Inorganic Chemistry 1

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◘ **Office hour:** by appointment

❑ Objectives of this course:

As a first half of the inorganic chemistry class for chemistry majoring students, basic inorganic theories and principles will be covered during this lecture.

This includes ,,,

Ch1. Intro. to Inorg. Chem.,

Ch2. Atomic structure,

Ch3. Simple bonding theory,

Ch4. Symmetry and group theory,

Ch5. Molecular orbitals,

Ch6. Acid-base and donor-acceptor chemistry,

Ch7. The crystalline solid state

☐ Text books:

1) Inorganic Chemistry, Gary L. Miessler; Donald A. Tarr, Pearson, 5th Edition

2) Inorganic Chemistry, James E. Huhey, Harper Collins, 1993

3) Molecular Symmetry and Group Theory, Alan Vincent, Wiley, 1998

4) Inorganic Structural Chemistry, Ulich Mueller, Wiley, 2002

□ Tentative Class Schedule

	Quiz (X 6)
1 - 2 week: Ch.1 Introduction to Inorganic Chemistry	
Ch.2 Atomic Structure	3/8(T) – Ch.2
3 - 4 week: Ch.3 Simple Bonding Theory	3/15(T) – Ch.3
5 - 6 week: Ch.4 Symmetry and Group Theory	3/29(T) – Ch.4
7 week: **Team Present1(4/12(T))**	
8 week: <u>Mid-term Exam. (4/19(T))</u> + KCS	
9 -10 week: Ch.5 Molecular Orbitals	4/26 (T) – Ch.5
11-12 week: Ch.6 + **Team Present2 (5/18(W))**	5/4 (W) – Ch.6
13-14 week: Ch.7 The Crystalline Solid State	5/17(T) – Ch.7
15 week: <u>Final Exam. (6/7(T))</u>	

▣ Grading: total 300

1) mid-term: 100

2) final exam: 100

2) team present*: 50

3) attendance + attitude: 25

4) quiz**: 25

▣ **Quiz:

1) Quiz will be given <u>6 times</u> on the scheduled days.

2) Homework (Chapter summary) will be evaluated via quiz.

3) Quiz problems will be selected from <u>homework (summary topic) topics</u>.

4) < 10 min. (2-3 questions)

❑ *Presentation:

1) one group of **5-6 classmates** (10 groups)

2) If you cannot choose a topic or articles, consult with Prof. You.

3) Topics related to Inorganic Chemistry

4) 10 min. presentation (3 min. in English + 7 min. in Korean) + Q/A (5 min)

   - PPT presentation on class-related literature paper(s) from a reviewer′s perspective

   - Each rep. will be presenting, but a whole group should participate in a presentation.

   - The presentation will be graded by Prof. You.

   - *(The English Presentation can be helped by a **Native speaker lecturer** @ Office of International

    Services)

☐ Others

1) Class related information and lecture slides will be available on KOCW (**http://www.kocw.net**) or e-campus (**http://ecampus.cbnu.ac.kr**)

2) Previous team presentation references (videos) are available on KOCW.

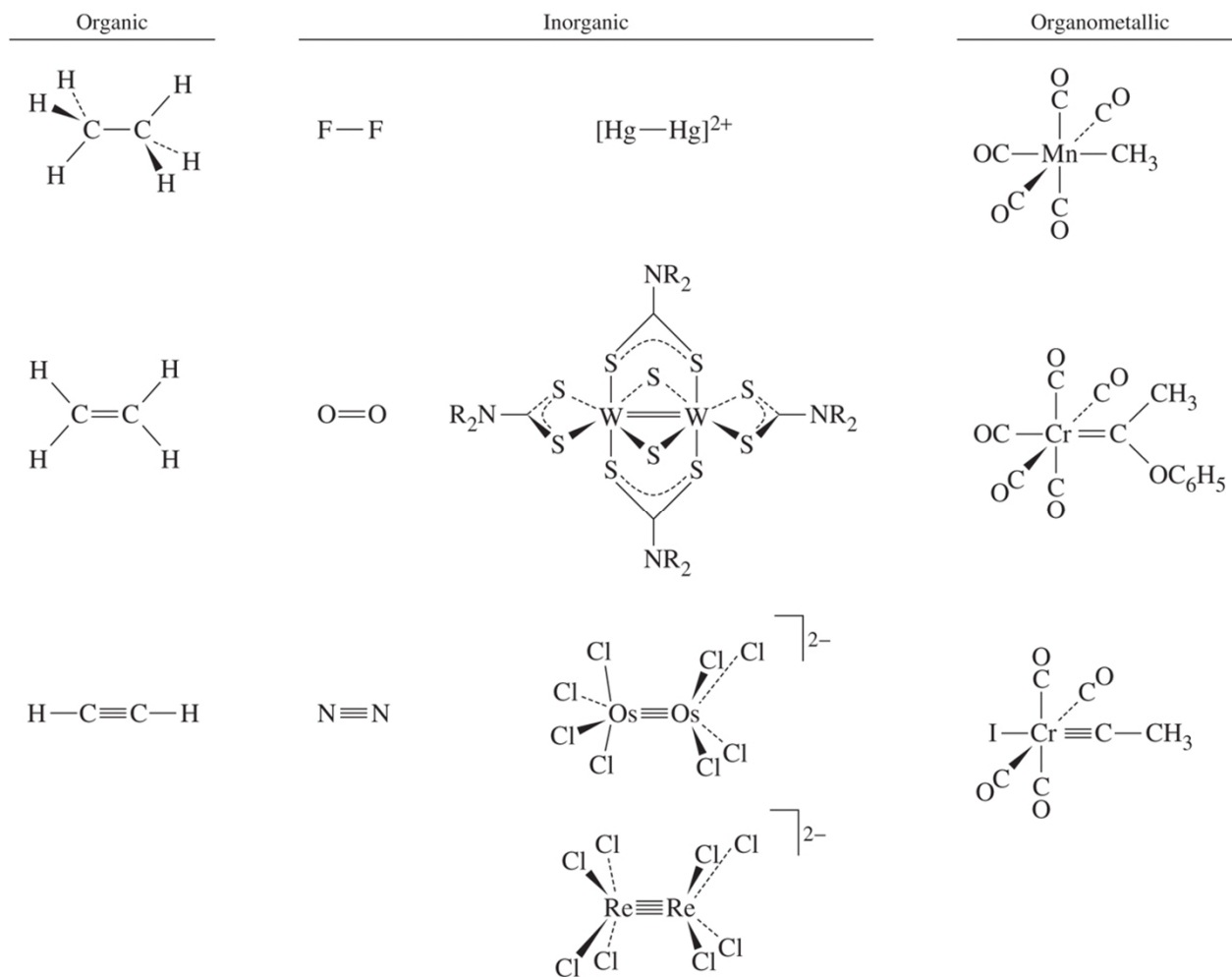3) **Summary topics** will be given prior to each chapter on e-campus.

