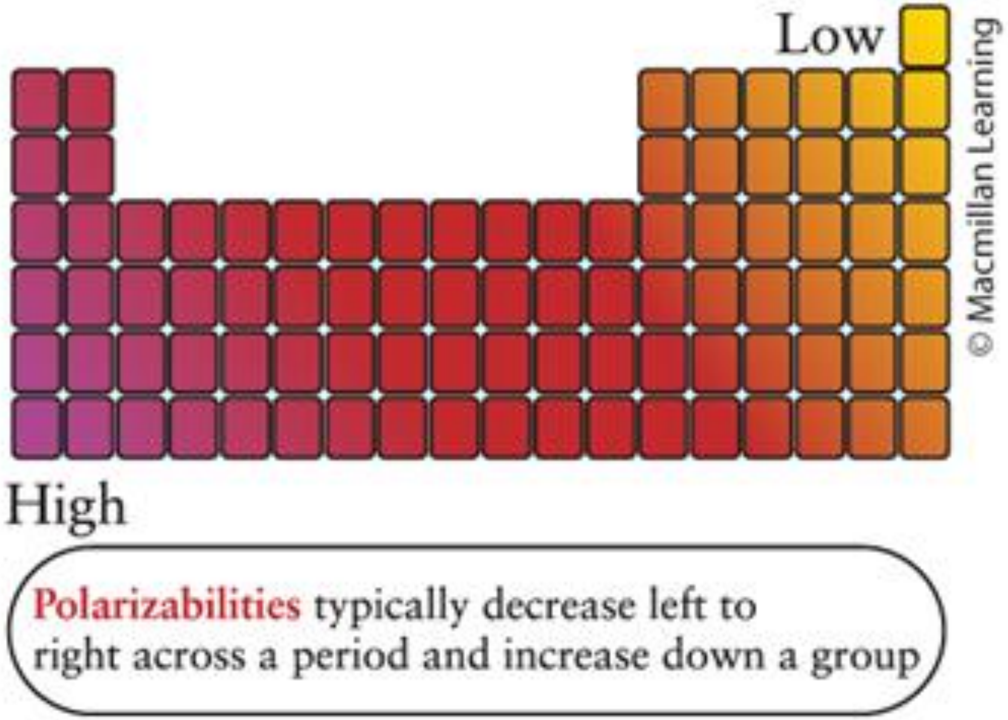
Trends in Electronegativity

- Electronegativities typically increase from left to right across a period and decrease down a group.
- Electronegativity is the tendency of an atom to attract electrons to itself.
- Atoms with a greater effective nuclear charge have a stronger pull on bonding electrons, resulting in higher electronegativities.



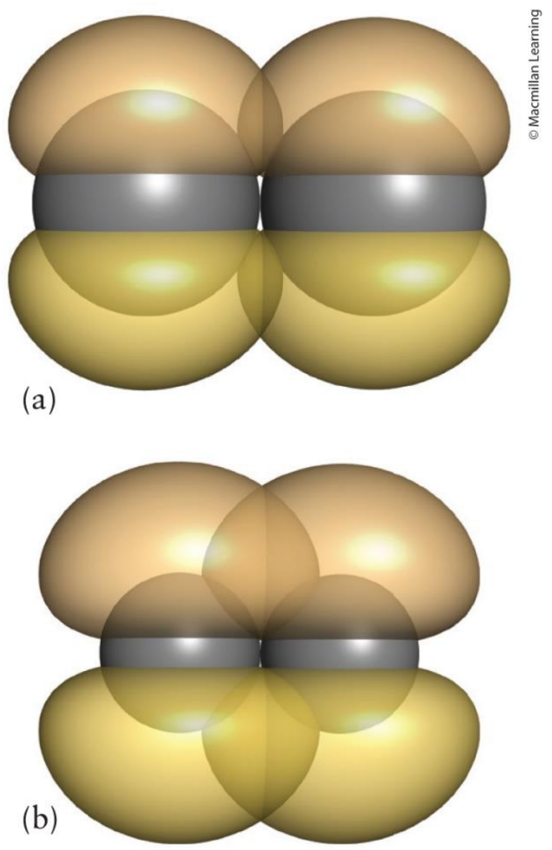
Trends in Polarizability

- Polarizabilities typically decrease from left to right across a period and increase down a group.
- Polarizability is the ease with which an electron cloud of an atom can be distorted.
- Electron-rich, heavier atoms are easily polarized.
- Atoms with a high polarizing ability are small-sized, highly-charged atoms.



Trends in Bonding

- The small radii of Period 2 atoms account for bonding differences compared to their congeners, the other members of the group.
- Period 2 atoms are small so their p-orbitals overlap effectively; the reason for multiple π-bonds.
- Period 3 atoms are bigger, their p-orbitals are held apart so have very little overlap.

