Chem 241

Lecture 18

Announcement

March 10 → LGRT 0323
March 26 → Second Exam

Recap

Steric effects
Redox reactions
Inner v Outer Sphere
Photochemical

Standard Cell Potenial

$Ag^+(aq) + e^- \rightarrow Ag(s)$ $E^o = 0.799$ V

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $E^o = -0.337$ V

$2Ag^+(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2Ag(s)$ $E^o = 0.462$

$\Delta G^o = -nFE^o$ $F = 96.48$ kC mol^{-1}

Nernst Equation:

$$E = E^0 - \frac{RT}{nF} \ln Q$$

Standard Cell Potenial

$$[H_2VO_4]^-(aq) + 4\ H^+(aq) + e^- \rightarrow VO_2^+(aq) + 3\ H_2O(l)$$

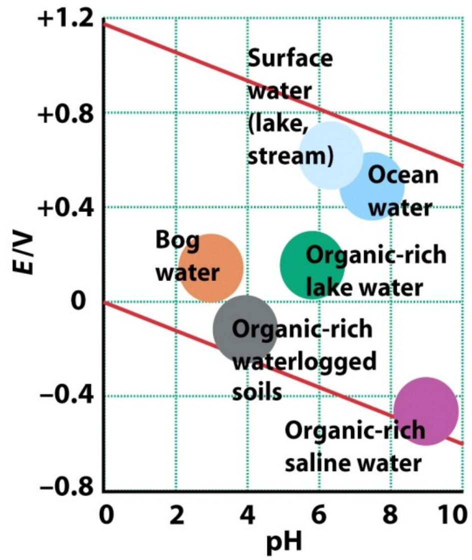
$$VO_2^+(aq) + 2\ H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)$$

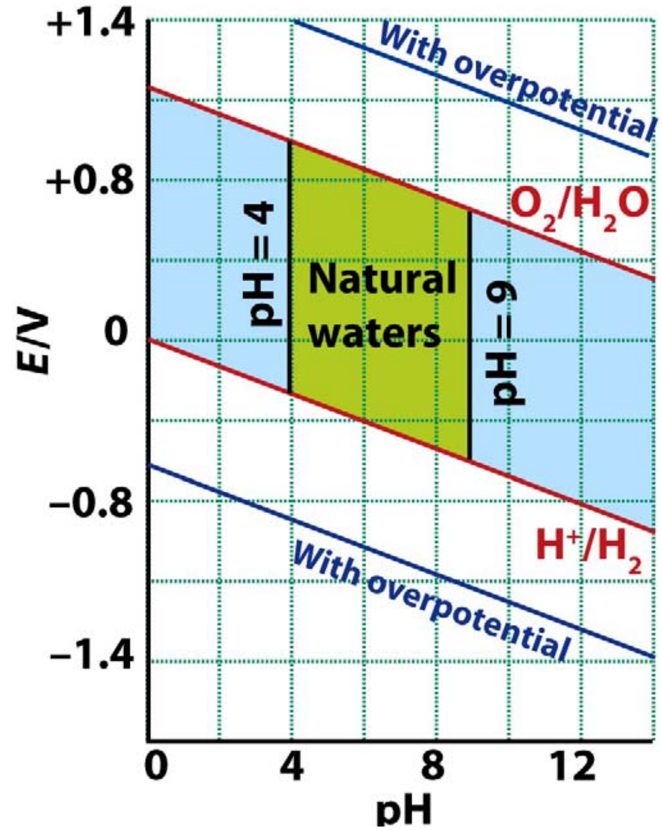
$$V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$$

Solvent

$H_2O(l)$ + e^- → $½H_2(g)$ + OH^-

$2\ H_2O(l)$ → $O_2(g) + 4\ H^+(aq) + 4e^-$





$M(s) + nH^+(aq)$ → M^{n+} + $n/2\ H_2(g)$

$4\ Fe^{2+}(aq)$ + O_2 + $4H^+(aq)$ → $4Fe^{3+}(aq)$ + $2H_2O(l)$

Reactions with Itself

Disproportionation: a redox reaction in which the oxidation number of an element is simultaneously raised and lowered.