1.1 What is Inorganic Chemistry?

- organic chemistry: hydrocarbon compounds and their derivatives

- <u>inorganic chemistry</u>: everything else including all remaining elements in the periodic table, as well as carbon

- research area included in inorganic chemistry

   1) organometallic chemistry: bridging organic and inorganic chemistry area

   2) bioinorganic chemistry: bridging biochemistry and inorganic chemistry

   3) environmental chemistry: including inorganic and organic compounds

   4) <u>solid–state chemistry</u>: including inorganic and physical chemistry

- both: single, double, triple covalent bonds

- inorganic chemistry: including direct <u>metal-metal</u> bonds, <u>metal-carbon</u> bond
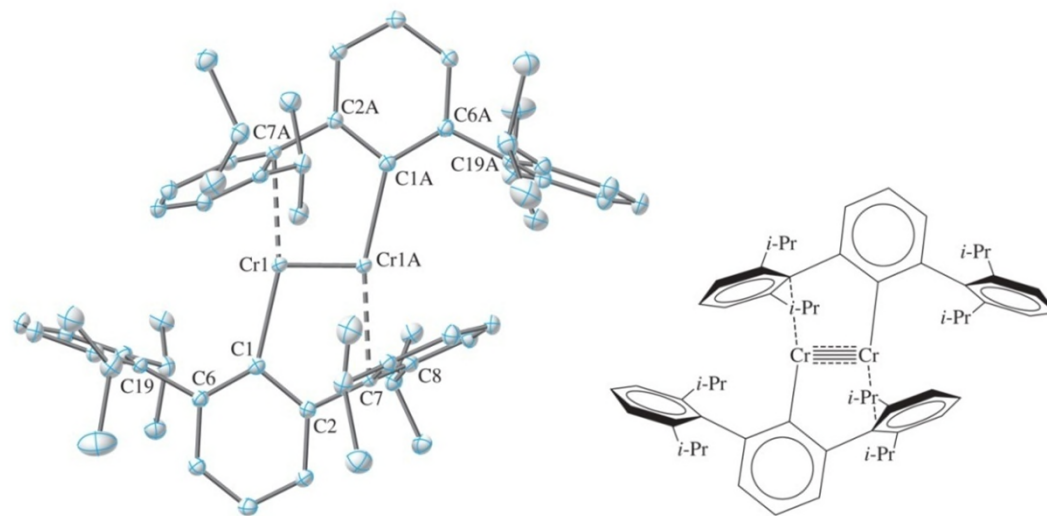

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Fig1.1

- organic chem.: max. number of bonds b/w two carbons → 3

- inorganic chem.: <u>quadruple</u> bonds b/w metals are possible

      : (1 x σ (sigma), 2 x π (pi), 1 x δ (delta))

      : δ is possible due to the d orbital of metal atoms used in bonding (Fig1.2)