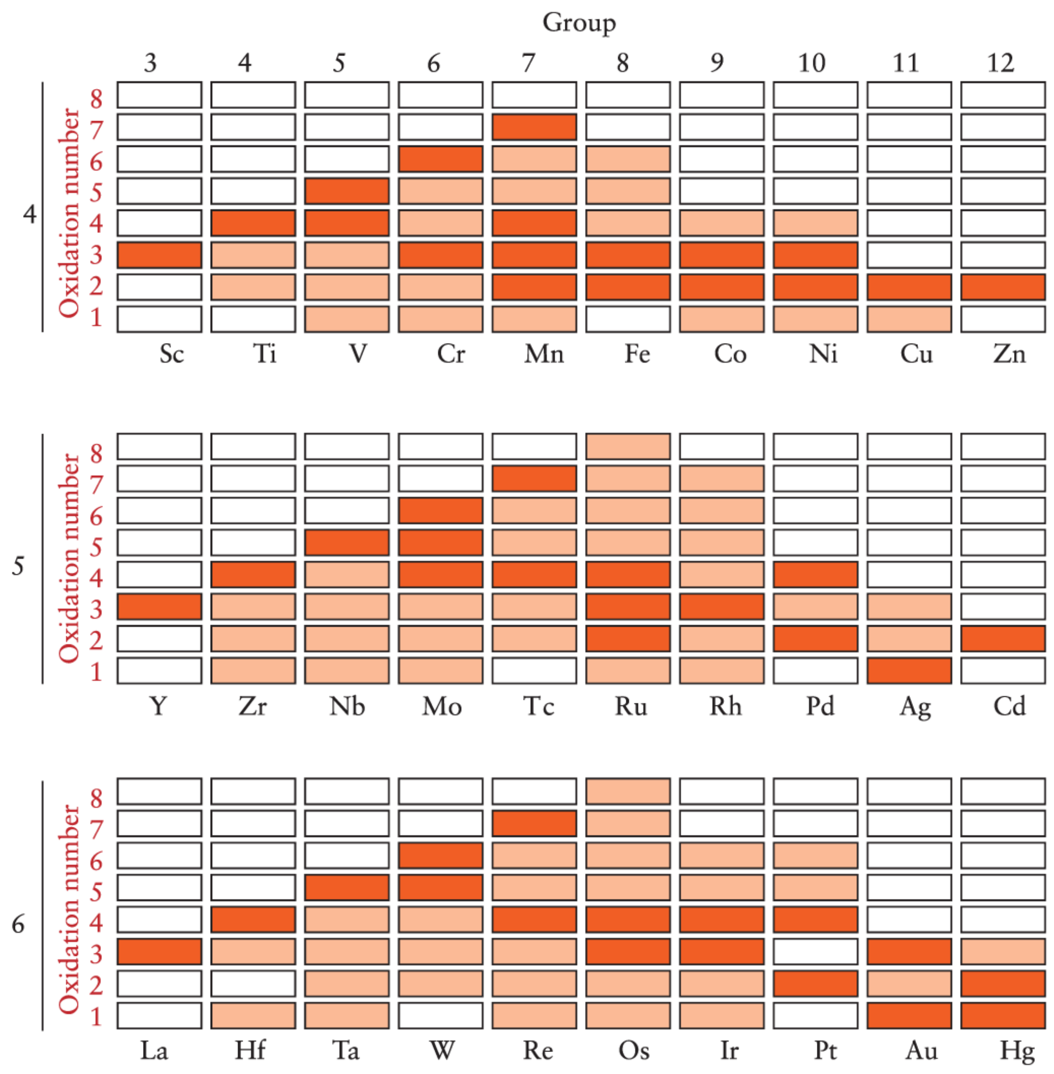


Period 2

Period 3

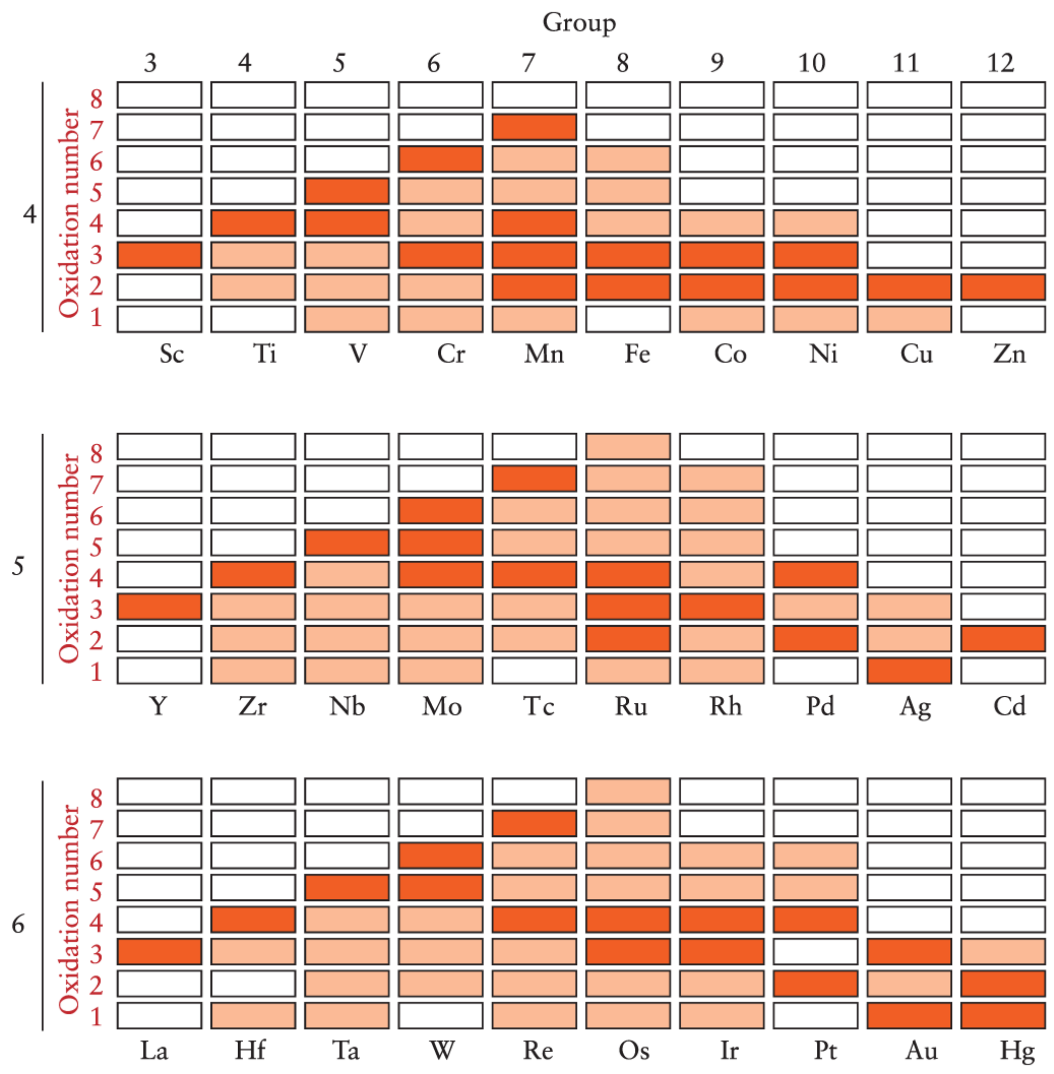
Oxidation States of d-Block Elements

- The d-block elements tend to lose their valence s-electrons first when forming compounds.
- Most lose a variable number of d-electrons and exist in a variety of oxidation states.



Oxidation States of d-Block Elements

- Elements in the center of each row have the widest range of oxidation states.
- Elements in the second and third rows reach higher oxidation states.



Trends in Chemical Properties: Hydrides

- All the main-group elements, except the noble gases, and possibly indium and thallium, form binary compounds with hydrogen called hydrides.

- Hydride formulas are related to group numbers.
- Carbon (Group 14/IV) forms CH_4.
- Nitrogen (Group 15/V) forms NH_3.
- Oxygen (Group 16/VI) forms H_2O.
- Fluorine (Group 17/VII) forms HF.

Trends in Chemical Properties: Hydrides

Saline Hydrides

- Most Group 1 and 2 elements, except for beryllium, form ionic compounds with hydrogen called saline hydrides or salt-like hydrides.

- They are formed by heating the metal in hydrogen gas.

$$2\ \mathrm{K}\ (\mathrm{s}) + \mathrm{H_2}(\mathrm{g}) \xrightarrow{\Delta} 2\ \mathrm{KH}\ (\mathrm{s})$$

$$2\ \mathrm{Cu}\ (\mathrm{s}) + \mathrm{H_2}(\mathrm{g}) \xrightarrow{\Delta} 2\ \mathrm{CuH}\ (\mathrm{s})$$

Metallic Hydrides

- Metallic hydrides release their hydrogen (as H_2 gas) when heated or treated with acid. Metallic hydrides are being studied as a possible way to store and transport hydrogen.

$$2\ \mathrm{CuH} \longrightarrow x\mathrm{Cu}(2-\mathrm{x})\mathrm{CuH} + {}^{1}/_{2}\, x\, H_2 \quad (0 < x < 2)$$

$$\mathrm{CuH}\ +\ HCl \longrightarrow \mathrm{CuCl}\ + H_2(\mathrm{g})$$

- Metallic hydrides are black, powdery, electrically conducting solids formed by heating certain d-block metals in hydrogen.

