

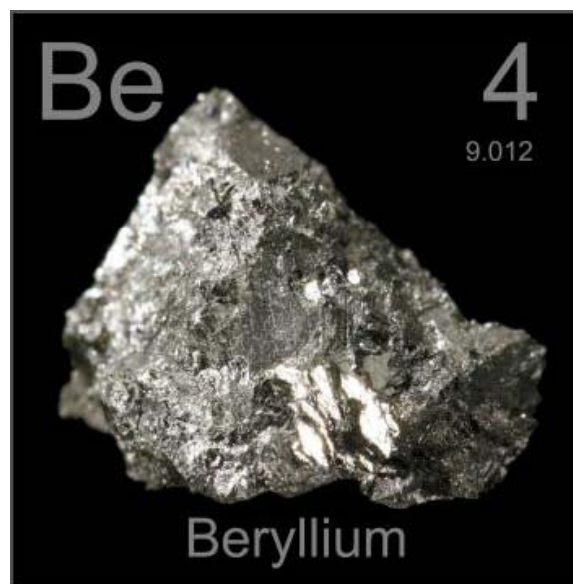
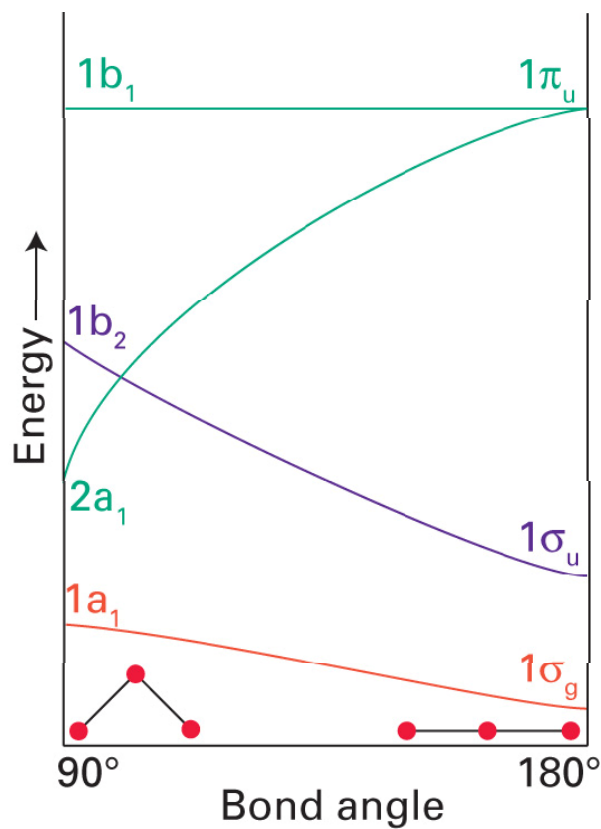
Lecture 7

Crystal structure and bonding thermodynamics

Reminder: Journal Club next Monday

Quiz 1: Worth 3 extra points on homework #1.

1. Write Your Name
2. Based on this correlation diagram, indicate which shape (linear or bent) BeH_2 is expected to adopt.