      : even "five-fold" bond b/w transition metals is reported → <u>quintuple</u> (Fig.1.3)
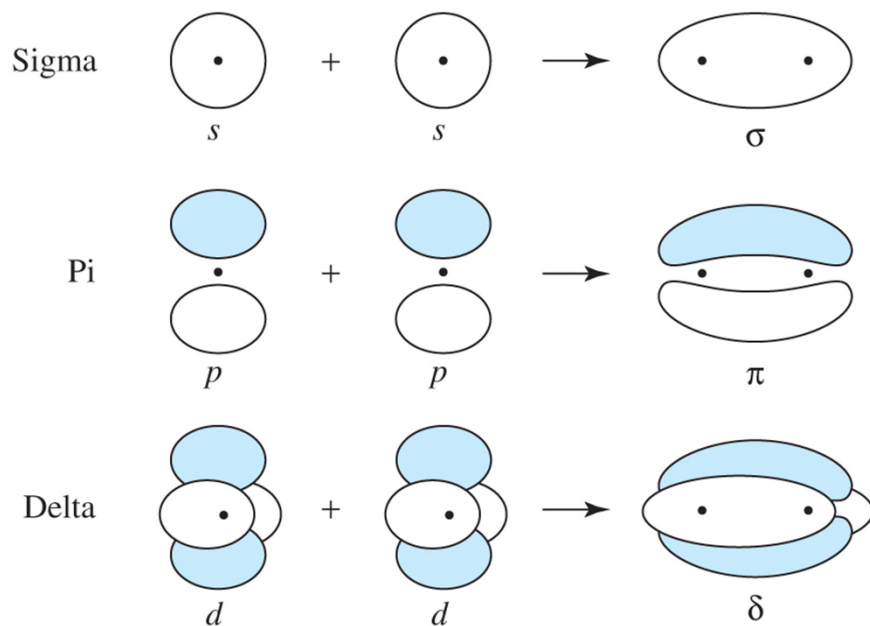
Fig1.2

Fig1.3

- H atoms : 1) organic chem.: H bonded to a single carbon

2) inorganic chem.: <u>bridging</u> two or more other atoms

ex) in metal cluster compds. – bridging across edges or faces of polyhedra of metal atoms

- alkyl group: 1) organic chem.: rarely act as bridge

2) inorganic chem.: some examples
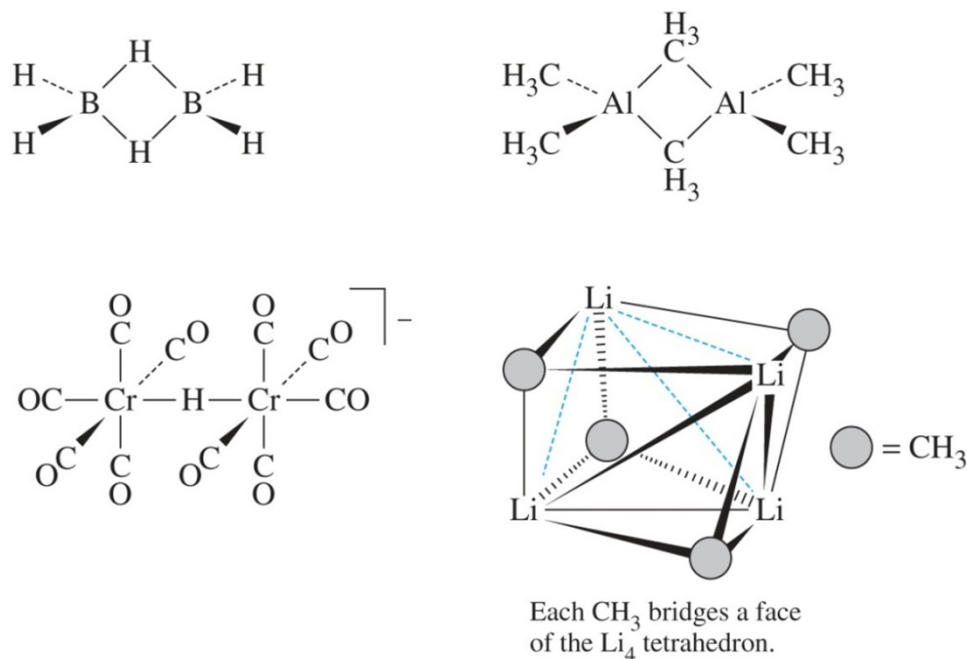
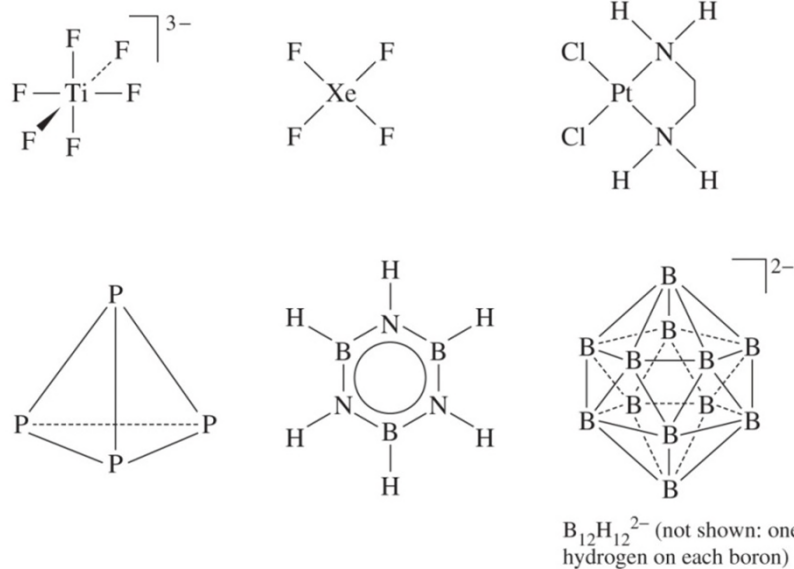© 2014 Pearson Education, Inc.