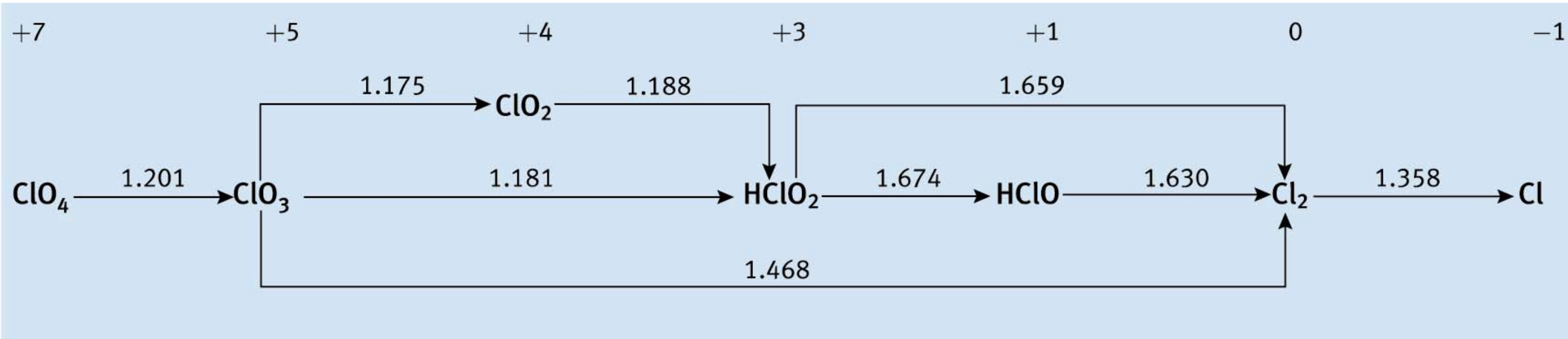
2 Cu^{+} (*aq*) → Cu^{2+}(aq) + Cu(s)

$$Cu^{+}(aq) + e^{-} \rightarrow Cu(s) \qquad E = 0.52\ V$$
$$Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + e^{-} \qquad E = -0.16V$$

Comproportionation: a redox reaction in which two species of the same element in different oxidation states form a product in which the element is in the same oxidation state,