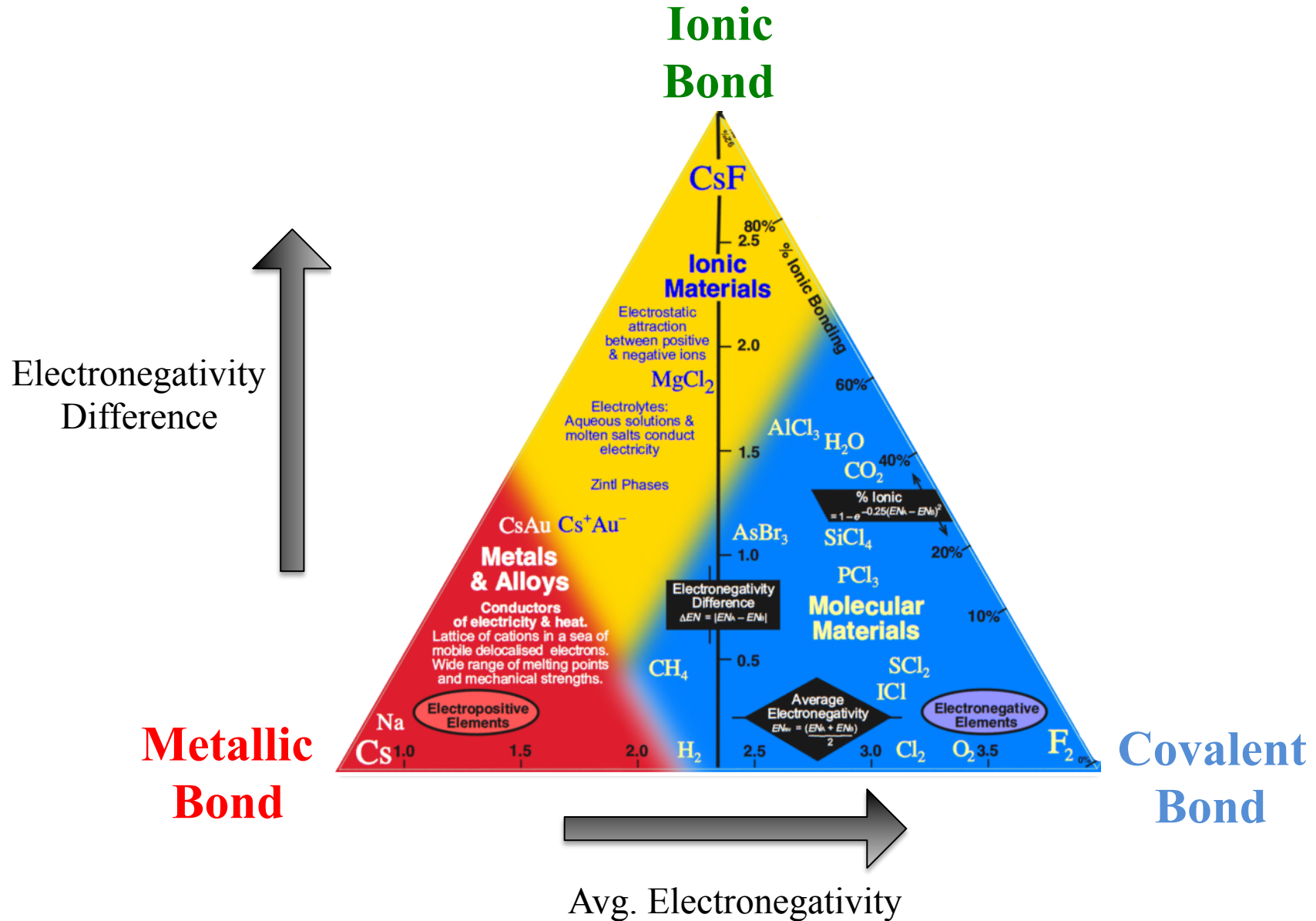
Hint: $Z_{\text{Be}}=4$

Bonding in solids

Bonds are distinguished based on the electron distribution functions in the molecules

		e ⁻ distribution	characteristics	examples	strength (eV/atom)
single-element solids	Covalent	Highest between pairs of nearest neighbors	Hard solids with low electrical conductivity	C, Si, Ge, H	4-8
	Metallic	Spread more uniformly (sea of e ^s)	Close-packed crystals with high conductivity	Na, Li, Fe	1-9
	Van der Waals	Dipole interactions	Low melting point	Ar, polymers	0.02-0.3
multi-elemental	Ionic	Transfer of valence electrons between atoms	Low electrical conductivity, high ionic conductivity	NaCl, MgO, Ag ₂ S	5-10
	Hydrogen	H ⁺ interacting with lone pair of e ^s	Molecular crystals	H ₂ O, DNA	0.1-0.4

Ketelaar Triangle

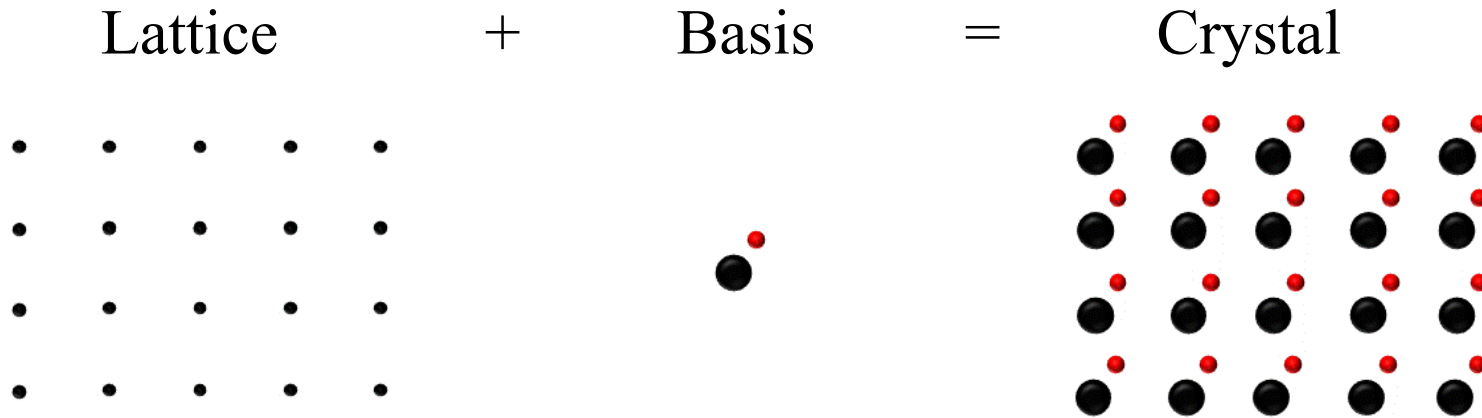


Arrangement of atoms in a solid

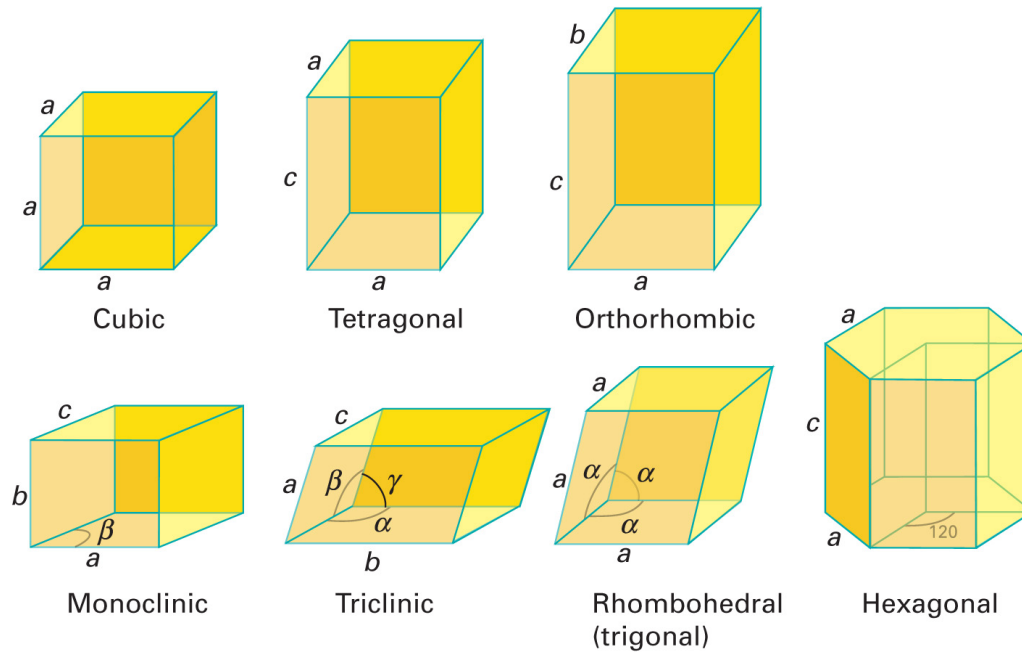
- 1611 – Kepler suggests hexagonal symmetry of snowflakes is due to “regular packing of the constituent particles”
- 1665 – Hooke suggests that crystals are composed of packed spheres
- 1913 – W.H. and W.L. Bragg prove with X-ray diffraction that salt is composed of Na^+ and Cl^- ions in a periodic lattice (Nobel prize in 1915)