Fig1.4

- coordination number and geometry

    1) carbon: maximum coordination number → 4 (4 atoms bonded to C, e.g., CH_4)

    2) inorganic compds: central atom w/ <u>5,6,7,,, higher</u> coordination number

        ex) most common coordination geometry for TM: <u>octahedron</u>, e.g., $[TiF_6]^{3-}$

        metal atoms

- different coordination geometry: 1) 4-coordinated carbon: tetrahedral

   2) inorganic chem.: <u>tetrahedral & square-planar</u>

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Fig1.5

- coordination complex: central metal w/ anions or neutral molecules bonded to them

       through N, O, S

- organometaliic complex: metal atoms or ions w/ directly bonded to carbons

- tetrahedral geometry: 1) carbon compds.: 4-coordinated compds. (CH_4)

        2) elemental phosphorous: tetratomic w/o a central atom (P_4)
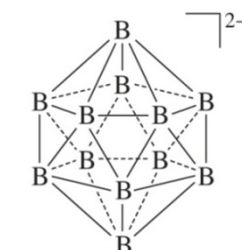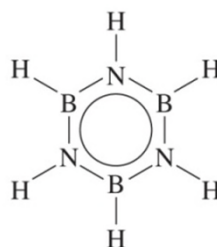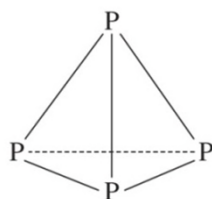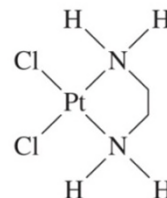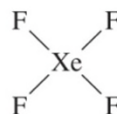
$B_{12}H_{12}{}^{2-}$ (not shown: one hydrogen on each boron)

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Fig1.5

- aromatic rings: 1) organic chem.: aryl group sigma bonded to metals

2) inorganic chem.: <u>rings pi-bonded</u> to metals (Fig. 1.6)

- metal atom bonded above the center of the ring

- metal atoms sandwiched b/w two aromatic rings

- multiple-decker sandwiched
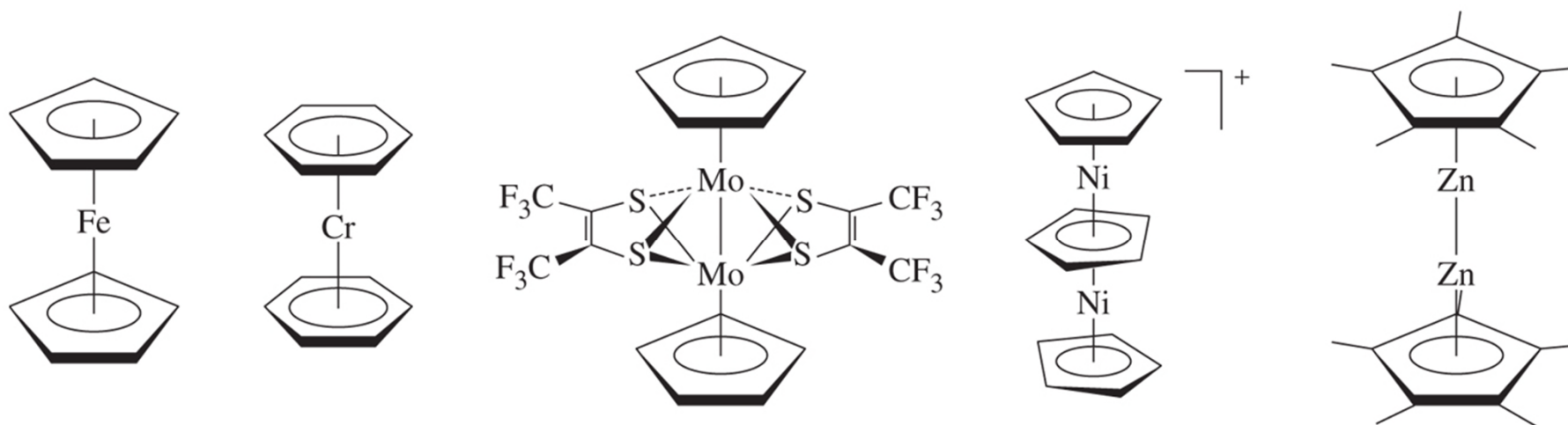
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Fig1.6

- Carbon centered metal cluster: C is at the center of a polyhedron of 5, 6, or more surrounding metal atoms
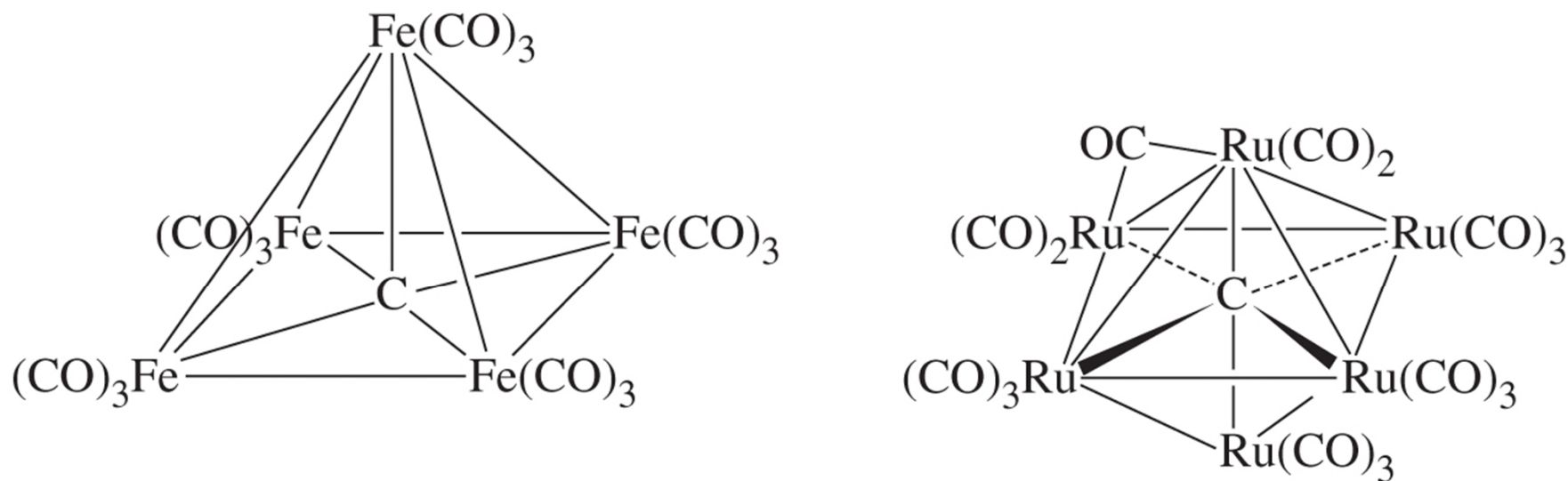
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Fig1.7