$$Ag^{2+}(aq) + Ag(s) \rightarrow 2Ag^{+}(aq) \quad E = 1.18\ V$$

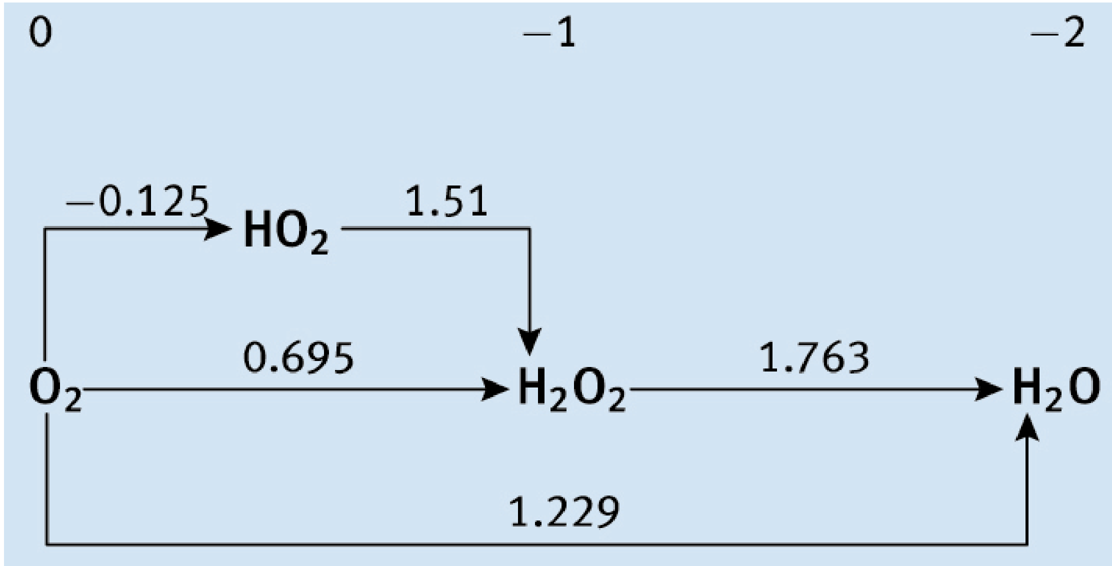
Latimer Diagram



$$ClO_4^-(aq) + 2H^+(aq) + 2e^- \rightarrow ClO_3^-(aq) + H_2O(l)$$

$$E^0(a+b) = \frac{n_a E^0(a) + n_b E^0(b)}{n_a + n_b}$$

Latimer Diagram



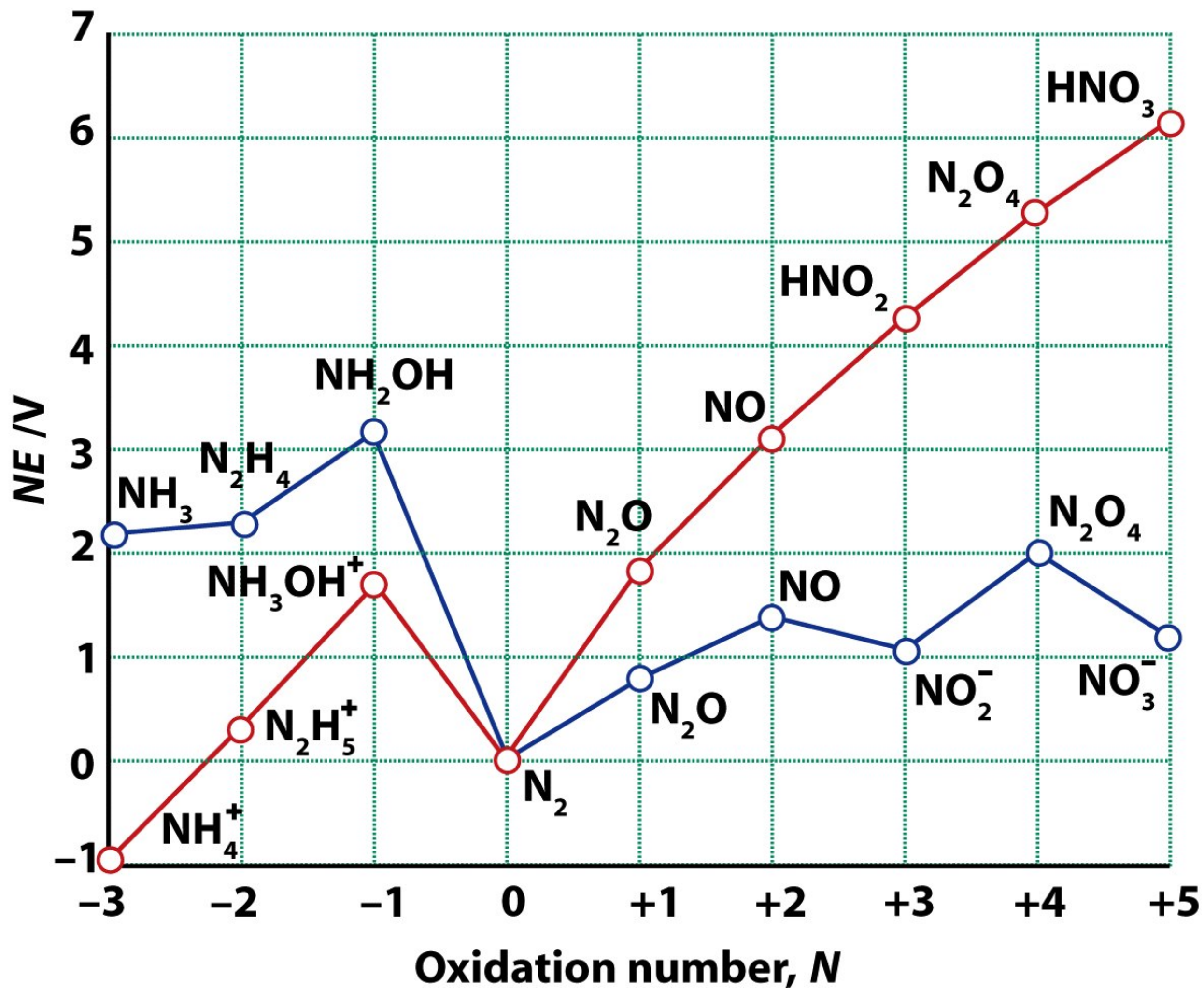
$2H^+(aq) + 2e^- + H_2O_2(aq) \rightarrow H_2O \quad E_{Right} = 1.76V$

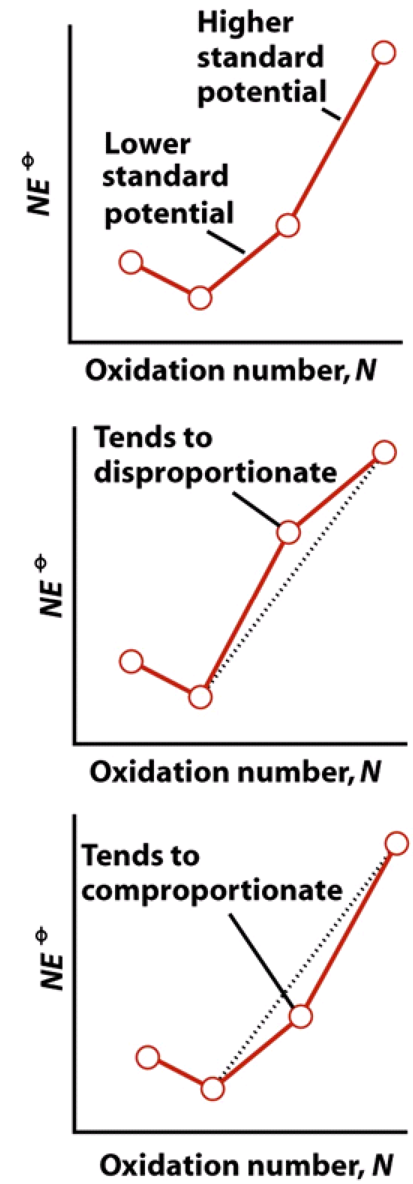
$O_2 + H^+(aq) + 2e^- \rightarrow H_2O_2(aq) \quad E_{Left} = 0.70V$

$E_{Right} > E_{Left}$: Then reaction will be spontaneous, species tend to disproportionate.