Molecular Hydrides

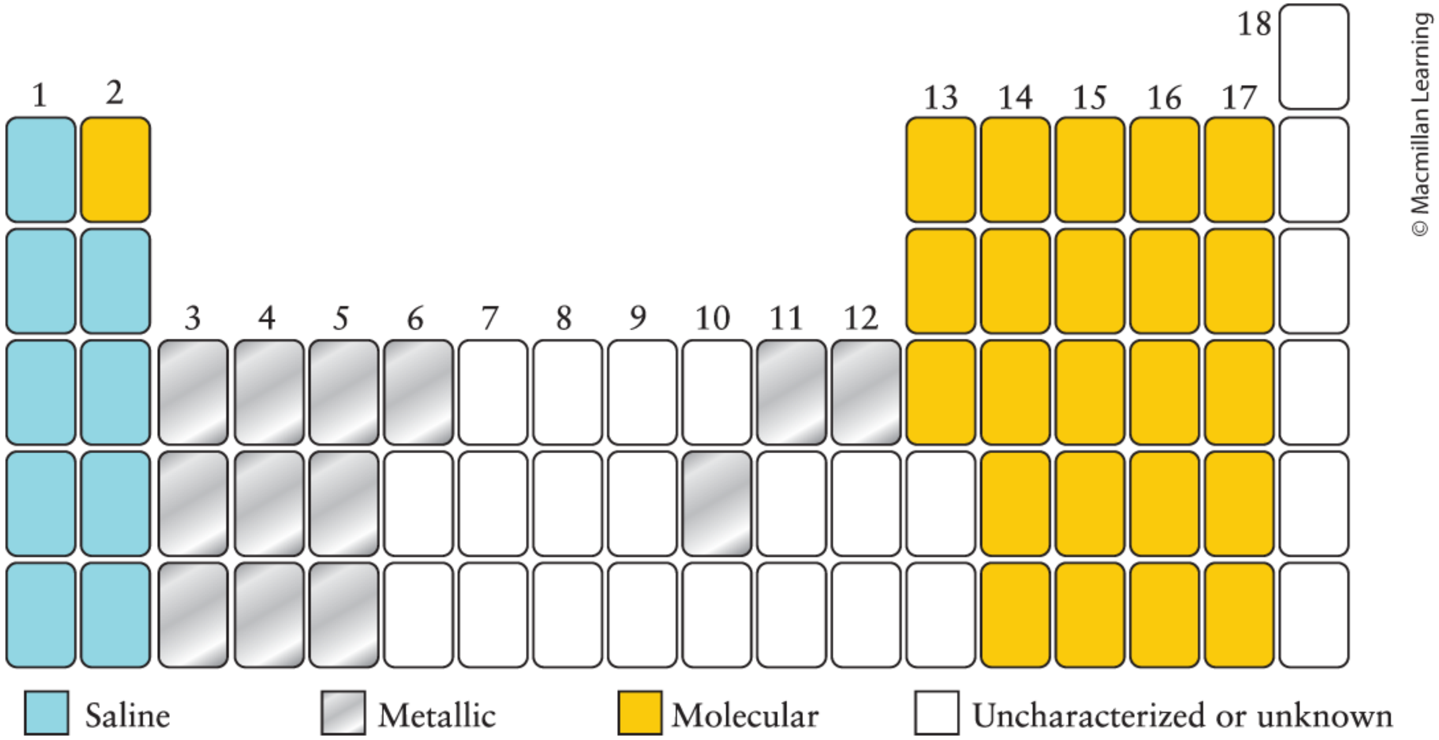
- Nonmetals form covalent molecular hydrides. Many are volatile, and some are Brønsted acids.

- Hydride gases include ammonia, the hydrogen halides (HF, HCl, HBr, HI), and lighter hydrocarbons such as methane, ethane, ethene, and ethyne.

- Liquid molecular hydrides include water and hydrocarbons such as octane and benzene.

The Pattern of Hydrides

	s-block	d-block	p-block
Type:	saline	metallic	molecular



Trends in Chemical Properties: Oxides

- All main-group elements, except noble gases, react with oxygen to form oxides. Oxides demonstrate periodic trends in the chemical properties of elements.

- Ionic oxides on the left of the periodic table are soluble.

- Left side p-block oxides are insoluble, high-melting-point solids.

- Right side p-block oxides are low-melting-point, often gaseous, molecular oxides.

Metal Oxides

- Metallic elements with low ionization energies commonly form basic oxides.

- Elements with intermediate ionization energies like Be, B, Al, and the metalloids, form amphoteric oxides, meaning:
  - They do not react with or dissolve in water.
  - They do dissolve in both acidic and basic solutions.

Molecular Oxides

- Many oxides of nonmetals, such as CO_2, NO, SO_3, are gaseous molecular compounds and can act as a Lewis acid.

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

Molecular Oxides

- Many oxides of nonmetals, such as CO_2, NO, SO_3, are gaseous molecular compounds and can act as a Lewis acid.

$$H_2O + \ CO_2 \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

- Acid anhydrides form acidic solutions when in water. For example, SO_3 forms H_2SO_4 in water. Also, N_2O_5 forms HNO_3 in water.

$$N_2O_5\ (g) + \ H_2O\ (l)\ \rightarrow\ 2\ HNO_3\ (aq)$$

- Formal anhydrides do not react with water. Although CO does not react with cold water, it is the formal anhydride of formic acid HCOOH, because it can be obtained by removing the elements of water from the molecular formula of the acid.

Trends in Chemical Properties: Oxidation Numbers

- The pattern of oxidation numbers underlies trends in the chemical properties of the d-block elements.
- An element with a high oxidation number is easily reduced, and probably a good oxidizing agent like MnO_4^-.
- An element with a low oxidation number is probably a good reducing agent like Cr^{2+}.

Oxidation Numbers and Acid-Base Behavior

- The pattern of oxidation numbers correlates with the pattern of acid-base behavior. Most d-block metals are basic, but oxides of a given element shift toward acidic character as the oxidation number increases.

CrO	+2	basic
Cr_2O_3	+3	amphoteric
CrO_3	+6	acidic

Classification of Solids Electrically

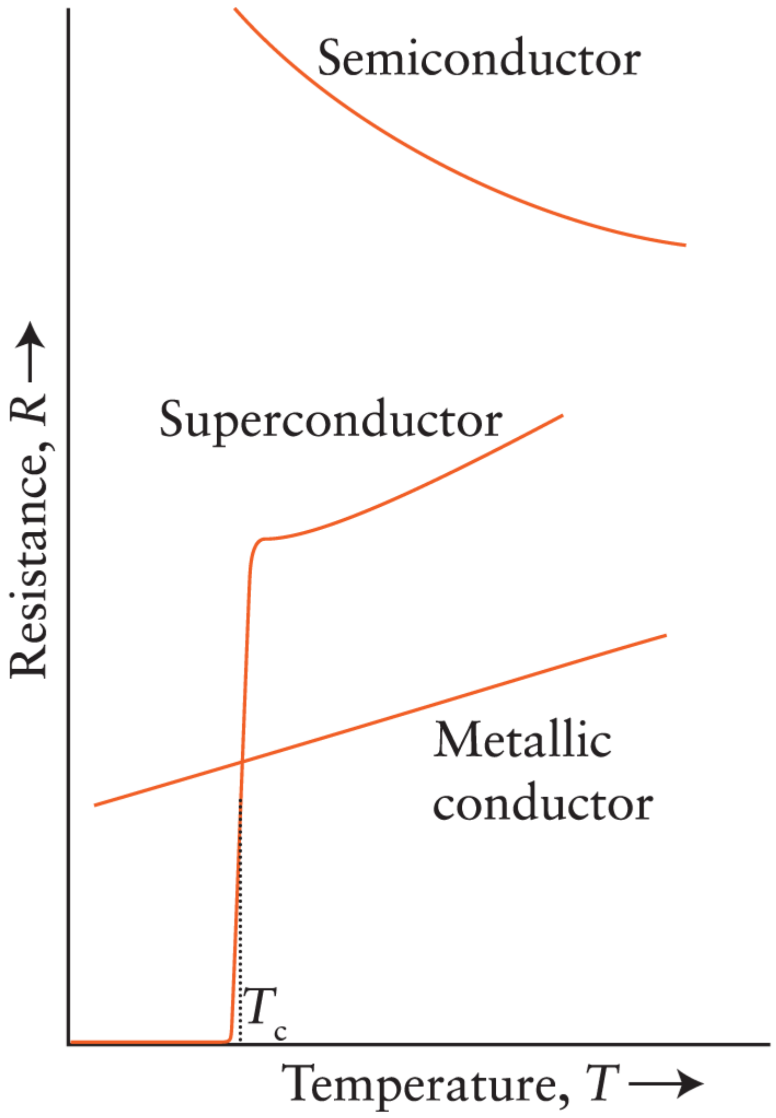
- An electric current is the flow of electric charge. The charge is carried by electrons in electronic conduction. Electronic conduction is the type of conduction in metals and graphite.