- <u>elemental carbon</u>: the past quarter century is the realm of chemistry of elemental carbon.

   ex) fullerene C_{60} ("buckminster fullerene")
      fullerene compds.
      carbon nanotube   ⟶   interested in applications in fields
      graphene   as divers as nanoelectronics,
                                            body armor, drug delivery
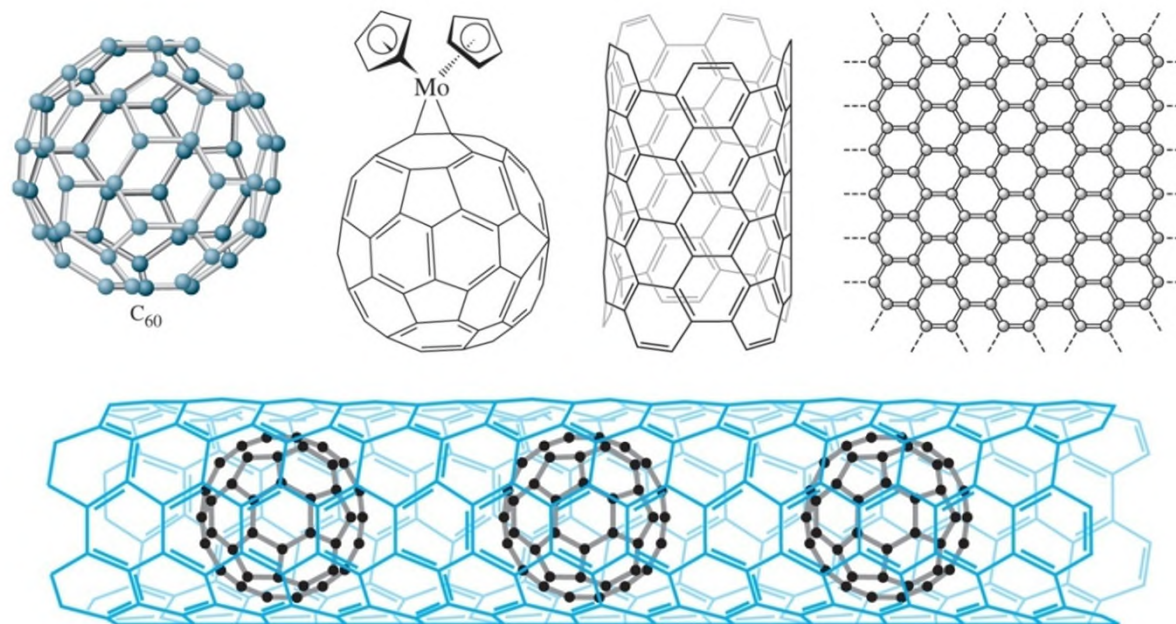
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Fig1.8

- <u>No sharp dividing</u> lines b/w subfield in chemistry

   1) acid-base chem., organometallic chem. → also for organic chem.

   2) oxidation-reduction reaction, spectra, solubility relations → analytical chem.

   3) structural determination, spectra, conductivity, theories of bonding → physical chem.

   4) metal-containing enzyme → biochem.

   5) organometallic catalysts → petroleum & polymer chem.

- Before alchemy era: in the metallic state – gold, copper

  : copper – obtained by reduction of malachite ($Cu_2(CO_3)(OH)_2$)

  : Ag, Sn, Sb, Pd – 3000 BCE

  : Fe – classical Greece, Mediterranean Sea 1500 BCE

  : colored glass, ceramic glaze – SiO_2 as major component & other

  metal oxides

- Alchemy era: 1) 1st CE – alchemists in China, Egypt,,,

  - tried to "transmute" metal into gold

  - developed distillation, sublimation, crystallization,,,

  2) 1000- 1500 CE – alchemists shifted to the Arab and Europe

  1150 CE – gunpowder in Chinese firework

  3) 1600 CE – chemistry was beginning to take shape as a science

The Lycurgus Cup (made of glass)

- When illuminated from outside, it appears green. However, when Illuminated from within the cup, it glows red.