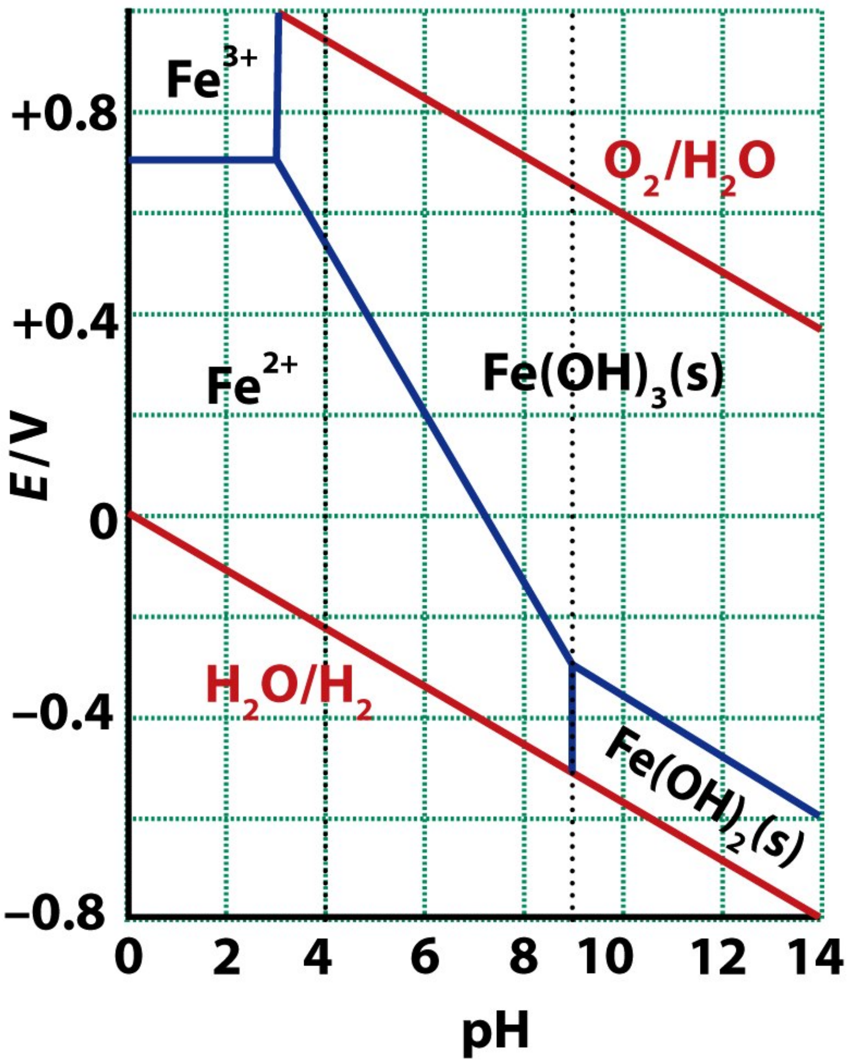
$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Frost Diagram