Crystal structure basics

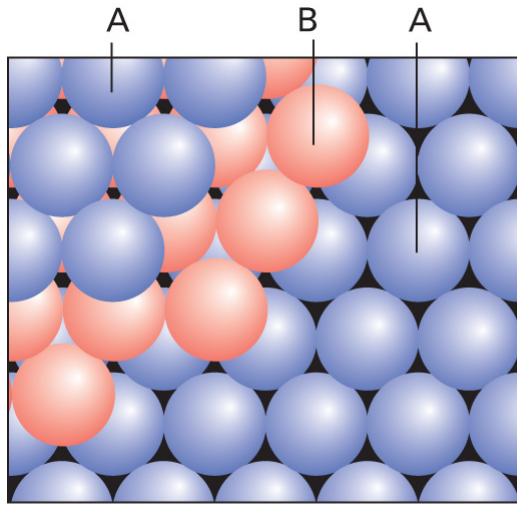


3D crystal systems:

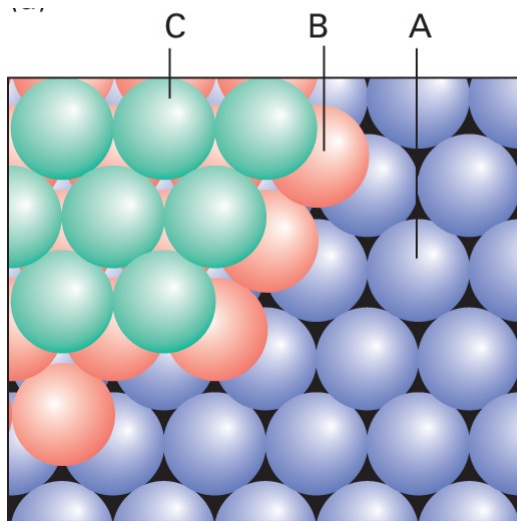
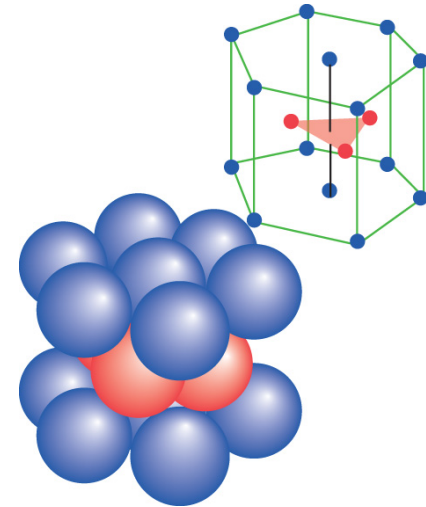


Close packing of spheres

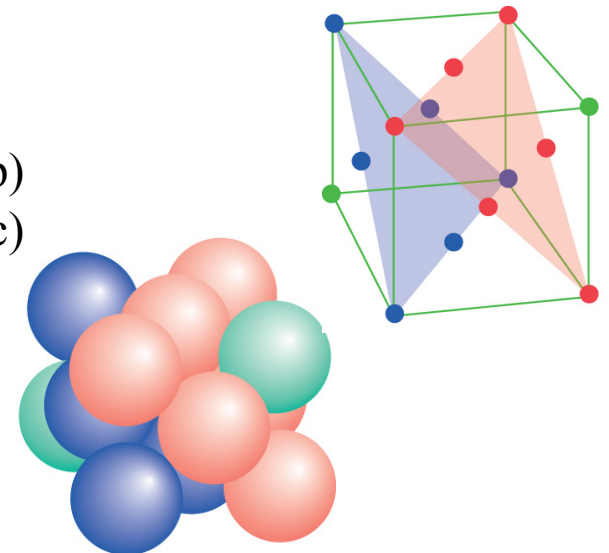
- Atoms/ions treated as hard spheres



ABAB...
hexagonal close-packed
(hcp)