- Red color is due to very small amounts of gold (Au) powder. (about 40 parts per million)

- 17th C: strong acids – nitric acid, sulfuric acid, hydrochloric acid

     - salts (acid + base)

     - properties of gases

     - atomic & molecular weight were determined

     - groundwork for the periodic table

- 1869: the concept of atoms & molecules → Mendeleev & Meyer (periodic table)

- 1896: the concept of radioactivity by Becquerel

- 1913: atomic theory including subatomic particles, spectra, electricity (by Bohr)

- 1926, 1927: quantum mechanics by Schrödinger & Heisenberg

<Inorganic Chemistry>

 : originally important for <u>mineral sources</u> for qualitative analysis (identify mineral, assess purity and value)

- 20th C: <u>ammonia</u>, nitric acid, sulfuric acid, sodium hydroxide → large scale production

     : coordination chemistry by Werner & Jørgensen

     : <u>organometallic chemistry</u>

- World War Ⅱ: military projects rejuvenated inorganic field

               → <u>Manhattan project</u> (fission bomb, fusion bomb)

- 1940s: great expansion of inorganic chem.

- 1950s: crystal field theory (describing the spectra of metal ions surrounded by negatively charged ion in crystal)

     ↓

 ligand field theory (by molecular orbital theory)

<Inorganic Chemistry>

- 1955: organometallic catalyst by <u>Ziegler & Natta</u>

 → <u>polymerization of ethylene</u> at lower temp. & press.

 → rapid expansion of this field

- <u>biological materials</u> containing metal atoms: model compds. by theoretical work

        → new synthetic technique
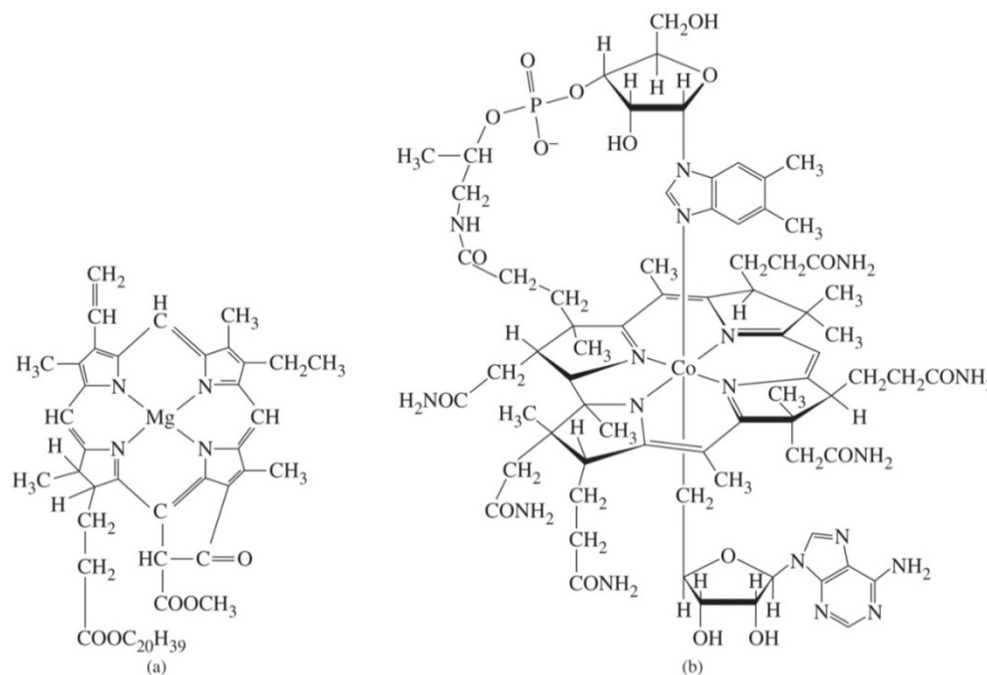
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Fig1.10

<Inorganic Chemistry>

- Conversion nitrogen to <u>ammonia</u>: bridging organometallic chem. & bioinorganic chem.

$$N_2 + 3H_2 \rightarrow 2NH_3$$
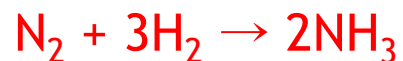
: reaction requires 400° & 200 atm → 15 % yield

: bacteria (by nitrogenese enzyme using iron-molybdenum-sulfur protein) → RT & 0.8 atm

- Medical application: platinum-containing antitumor agents

e.g.) <u>cisplatin</u> ($Pt(NH_3)Cl_2$), satraplatin
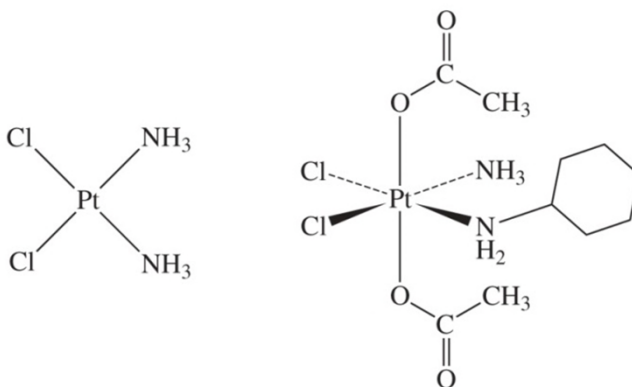
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Fig1.11

Summary Topic

Chapter2. Atomic Structure

1) Balmer's equation

2) Niels Bohr's quantum theory

3) In Figure 2.2, how can you get $-1/4R_H$ for $n = 2$?