- In ionic conduction, the charge is carried by ions. Ionic conduction is the mode of electrical conduction in molten salts or electrolyte solutions. Most ions are too bulky to travel easily through most solids. However, solid electrolytes allow ions to move through their lattices.

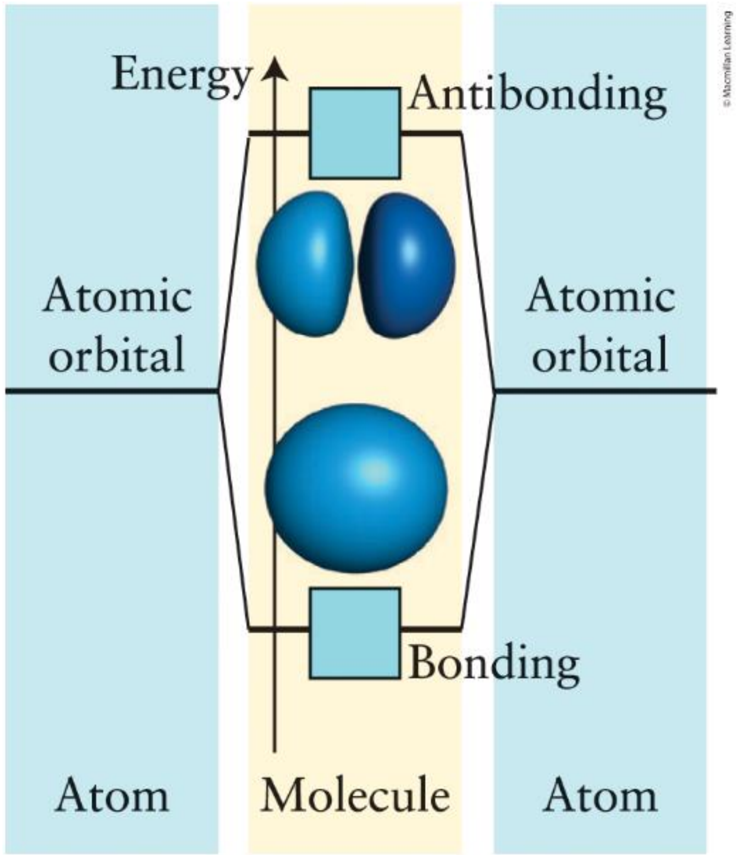
- Solid electrolytes are important components of rechargeable batteries, like lithium-ion batteries.

Classification of Solids Electrically

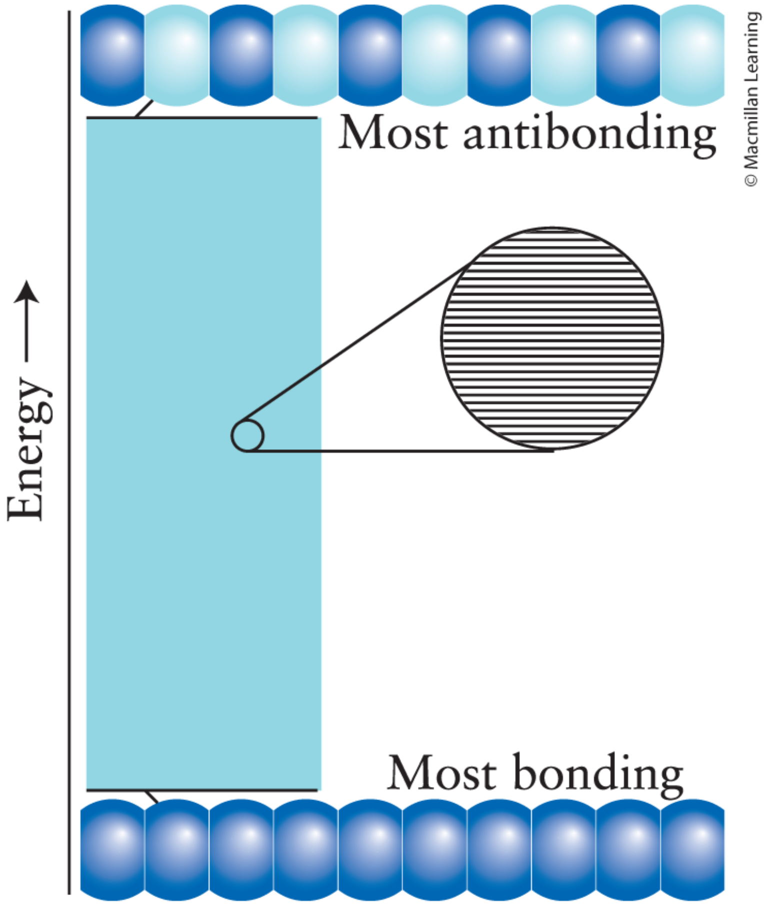
- Insulators have such a high resistance they do not conduct electricity.
- Solids can be classified according to how their resistance varies with temperature.
- Metallic conductor: resistance increases when temperature increases
- Semiconductor: resistance decreases when temperature increases
- Superconductor: conducts electricity with zero resistance at temperatures lower than a critical temperature, Tc (usually very low)



Molecular Orbital Theory and Conduction

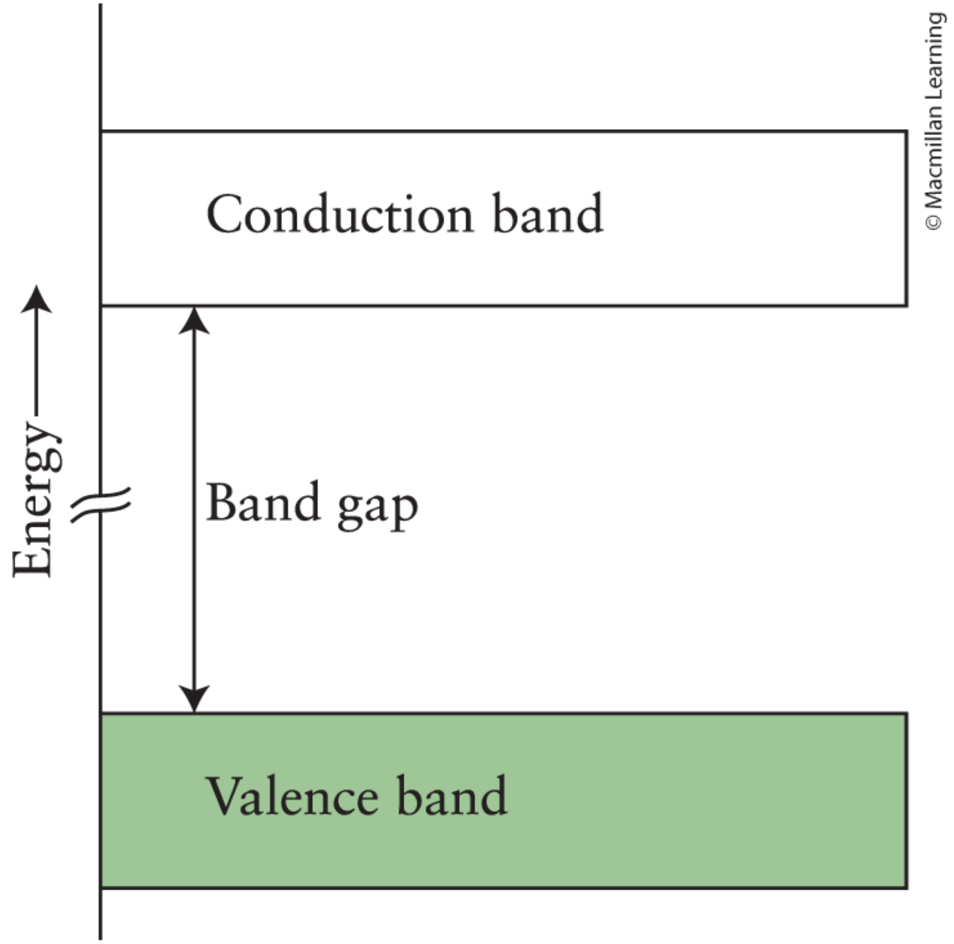


- When N atomic orbitals merge together, they form N molecular orbitals.
- The same thing happens in a solid, but N is enormous (for example, about 1023 for 10 g of copper). More molecular orbitals means MOs are closer together in energy, forming a nearly continuous band.
- In metals, half the MOs are bonding and half are antibonding.