Pourbaix Diagram

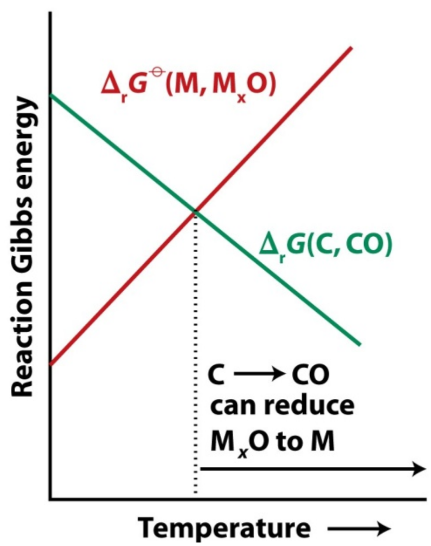


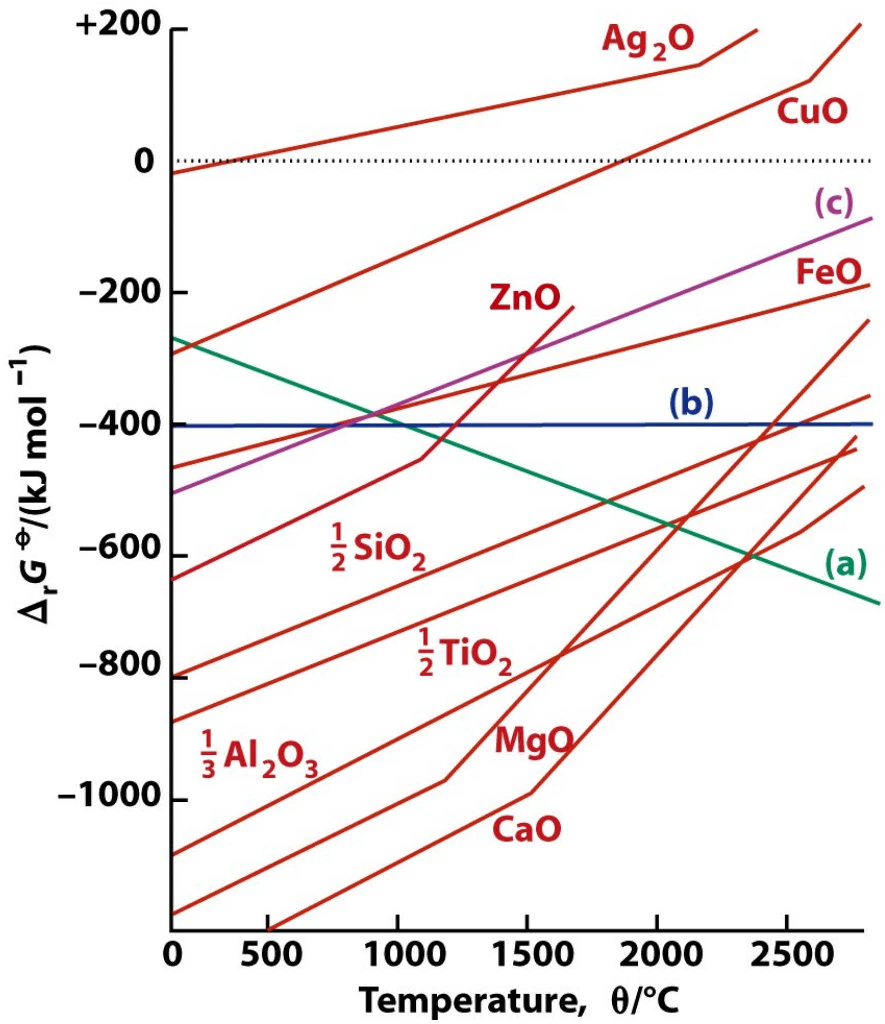
Ellingham Diagram

$M_xO + C(s) + \text{heat} \rightarrow xM(s,l) + CO(g)$

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$
$\frac{1}{2}C(s) + \frac{1}{2}O_2(g) \rightarrow \frac{1}{2}CO_2(g)$
$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

$M_xO(s) \rightarrow xM(s,l) + \frac{1}{2}O_2(g)$





Homework

Chapter 5

Exercises: 2, 3, 6, 7, 9

Inorganic Solids

What? And Why?

A. Understanding the structure and bonding of solid state compounds is important for understanding

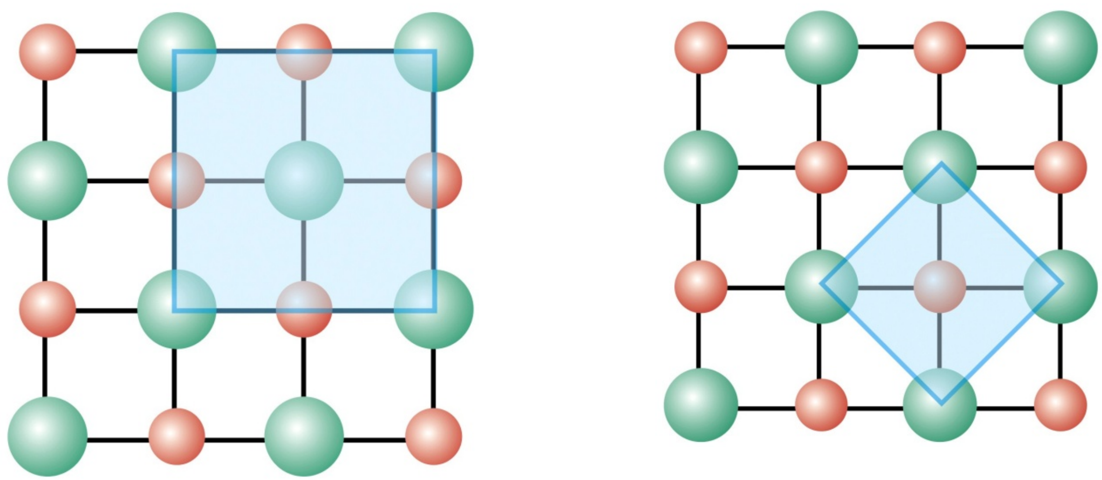
1. inorganic materials such as metals, alloys, salts, such as
    a. Pigments
    b. Nanostructured materials (zeolites)
    c. High-temperature super conductors
    d. minerals
2. Trends in structure and reactivity.
3. Electronic structures of conductors, semi-conductors and insulators.

Inorganic Solids

Aarrangement of atoms (or ions) in a simple solid structure can often be represented by different arrangements of **hard spheres.**