4) Heisenburg's uncertainty principle

5) Hamiltonian in Schroedinger's equation

6) The energy levels predicted by the particle in-a-box model for any particle in

   a one-dimensional box of length a.

7) Four quantum numbers (symbols, names, values, roles)

8) How to find out the nodal surfaces?

9) Pauli's exclusion principle

10) Hund's rule

11) Slater's effective nuclear charge Z^*

12) Ionization energy

- The theory of atomic and molecular structure depend on quantum mechanics to describe atoms and molecules in mathematical terms. Fortunately, it is possible to gain a practical understanding of the principles of atomic and molecular structure with only a moderate amount of mathematics rather than the mathematical sophistication involved in quantum mechanics.

- This chapter presents the fundamentals needed to explain atomic and molecular structures in qualitative or semiquantitative terms.

Finding of the subatomic particle:
Balmer's Equation

→

원자의 subatomic particle인 전자가 E를 방출하거나 흡수할 수 있음.

→

Generalized by Niels Bohr

→

하지만 이러한 이론은 전자의 wave nature 때문에 H 외에는 잘 맞지 않음.

↓

3-D Schrodinger equation의 solution이 바로
atomic orbitals

←

Schroedinger equation의 realistic solution을 위한 조건들을 적용한 예:
Particle in a box (1-D)

←

그래서 wave property를 잘 나타내는 equation 사용하기로 함:
Schroedinger equation

←

Heisenberg's Uncertainty principle

↓

Quantum number로
AO 표현함.

→

Ψ 표현하는 두 가지 방법:
1) Cartesian,
2) Spherical

→

QN 의 제한으로 인해 aufbau principle 필요:
1) Pauli's
2) Hund's

→

If more than 1 e⁻, shielding effect: Z

↓

Ionization energy, electron affinity, covalent/ ionic radii.

- Many Chemists had considered the idea of <u>arranging the elements</u> into a periodic table.

- But, due to either <u>insufficient data</u> or <u>incomplete classification scheme</u>, it was not done until Mendeleev and Meyer's time.

- Using similarities in <u>chemical behavior and atomic weight</u>, Mendeleev arranged those families in rows and columns,,,

- and, he <u>predicted</u> the properties of unknown elements, such as Ga, Sc, Ge, Po.

- In the modern periodic table :

  : **periods** (horizontal row of elements)

  : **group/family** (vertical column)

- 3 different ways of designations of groups:

  : IUPAC, American, European

  1) American: main group → IA – VIIIA;

  　　　　　TMs → IIIB – VIIIB – IIB

  2) IUPAC: numbering **from 1 through 18**

  　　　　for all group

Fig2.1

- During the 50 years after the Mendeleev's periodic table was proposed, there had been experimental advances and discoveries as shown in Table 2.1.

TABLE 2.1 Discoveries in Atomic Structure

1896	A. H. Becquerel	Discovered radioactivity of uranium
1897	J. J. Thomson	Showed that electrons have a negative charge, with charge/mass $= 1.76 \times 10^{11}$ C/kg
1909	R. A. Millikan	Measured the electronic charge as 1.60×10^{-19} C, therefore the mass of the electron is 9.11×10^{-31} kg, $\dfrac{1}{1836}$ the mass of the H atom
1911	E. Rutherford	Established the nuclear model of the atom; a very small, heavy nucleus surrounded by mostly empty space
1913	H. G. J. Moseley	Determined nuclear charges by X-ray emission, establishing atomic numbers as more fundamental than atomic masses

- The discovery of atomic spectra showed that each elements emits **light of specific energy** when excited.

  : **Balmer's equation** (1885) → **energy** of visible light emitted by **H atom**

$$E = R_H \left(\frac{1}{2^2} - \frac{1}{n_h^2} \right)$$

n_h: integer, with $n_h > 2$

R_H: Rydberg constant for hydrogen = 1.097 X 10^7 m^{-1} = 2.179 X 10^{-18} J

----

* E is related to the wavelength, frequency, and wave number of the light!!

$$E = h\upsilon = \frac{hc}{\lambda} = hc\bar{\upsilon}$$

h = Planck constant = 6.626 X 10^{-34} Js

υ = frequency of the light, in s^{-1}

c = speed of light = 2.998 x 10^8 ms^{-1}

λ = wavelength of the light, frequently in nm

$\bar{\upsilon}$ = wavenumber of the light, usually in cm^{-1}

- Balmer's equation becomes more general by **replacing 2^2 by n^2_l.** ($n_l < n_h$)

- **Niels Bohr's quantum theory** of the atom : - negative e^- in atoms move in circular orbitals around positive nucleus.