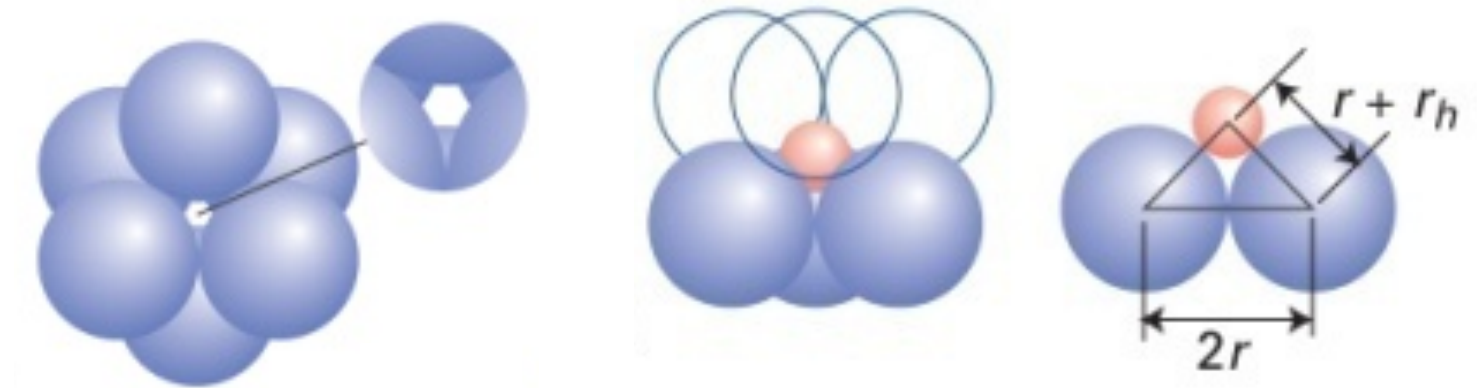
ABCABC...
cubic close-packed (ccp)
face-centered cubic (fcc)



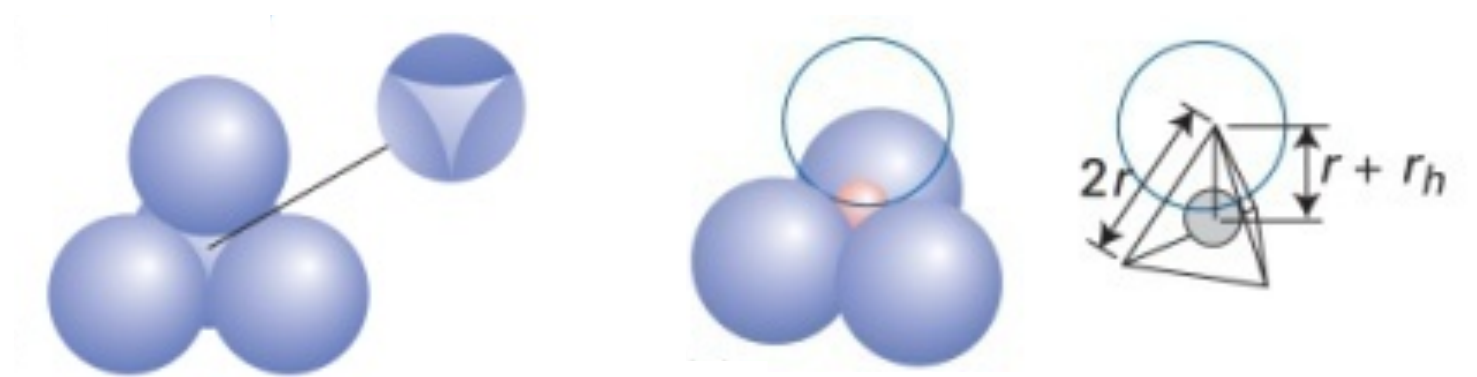
Interstitials

Unoccupied spaces between spheres can be occupied by other smaller atoms

- Octahedral hole



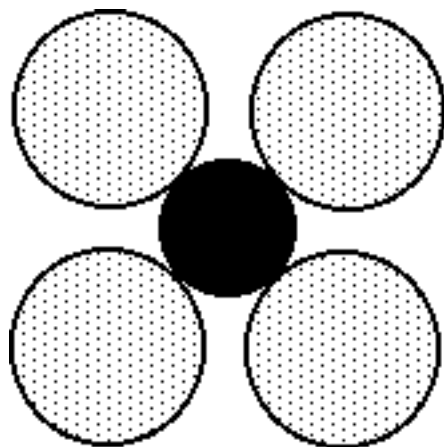
- Tetrahedral hole



Predicting structures of ionic compounds

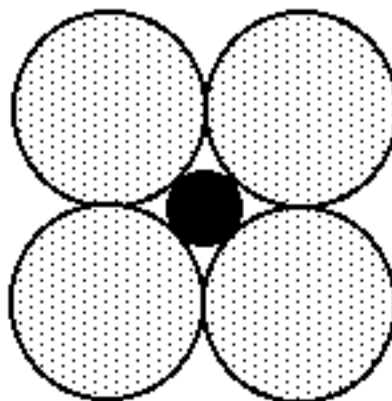
- The radius ratio indicates the likely coordination numbers of the ions in a compound

$$\text{Radius Ratio} = \frac{r_{\text{small}}}{r_{\text{large}}} \quad (\text{usually}) = \frac{r_{\text{cation}}}{r_{\text{anion}}}$$



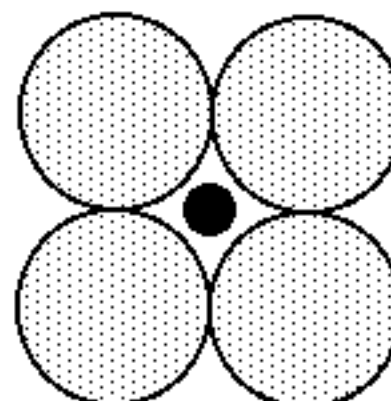
$$r_{\text{cation}}/r_{\text{anion}} > \text{ideal}$$