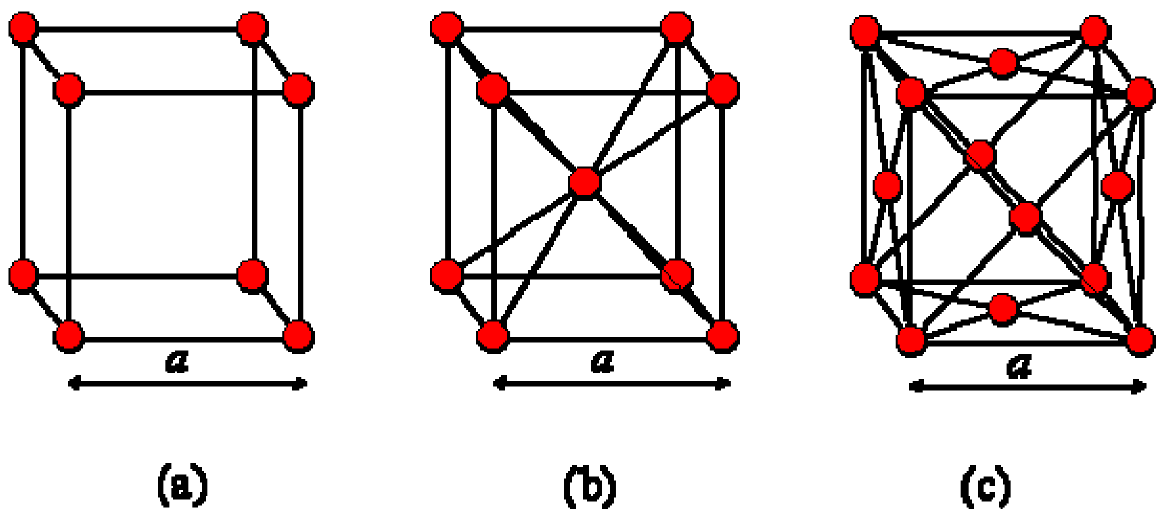
A crystal of an element or compound is constructed from repeating elements. The **crystal lattice** is the pattern formed by these repeating structural elements.

Unit Cell



Centering the Unit Cell

A. **Primitive (P)**
B. **Body Centered (I)**
C. **Face Centered (F)**
D. **Base Centered (C)**

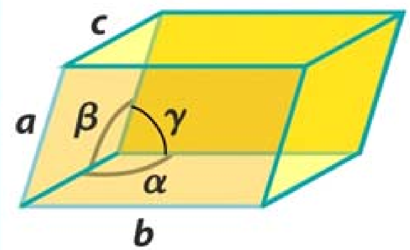


Seven Crystal Systems

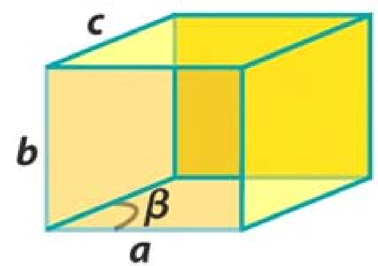
Unit Cell is the repeating parallelepiped

Table 3.1 The seven crystal systems

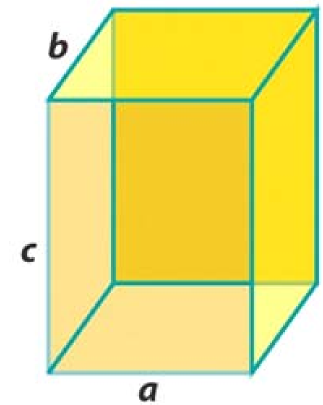
System	Relations between lattice parameters	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°\ \ \beta \neq 90°$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Hexagonal	$a = b \neq c$	$\gamma = 120°$
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$



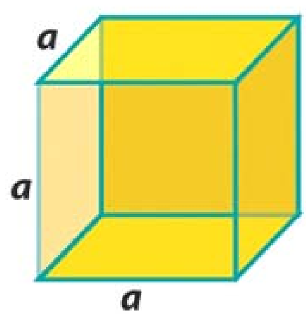
Triclinic



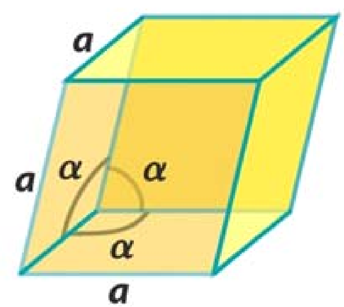
Monoclinic



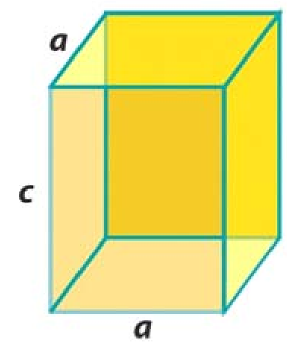
Orthorhombic



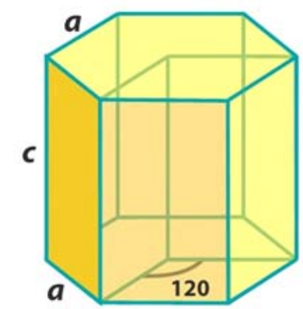
Cubic



Trigonal



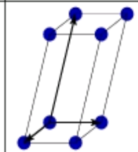
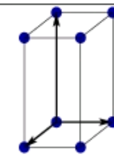
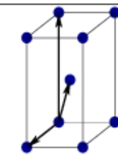
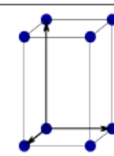
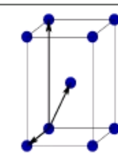
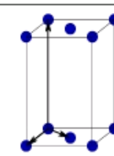
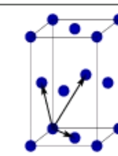
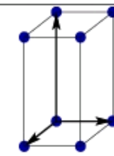
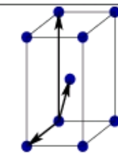
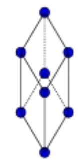
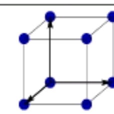
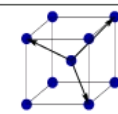
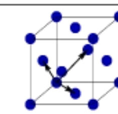
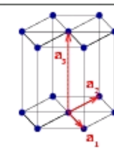
Tetragonal