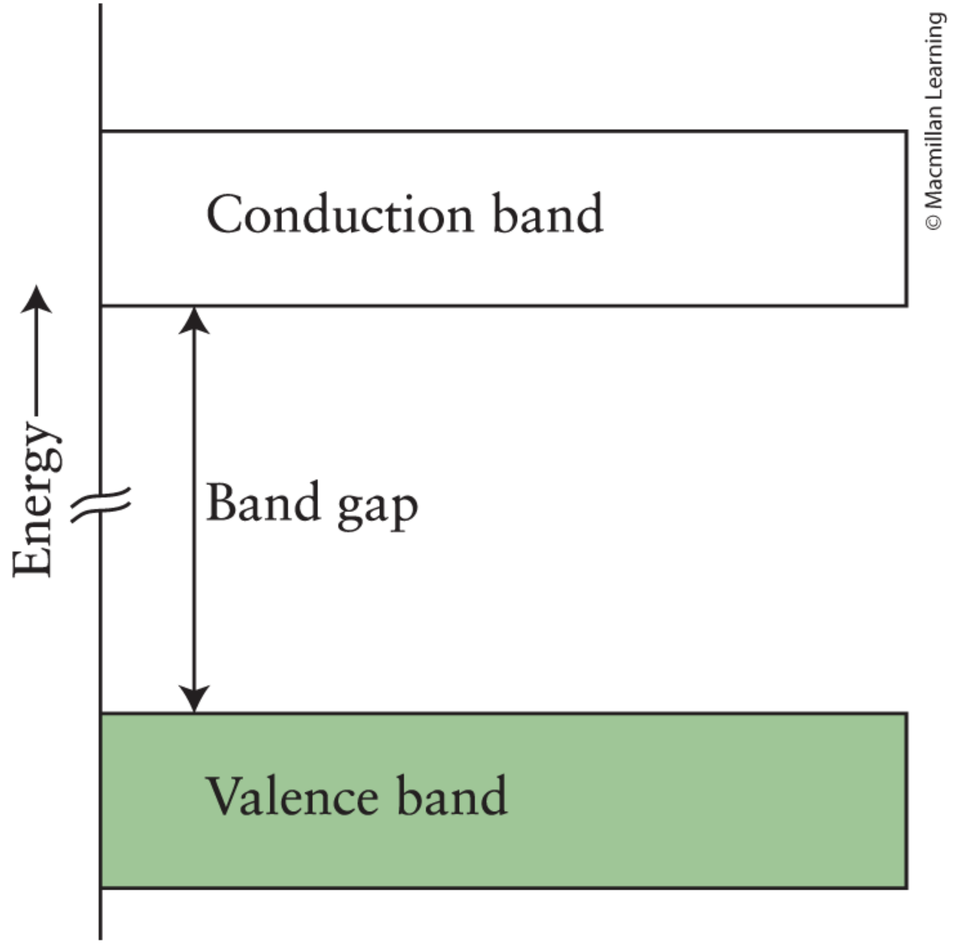
Conduction Bands

- Neighboring orbitals are so close in energy that little additional energy is needed to excite metal electrons from the topmost filled MO to empty orbitals of the conduction band. Conduction band electrons move freely.
- When a metal is heated, atoms vibrate more vigorously, which impedes the migration of electrons, increasing the resistance.
- Conduction bands are empty or incompletely filled bands of molecular orbitals.



Valence Bands

- In insulators, the valence electrons fill all available molecular orbitals to give a full band valence band. Here there is a substantial band gap, a range of energies for which there are no orbitals, before the next band, the conduction band composed of empty orbitals, begins.
- Electrons need a very large injection of energy to reach the conduction band.
- If the energy gap is too large, electrons are not mobile and the solid does not conduct electricity.



Intrinsic and Extrinsic Semiconductors

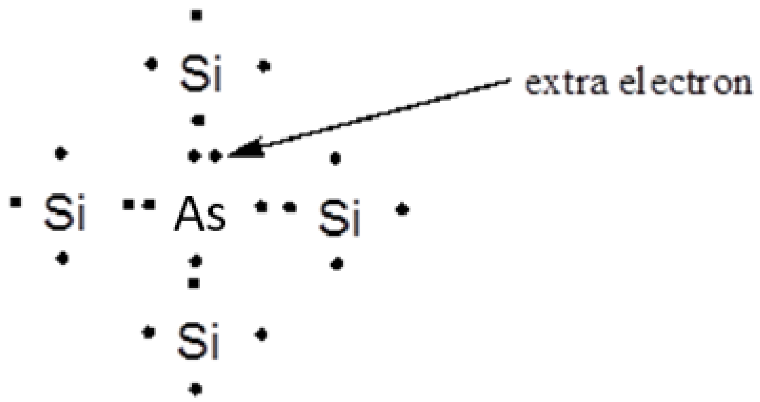
- In an intrinsic semiconductor, an empty conduction band lies close in energy to a full valence band.

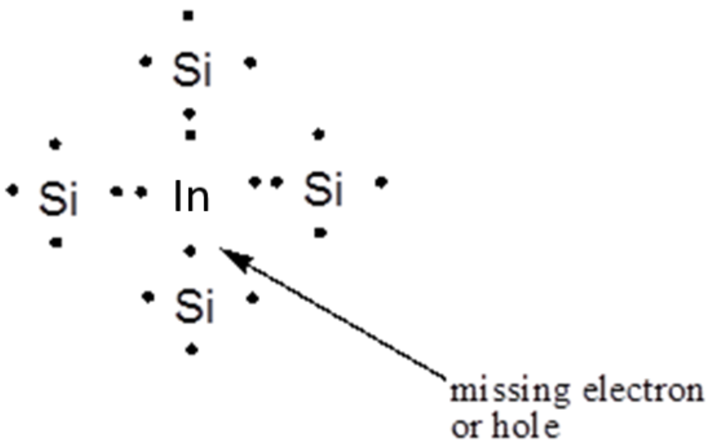
- As the solid is warmed, electrons can be excited from the valence band into the conduction band; resistance in the semiconductor decreases as its temperature raises.

- Semiconductors are doped by spreading small impurities throughout a solid to modify their electrical carrying ability. This produces an extrinsic semiconductor.