Stable



$$r_{\text{cation}}/r_{\text{anion}} = \text{ideal}$$

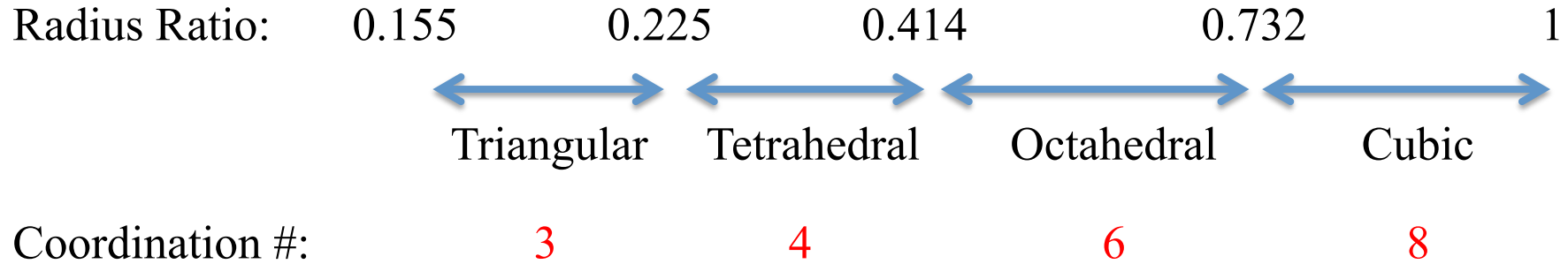
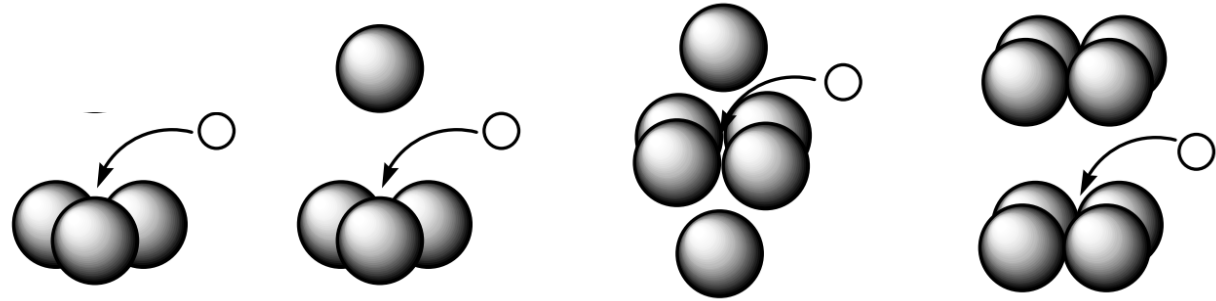
Stable



$$r_{\text{cation}}/r_{\text{anion}} < \text{ideal}$$

Unstable

Radius ratio rules for ionic crystals

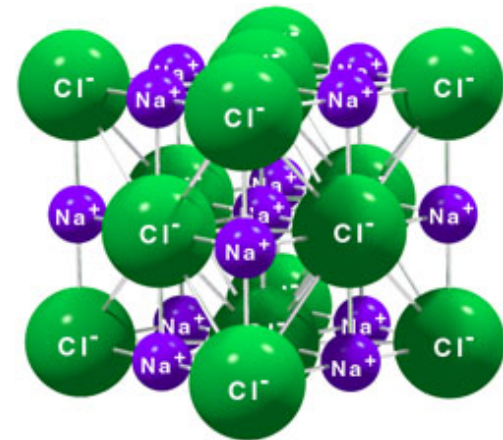


Example: Table salt, NaCl



Na⁺: 102 pm
Cl⁻: 181 pm

$$\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = 0.56$$



Thermo 101

- First law: energy can neither be created nor destroyed
- Second law: entropy increases during spontaneous processes
- Third Law: entropy of a perfect crystal is 0 at T=0K

For this class:

- A compound tends to adopt the crystal structure that corresponds to the lowest Gibbs free energy

$$G = H - TS = U + PV - TS$$

G = Gibbs free energy; H = enthalpy; S = entropy; U = internal energy

Reaction thermodynamics

- It is primarily changes in H, S, and G that are important in calculations of thermodynamic or chemical equilibria

ΔH = heat absorbed or released by a process

ΔS = change in the degree of disorder of the system

- For any isothermal, isobaric process:

$$\Delta G = \Delta H - T\Delta S$$

- And for a reaction:

$$\Delta G_{\text{rxn}} = \sum G(\text{products}) - \sum G(\text{reactants})$$

$$\Delta H_{\text{rxn}} = \sum H(\text{products}) - \sum H(\text{reactants})$$

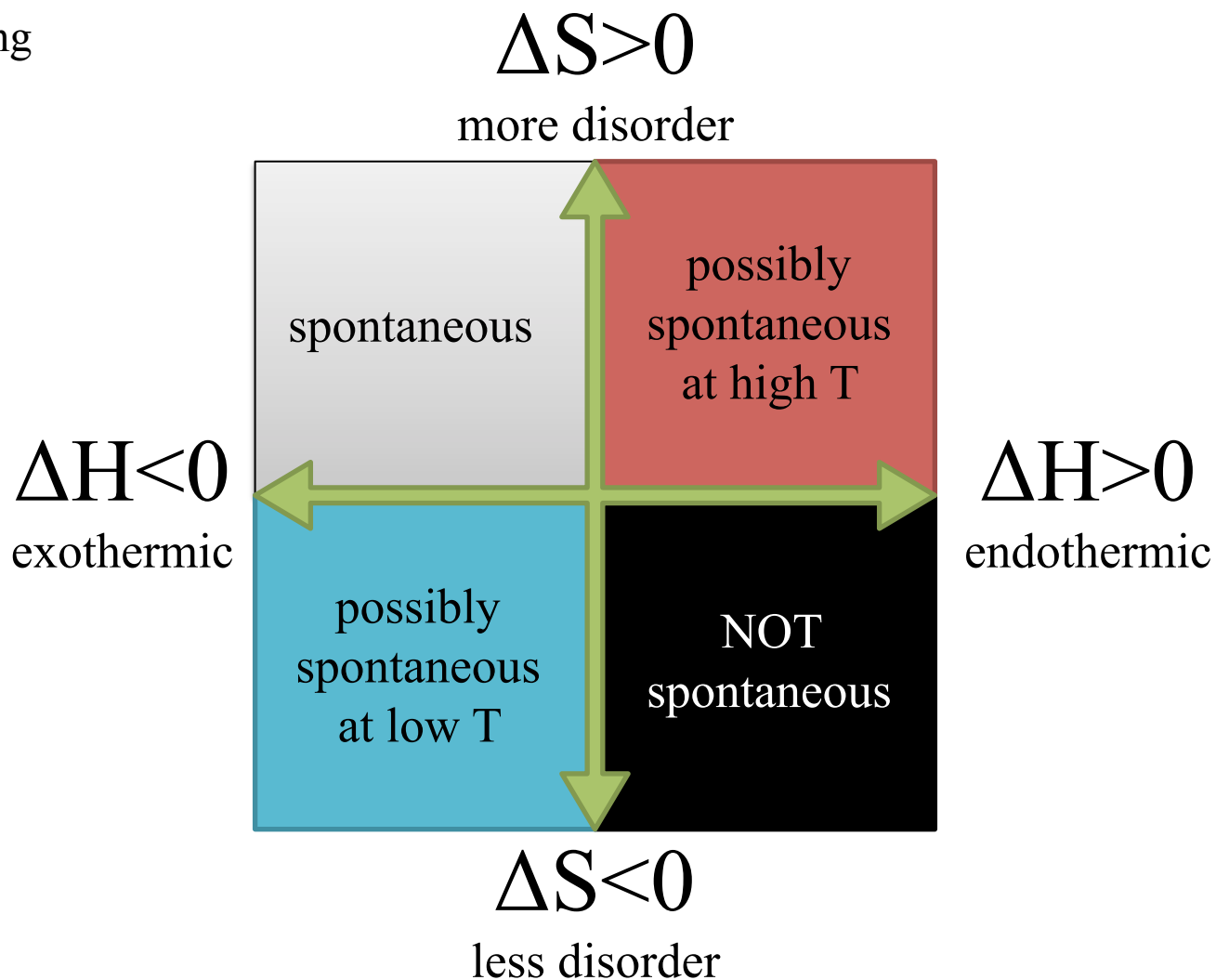
$$\Delta S_{\text{rxn}} = \sum S(\text{products}) - \sum S(\text{reactants})$$

Spontaneity

A process or reaction only proceeds spontaneously when ΔG is negative

$$\Delta G = \Delta H - T\Delta S$$

The thermodynamic driving force can be a decrease in enthalpy or an increase in entropy, or both



When $\Delta G = 0$ the system is in equilibrium

Standard states

- It is often more convenient to express free energy changes in terms of transformations of reactants and products from their standard states
- Standard state = equilibrium state at atmospheric pressure and the temperature in question
- Example: the standard Gibbs free energy of formation of a material $\Delta G_f^\circ(T)$ is the free energy change corresponding to the formation of a material from the elemental reactants in their standard states



$$\Delta G_f^\circ(\text{Si(s)}, 300\text{K}) = 0$$

$$\Delta G_f^\circ(\text{O}_2\text{(g)}, 300\text{K}) = 0$$

$$\Delta G_f^\circ(\text{SiO}_2\text{(s)}, 300\text{K}) = -853.3 \text{ kJ/mol}$$

$$\begin{aligned} \Delta G_{\text{rxn}}^\circ(300\text{K}) &= \Delta G_f^\circ(\text{SiO}_2\text{(s)}, 300\text{K}) - \Delta G_f^\circ(\text{Si(s)}, 300\text{K}) - \Delta G_f^\circ(\text{O}_2\text{(g)}, 300\text{K}) \\ &= -853.3 \text{ kJ/mol} \end{aligned}$$

Energetics of ionic bonding

- Solid formation from a gas of ions:



This reaction is usually so exothermic ($\Delta H \ll 0$) that at and near room temperature the contribution of the entropy change to the change in Gibbs free energy can be neglected

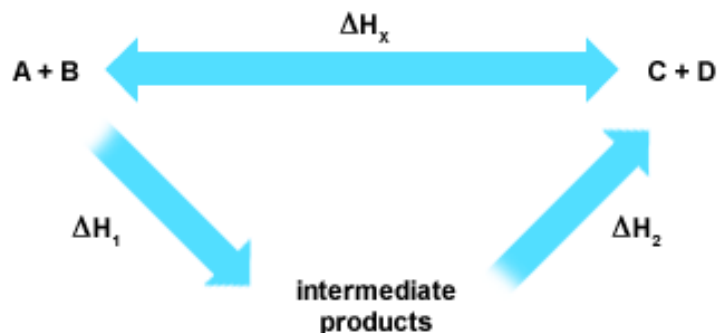
- Lattice enthalpy: standard molar enthalpy change accompanying the formation of a gas of ions from the solid



The most stable crystal structure of the compound is that with the greatest lattice enthalpy