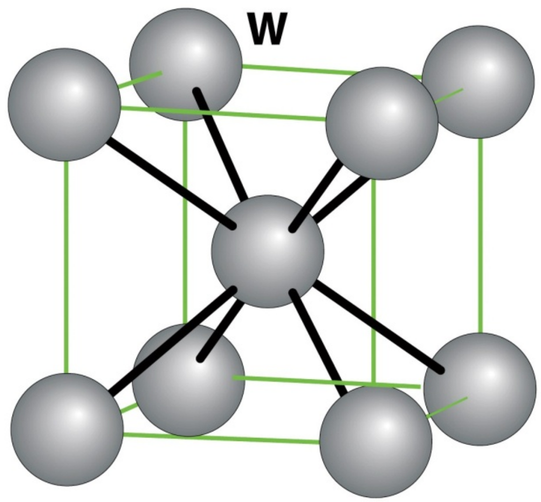
Hexagonal

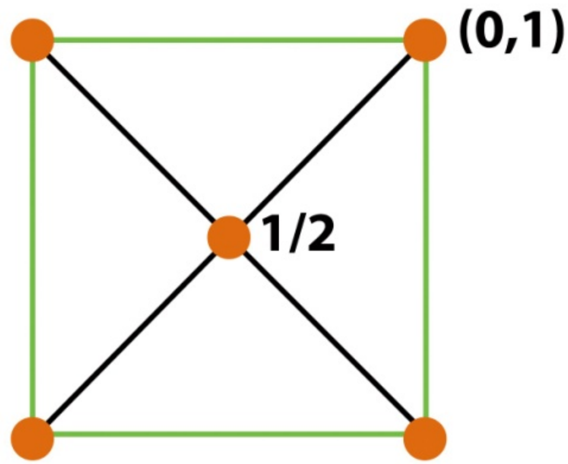
Bravais Lattice

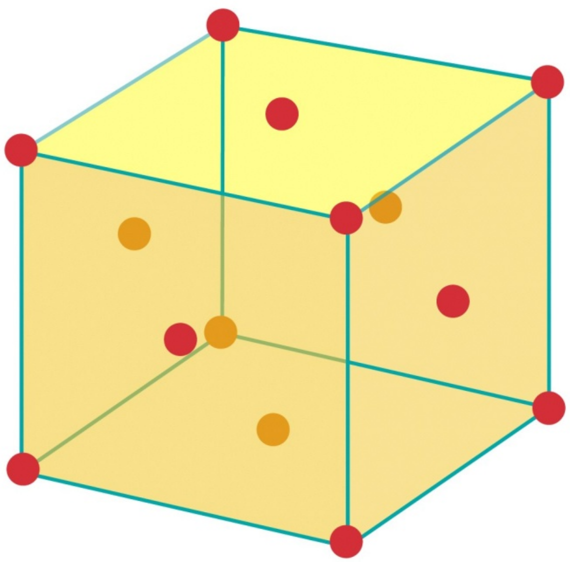
A. **Primitive (P)**
B. **Body Centered (I)**
C. **Face Centered (F)**
D. **Base Centered (C)**

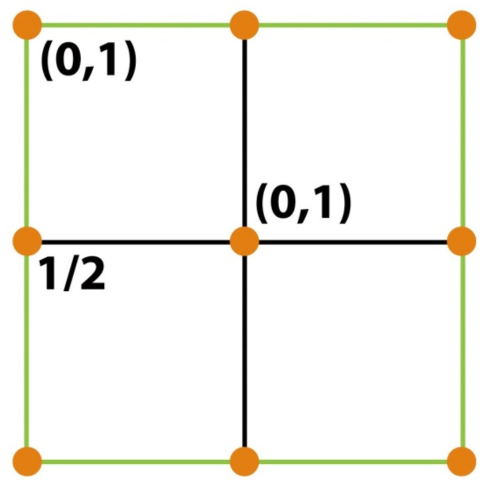
Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