Doping Semiconductors

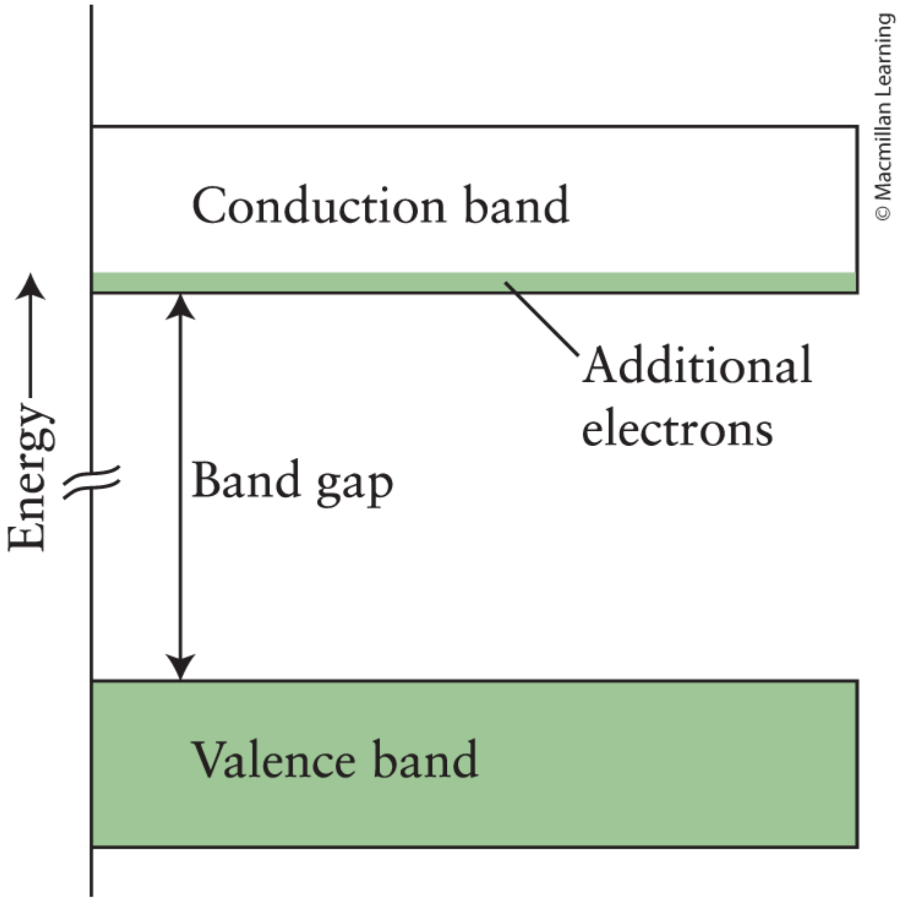
- Doping silicon with arsenic increases the number of electrons in the solid. This type of material is called an n-type semiconductor because it contains excess negatively charged electrons.

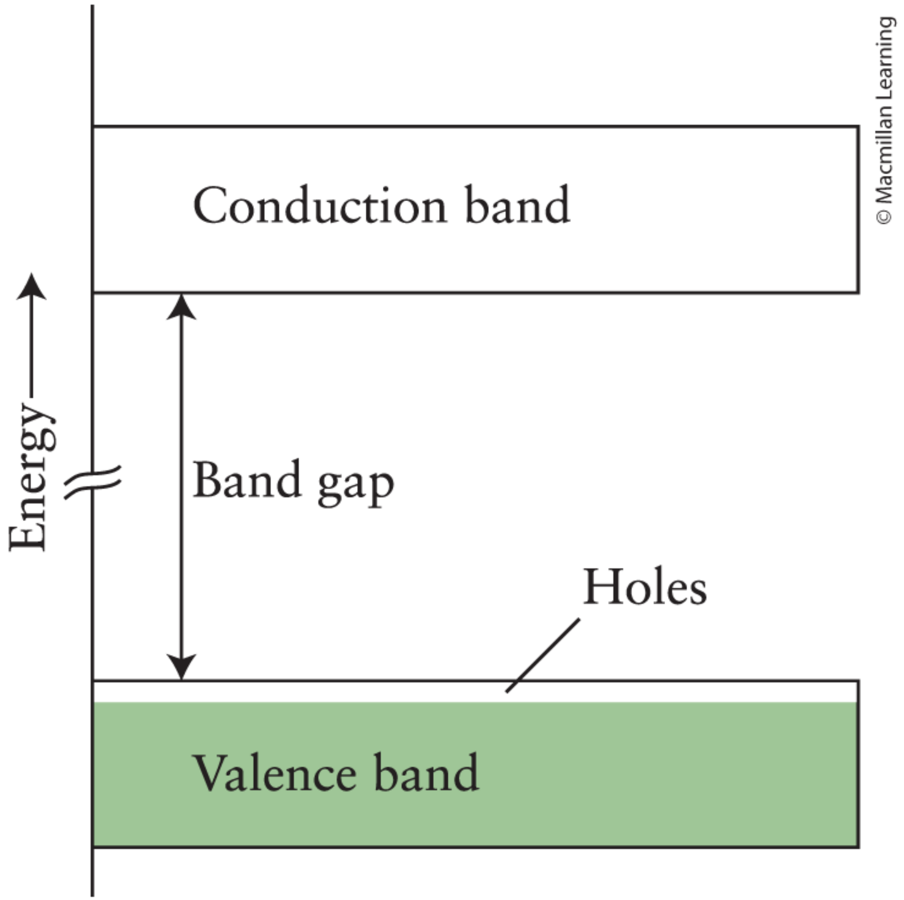




- Doping silicon with indium produces materials with “extra” holes. This type of material is called a p-type semiconductor because it contains positively charged holes.

Doping Semiconductors





- n-type semiconductor
- p-type semiconductor

p–n Junction

- The region in the semiconductor where the n-type and p-type semiconductors meet is called the p–n junction.

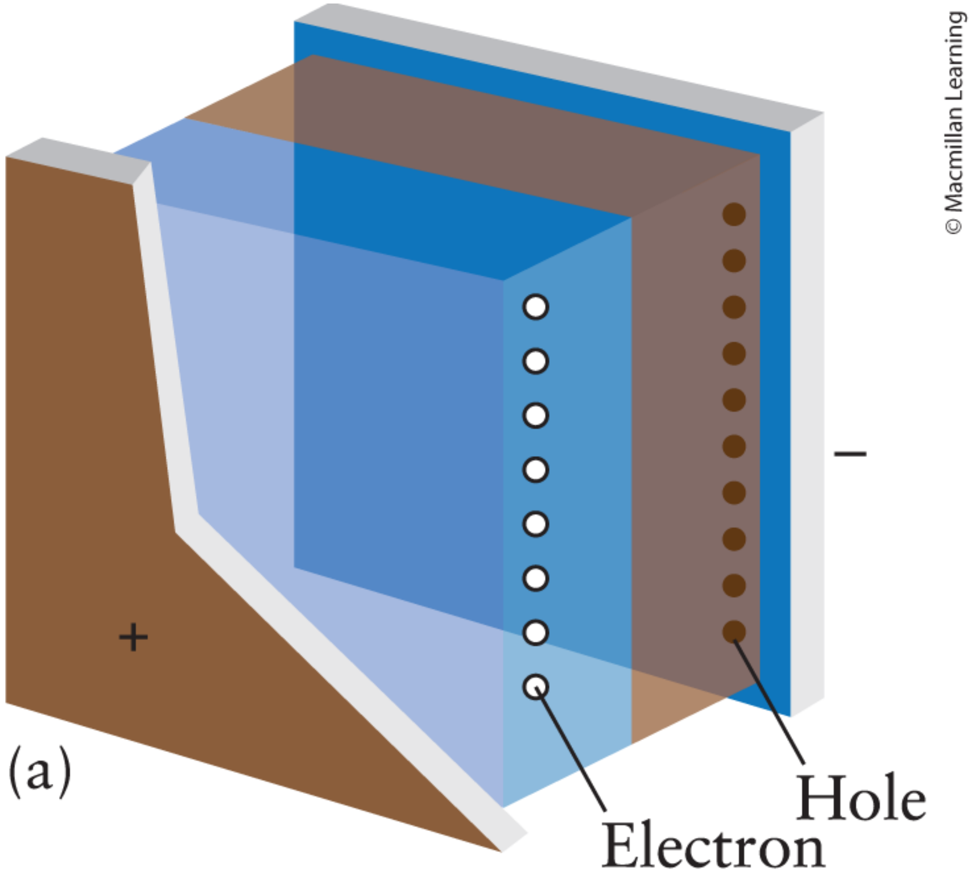
- At a p–n junction, electric current can only flow in one direction.
- An interesting interaction occurs at the p–n junction when the n-type layer comes into contact with the p-type layer. Electrons will only flow in one direction (forward biased) but not in the other (reverse biased).