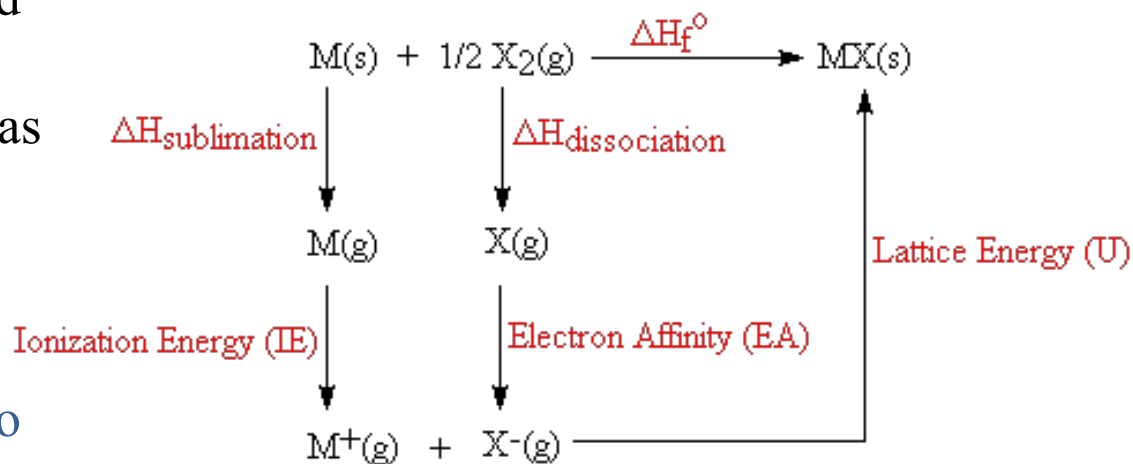
Born-Haber cycle

- Hess's law:



$$\Delta H_x = \Delta H_1 + \Delta H_2$$

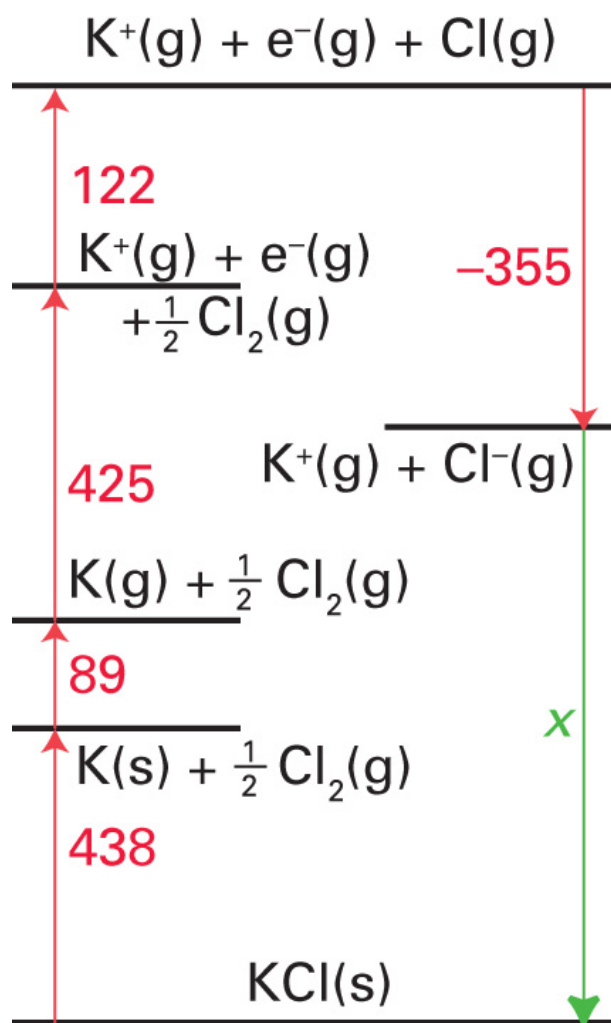
- Born-Haber cycle: a closed loop of reactions that includes lattice formation as one step



Enthalpy is a state property, so the sum of the enthalpy changes around a complete cycle is zero

Born-Haber cycle of KCl

kJ/mol



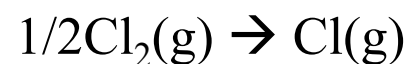
$$-\Delta H^\circ_f = 438$$



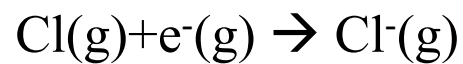
$$\Delta H^\circ_{\text{sub}} = 89$$



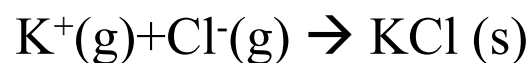
$$\Delta H^\circ_{\text{ion}} = 425$$



$$\Delta H^\circ_{\text{dis}} = 122$$



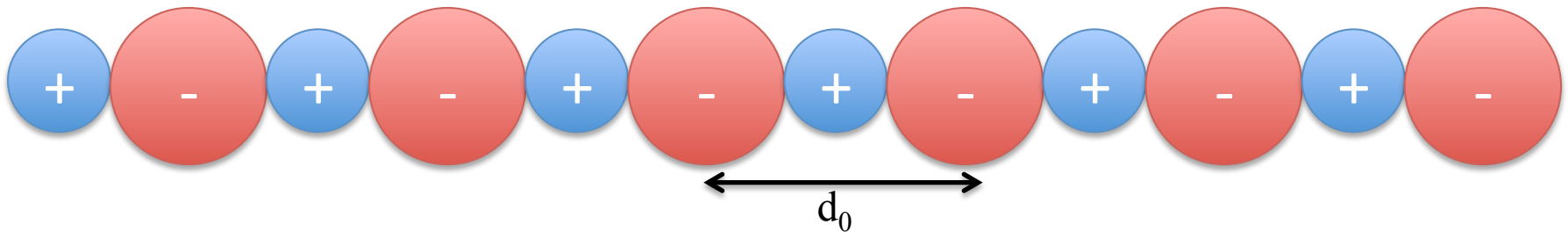
$$\Delta H^\circ_{\text{eg}} = -355$$



$$\Delta H^\circ_L = 719$$

Born-Mayer equation

- Used to calculate lattice enthalpies from first principles
- Example: 1-D line of alternating singly-charged cations and anions