Fractional Coordinates

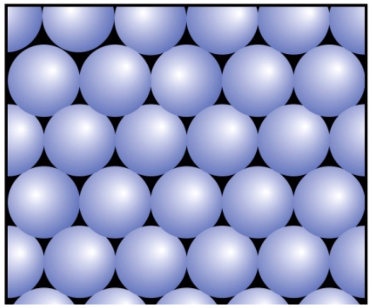




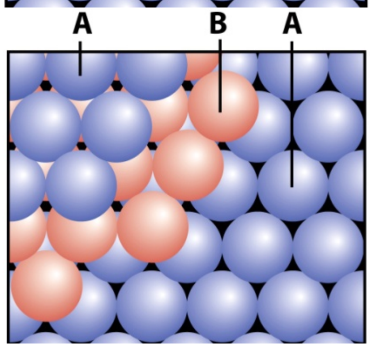




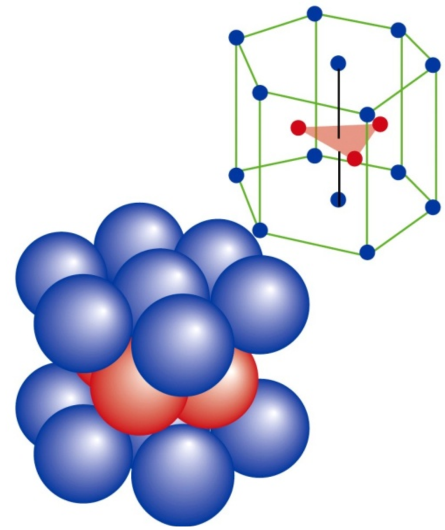
Packing

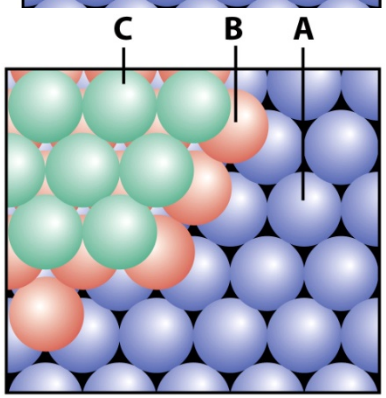


1st Layer

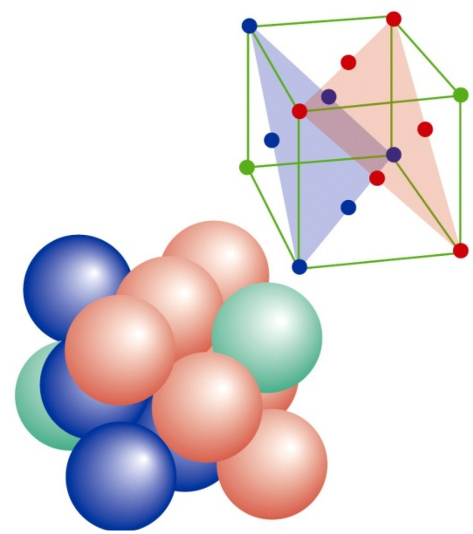


two layers (ABAB…) is hcp





packing in three layers (ABCABC…) is ccp.



Inorganic Solids

26% of the volume of a close packed structure is space.

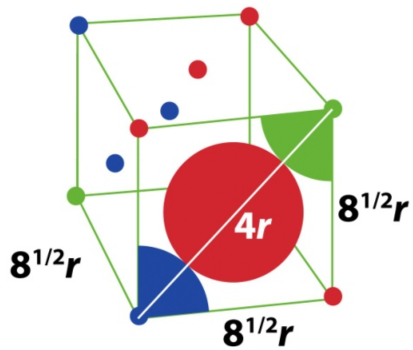
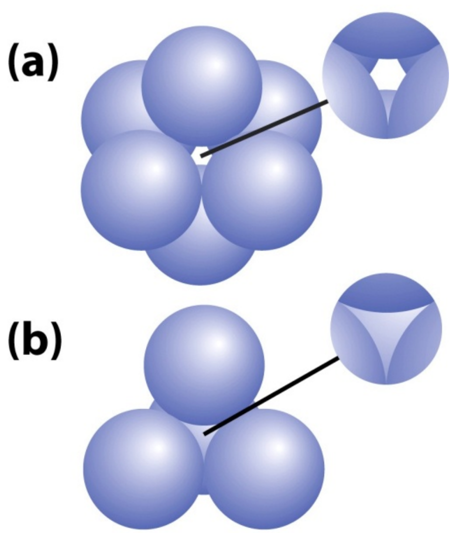


Figure 3-13
Shriver & Atkins Inorganic Chemistry, Fourth Edition

The space is made up of T_d and O_h holes.

a. There are 4 Oh holes in the unit cell and 8 Td holes.
b. Sizes of holes are 0.414r (Oh) and 0.225r (Td).



Inorganic solids

Metals and Alloys

- 1. often adopt close-packed structures
  - a. accounts for the high density of metals (Ir and Os are the most dense elements at STP.
  - b. Implies a lack of directional covalent bonds
    - Metallic bonding (cations in a sea of electrons, metals generally have low IE)
    - Or effectively enormous molecules with MOs that extend throughout the sample.
  - c. Good conductors because electrons are delocalized
  - d. Malleable and ductile: no directional bonding, electrons rapidly relocate. Forces between atoms is small.

Inorganic Solids

Which close packed arrangement is adopted by a metal depends on the electronic structure.

- a. hcp and ccp are not required. Another common arrangement is body-centered cubic (bcc).
- b. Polytypism is common. Ex. Above 500 C Co is ccp, but adopts a more random arrangement of layers upon cooling