- One type of a p–n junction is a light-emitting diode, or LED.

p–n Junction

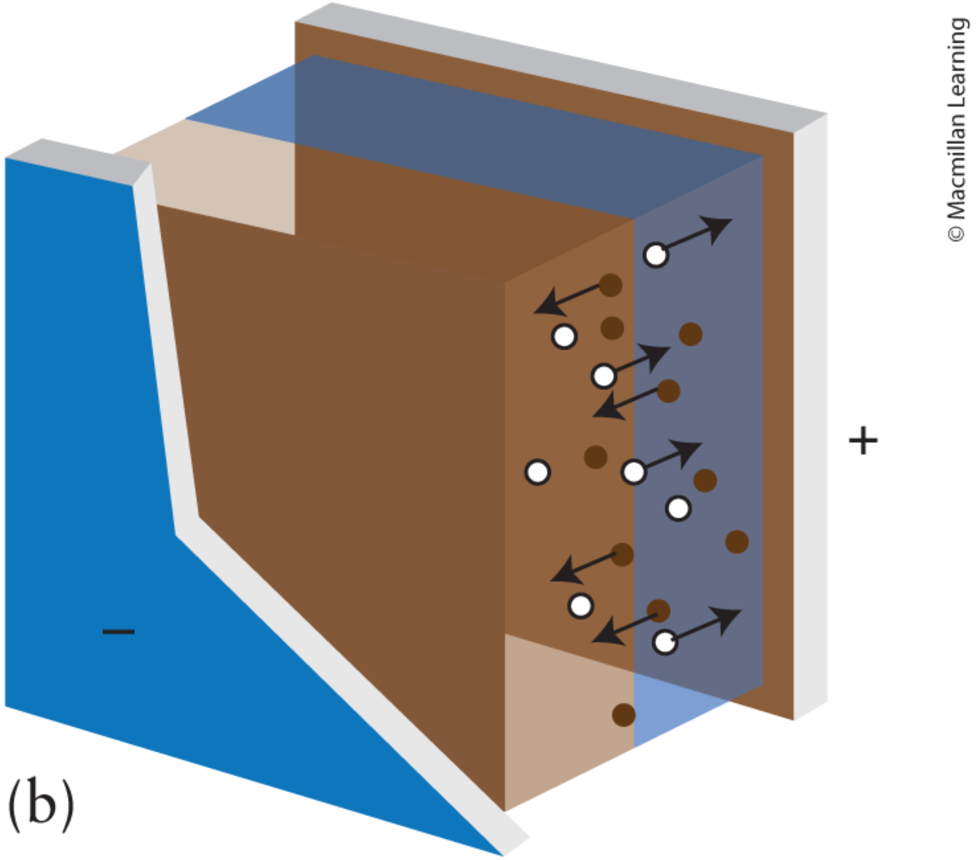
- When the p-type and n-type semiconductors are sandwiched together, at the point at which they touch, a sudden, mad rush of extra free electrons in the n-type layer fall into holes on the p-type side.

- Electrons stop moving when a p-type has a negative charged applied: the holes move to the “-” side, preventing the electrons on the n-type side from jumping the band gap.



p–n Junction

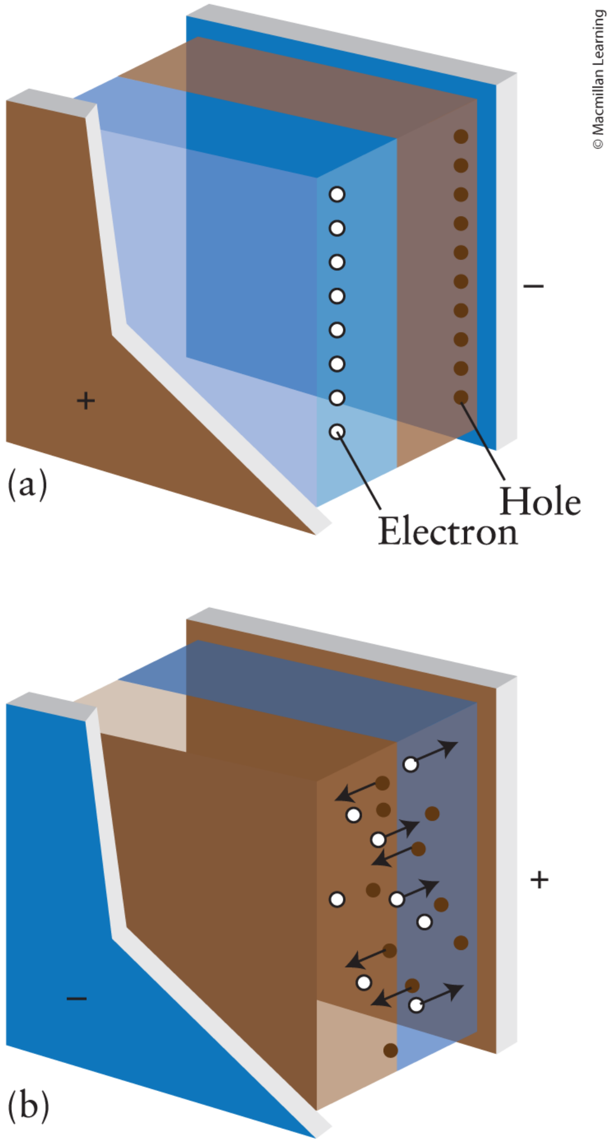
- Switching the charge, making the n-type negatively charged, will draw the holes to the n-type side, and electrons begin jumping the “junction” or flowing to the p-type side; the added potential can be either electrical or a photon.



(b)

p–n Junction

- Doping determines the size of the band gap and hence the voltage of the semiconductor.
- This is called a bias because electrons can only flow once the n-type has an applied negative voltage.



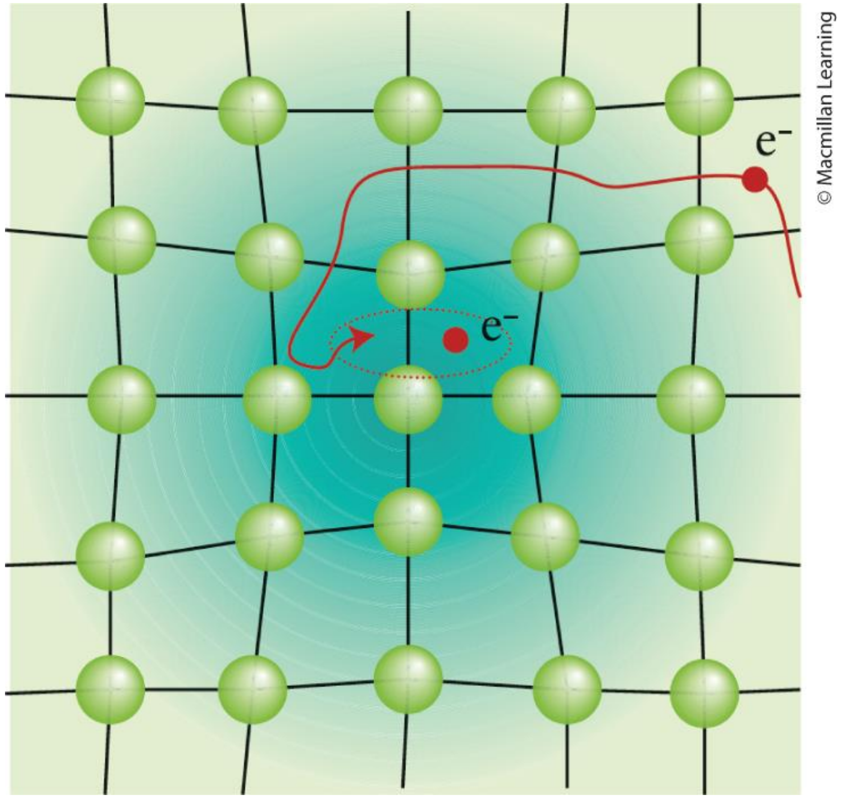
- (a) reverse bias, the current does not flow.
- (b) forward bias, charge carries can be regenerated

Superconductors

- In principle, superconductors have great potential to help reduce losses in power transmission.
- Superconductivity is the loss of all electrical resistance when a substance is cooled to its critical temperature (Tc).
- It is thought low temperatures reduce the effect of the vibrations of the atoms in their crystalline lattice. They do this by forming pairs of electrons called Cooper pairs.