For a given ion, the potential due to Coulombic interactions is:

$$V = \sum \frac{q_1 q_i}{4\pi\epsilon_0 r_1 - r_i} = \frac{e^2}{4\pi\epsilon_0} \left(-\frac{2}{d_0} + \frac{2}{2d_0} + \dots \right) = -\frac{2e^2}{4\pi\epsilon_0 d_0} \ln(2)$$

For the whole line (multiply by N_A , divide by 2):

$$V = -\frac{N_A e^2}{4\pi\epsilon_0 d_0} A$$

$A = \ln(2)$ is the Madelung constant for this particular geometry

Born-Mayer equation

- The attractive electrostatic force will be balanced by a repulsive force due to quantum interactions of the valence electrons of neighboring ions

$$V = -\frac{N_A e^2}{4\pi\epsilon_0 d_0} A + B \exp\left(-\frac{d}{d_0}\right) \quad \begin{array}{l} d = \text{range of repulsive interaction} \\ B = \text{magnitude of this interaction} \end{array}$$

- Using the fact that $dV/dd_0=0$ at the minimum, we find:

$$V = -\frac{N_A e^2}{4\pi\epsilon_0 d_0} \left(1 - \frac{d}{d_0}\right) A$$

Lattice enthalpy for arbitrarily charged ions:

$$\Delta H_L = -V = \frac{N_A |z_A z_B| e^2}{4\pi\epsilon_0 d_0} \left(1 - \frac{d}{d_0}\right) A$$

Consequences of lattice enthalpy

- Lattice enthalpies can explain trends in
 - Thermal stability
 - Oxidation state stability
 - Solubility
- First, the electrostatic parameter:

$$\Delta H_L \propto \frac{|z_A z_B|}{d_0} = \xi$$

Highly charged, closely spaced ions form more stable lattices

Thermal stabilities of ionic solids

Decomposition reaction (ie trends in carbonate decomposition):




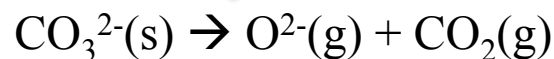
Decomposition becomes favorable when

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}} \leq 0 \qquad T \geq \Delta H_{\text{rxn}} / \Delta S_{\text{rxn}}$$

In discussing trends, ΔS_{rxn} is essentially constant (dominated by CO_2 production)

$$\Delta H_{\text{rxn}} \approx \Delta H_{\text{decomp}} + \Delta H_{\text{L}}(\text{MCO}_3, \text{s}) - \Delta H_{\text{L}}(\text{MO}, \text{s})$$

large,  constant



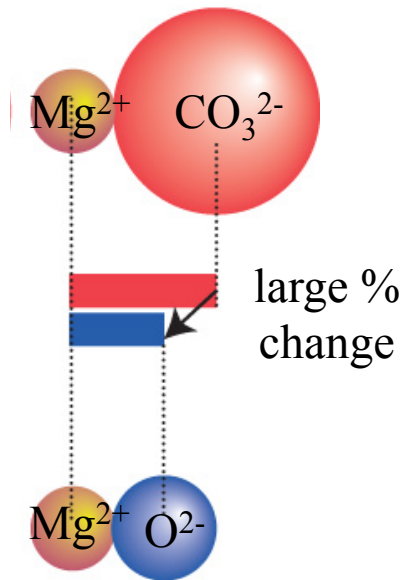
Thermal stabilities of ionic solids

- Which carbonate will be more stable, MgCO_3 or BaCO_3 ?

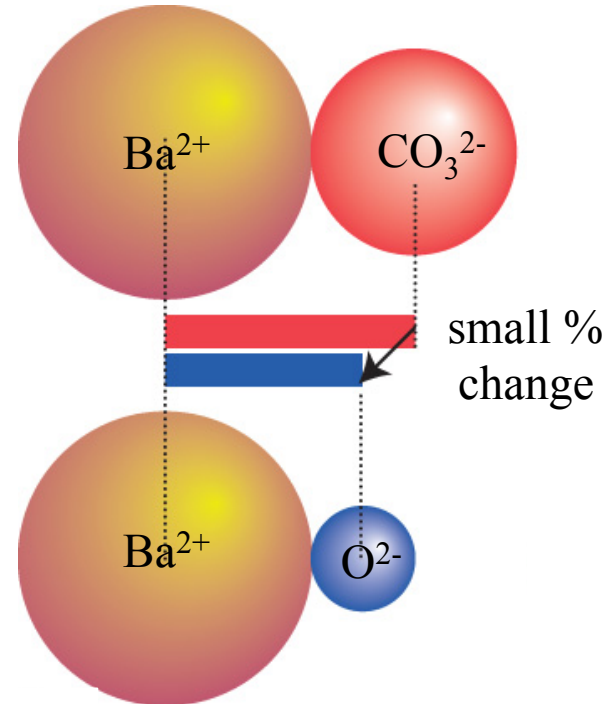
2	IIA	
4	9.0122	A
Be BERYLLIUM		
12	24.305	
Mg MAGNESIUM		
20	40.078	21
Ca CALCIUM		
38	87.62	39
Sr STRONTIUM		
56	137.33	55
Ba BARIUM		
88	(226)	85

↓
r

$$\xi_r = \frac{|z_A z_B|}{d_0}$$



$T_{\text{decomp}} = 573\text{K}$



$T_{\text{decomp}} = 1573\text{K}$

Stabilities of oxidation states

- The same argument is used to account for the fact that high oxidation states are stabilized by small anions



CuF_2 exists, CuI_2 does not:

F is smaller, thus the difference in lattice enthalpies is larger, and F is able to stabilize the higher oxidation state

Solubilities



- Dissolution is a complicated process, but lattice enthalpies and hydration enthalpies play important roles (don't forget about entropy!)
- Generally, the larger the difference in radii, the more soluble in water