  - e^- may absorb or emit **light of specific E**

$$E = R_H \left(\frac{1}{n_l^2} - \frac{1}{n_h^2} \right)$$

$$R = \frac{2\pi^2 \mu Z^2 e^4}{(4\pi\varepsilon_0)^2 h^2}$$

μ = reduced mass of the electron-nucleus combination

$*\Big($ m_e = mass of the electron

$m_{nucleus}$ = mass of the nucleus

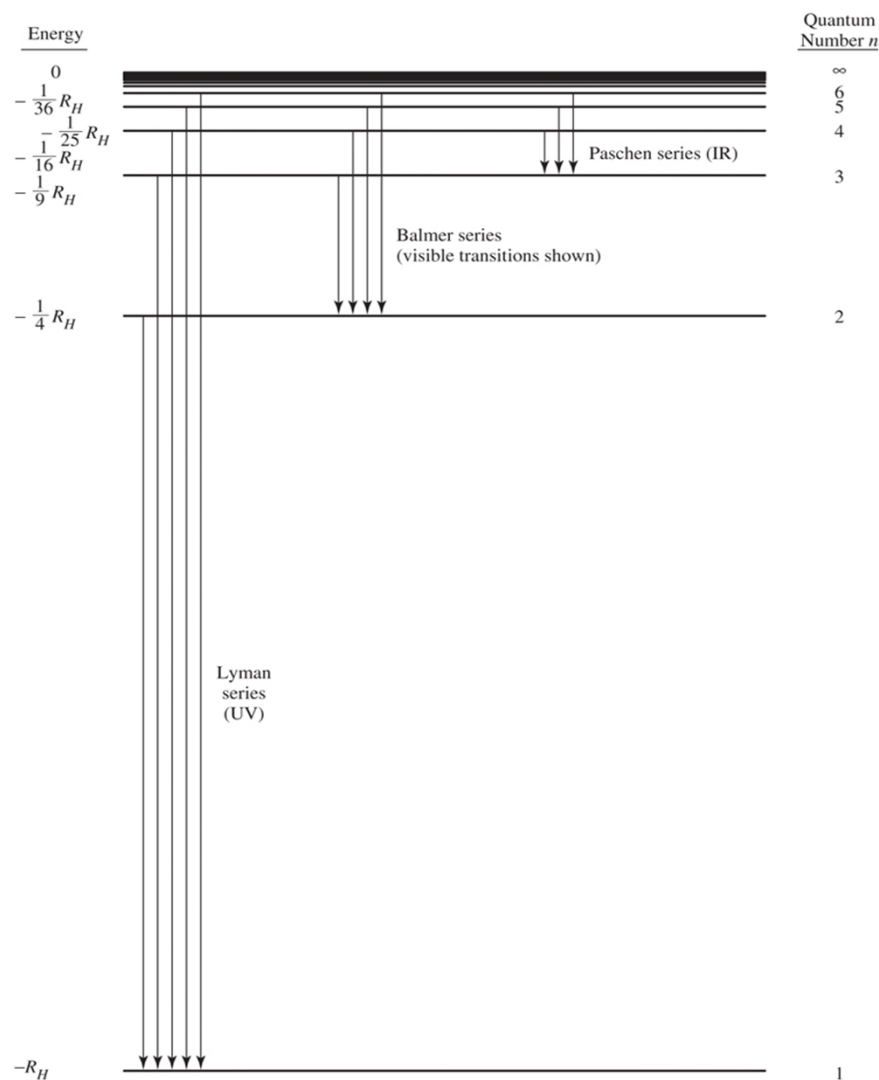Z = charge of the nucleus

e = electronic charge

h = Planck constant

----

n_h = quantum number of describing the **higher energy state**

n_l = quantum number of describing the **lower energy state**

$4\pi\varepsilon_0$ = permittivity of a vacuum

- **Electron transition** among *E* levels for the **hydrogen** atom (Fig. 2.2)

Fig. 2.2

- *E* release: as e⁻ drops from n_h to n_l

- If correct *E is absorbed*: e⁻ is raised from n_l to n_h

- According to Bohr's model and equation, *E* is inverse-squarely proportional to *n*.

- Thus, (at small *n* → large *E* gap
         at large *n* → small *E* gap

- Exercise 2.1

- However, Bohr's theory works only for H and fails to atoms w/ more e⁻ because of **the wave nature of e⁻.**

- de Broglie equation: all moving particles have **wave properties,** which can be expressed as shown below

$$\lambda = \frac{h}{m\upsilon}$$

λ = wavelength of the particle

h = Planck constant = 6.626×10^{-34} Js

m = mass of the particle

υ = velocity of the particle

- e⁻'s wave property is observable due to the **very small mass**.(1/1836 of the H atom)

- But, we can not describe the motion of e⁻ w/ the wave property precisely because of **Heisenberg's uncertainty principle**.

Heisenberg's Uncertainty Principle

$$\Delta x \, \Delta p_x \geq \frac{h}{4\pi}$$

Δx = uncertainty in the **position** of the electron

Δp_x = uncertainty in the **momentum** of the electron

- Thus, there is the inherent uncertainty in the **location** and **momentum** of e⁻

  (Δx is large)   (Δp_x is small)

- e⁻ should be treated <u>as **wave** (due to its uncertainty in location)</u>, not simple particles.

- We can't describe **orbits of e⁻**, but can describe **orbitals !!!**

  region that describe the <u>probable location of e⁻</u>

  electron density

- Therefore, one should use an equation which <u>describes **wave property** well</u> !!!

The Schrödinger equation

- The equation describes the wave properties of e$^-$ in terms of its <u>position, mass, total E and potential E</u>.

$$H\Psi = E\Psi$$

H = the Hamiltonian operator

E = energy of the electron

Ψ = the wave function

- <u>Hamiltonian operator (H)</u> includes derivatives that operate on the wave function.

- The result is a constant (E) times Ψ.