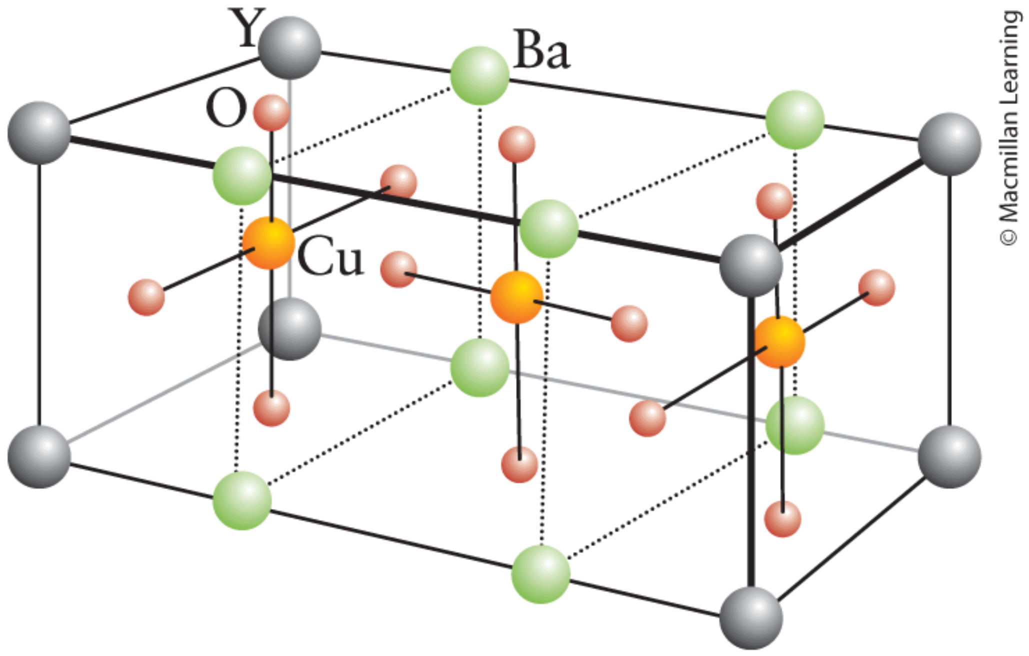
Cooper Pairs

- Cooper pairs form when one electron distorts the cationic lattice, drawing in a second electron.
- The two electrons are weakly attracted, and not shaken apart by the vibrations of the crystal lattice.



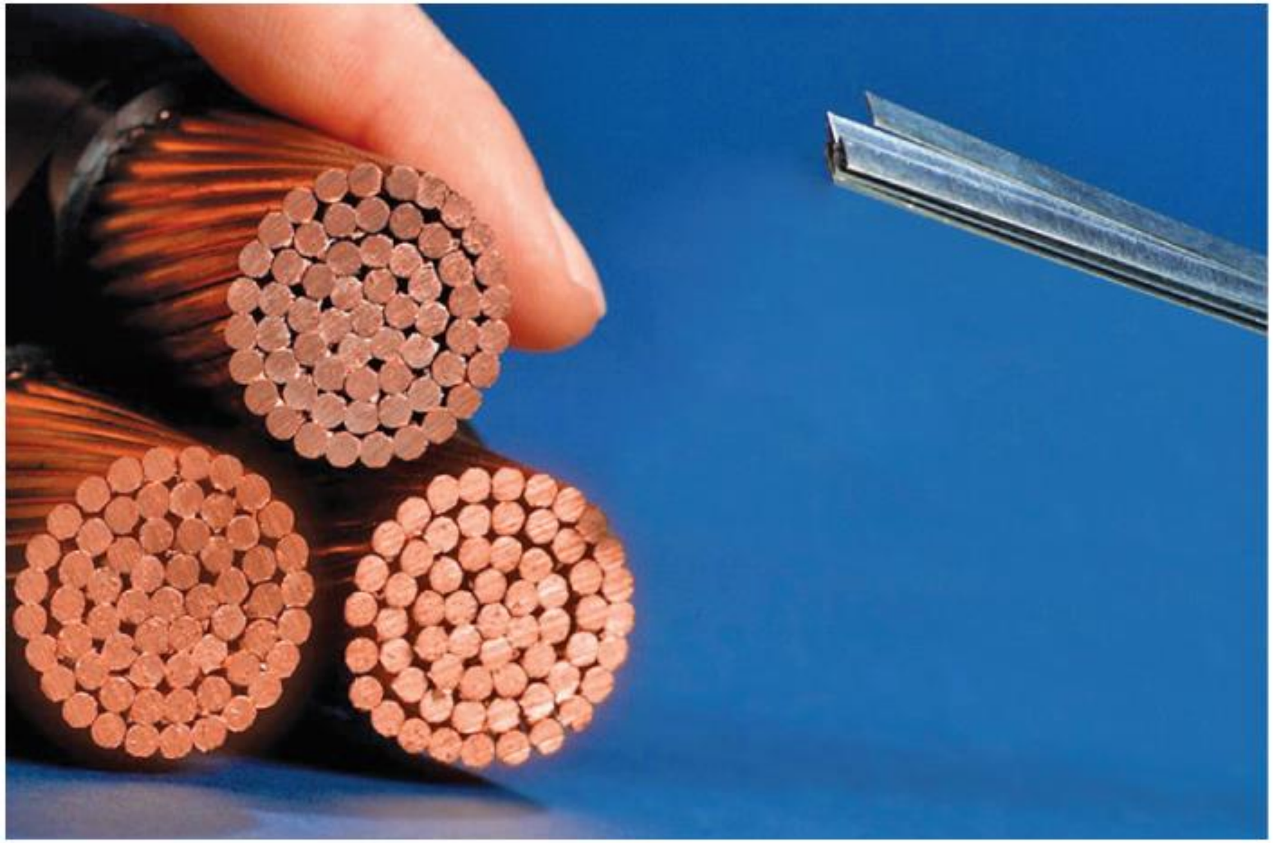
Superconductivity

- Superconductivity was first observed in 1911 in mercury, the T_c = 4 K and by 1988, materials were recording Tc of 125 K.
- By 2015, the highest transition temperature attained was 138 K.
- In 2020, a material was shown to have superconducting properties at 287 K, but it is unsuitable for practical applications because it requires very high pressures.



Superconducting Wire

- Twenty-five kilograms of the experimental conducting wire on the right can carry as much current as 1800 kg of the bulky copper wire on the left – a ratio of 72:1.



Courtesy American Superconductor (AMSC).

Summary

Periodic Trends

- The properties of elements are related to their location in the periodic table.
- The d-block elements have similar sizes.
- The lanthanide contraction leads to smaller atomic radii and higher densities than expected for elements in Period 6.
- The d-block elements can be found with a variety of oxidation numbers.
- The electrical conductivity can be explained in terms of the occupation of molecular orbitals.

Enjoy Halloween