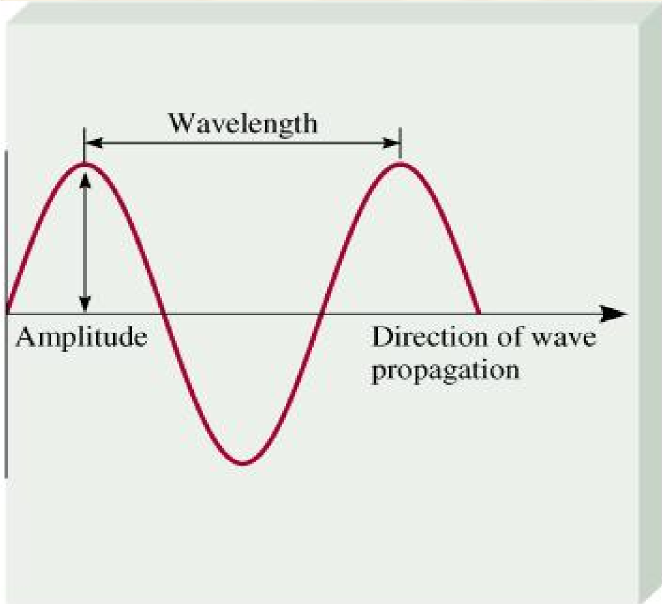
Chapter 6
Electronic Structure and The Periodic Table

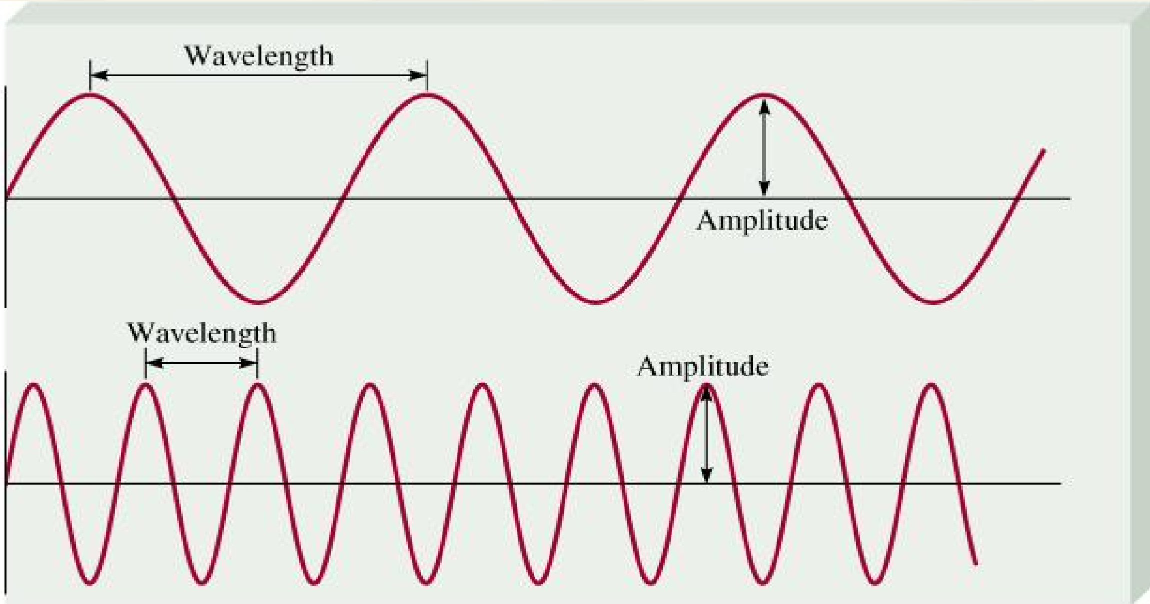
Ch.6 Electronic Structure and The Periodic Table

- **6-1： Light, photon energies, and atomic spectra**
- 1. The Wave Nature of Light：Wavelength and Frequency
- 2. The particle Nature of Light ；Photon Energies
- 3. Atomic Spectra
- **6-2： The Hydrogen atom 氫原子模型**
- 1. Bohr Model
- 2. Quantum Mechanical Model
- **6-3： Quantum number 量子數**
- 1. First Quantum Number , n；Principal Energy Levels
- 2. Second Quantum Number ,l；Sublevels（s, P,d,f）
- 3. Third Quantum Number ,ml；Orbitals
- 4. Fourth Quantum Number ,Ms ；Electron Spin
- 5. Pauli Exclusion Principle
- **6-4 ：Atomic orbitals；Shapes and size**
- **6-5 ：Electron configurations in atoms**
- 1. Electron Configuration from Sublevel Energies
- 2. Filling of Sublevels and the Periodic Table
- 3. Electron Configuration from the periodic Table
- **6-6： Orbital diagrams of atoms**
- **6-7 Electron arrangements in monatomic ions**
- 1. Ions with Noble-Gas Structures
- 2. Transition Metal Cations
- **6-8 Periodic trends in the properties of atoms**
- 1. Atomic Radius
- 2. Ionic Radius
- 3. Ionization Energy
- 4. Electronegativity

6-1 Light, Photon Energies, and atomic spectra

1.The wave Nature of light :Wavelength and Frequency





Wavelength (λ) The distance between two consecutive crests or troughs, most often measured in meters or nanometers(1nm=10^{-9}m)

Amplitude (Ψ) 水平點到波峰或波谷的高度

Frequency (ν): The number of wave cycles that pass a given point in unite time.
$\nu = 10^8/\,s\ = 10^8$ Hz (單位時間內所行經的波週數以秒的倒數(1/s)或赫茲(Hterz, Hz)表示)

1.Wave nature of Light

The speed at which a wave moves through space can be found by multiplying the length of a wave cycle by the number of cycles passing a point in unit time

The speed (c) of the wave = $\lambda \times \nu$

$$c = \lambda \times \nu = \frac{長度}{\cancel{波}} \times \frac{\cancel{波}}{時間} = \frac{長度}{時間}$$

Speed of light (*c*) in vacuum = 2.998×10^8 m/s

Ex6.1:The red light associated with the aurora borealis is emitted by excited oxygen atom at 630.0nm.What is the frequency of the light?

Sol:

$$l = 630\ nm \times \frac{1m}{10^{9}\ nm} = 6.300 \times 10^{-7}\ m$$

$$u = \frac{2.988 \times 10^{8}\ m/s}{6.300 \times 10^{-7}\ m} = 4.759 \times 10^{14}\ /s$$

$$= 4.759 \times 10^{14}\ HZ$$

2.The Particle Nature of Light ; Photon Energies

Max Planck(1900)－Blackbody radiation 波動性

Albert Einstein(1905)－Photoelectric effect 粒子性

$$E=h\nu=\frac{hc}{l}$$

h: Planck′s constant 蒲朗克常數

$=6.626\times10^{-34}$ J·s

Ex6-2:The wavelength is 557.5×10^{-9} m

(a) The energy, in Joules, of a photon emitted by an excited oxygen atom

(b) The energy, in kiloJoules, of a mole of such photons (以仟焦耳(KJ)表示1mol光子的能量)

(a) $E = hn = \frac{hc}{l}$

$$= \frac{(6.626\times10^{-34}\,J\times s)(2.998\times10^{8}\,m/s)}{557.5\times10^{-9}\,m} = 3.153\times10^{-19}\,J$$

$$E = 3.562\times10^{-19}\,J/個 \times \frac{1KJ}{10^{3}\,J} \times \frac{6.022\times10^{23}\,個}{1mol}$$

$$= 1.899\times10^{2}\,KJ/mol$$

The energy, in Joules, of a photon emitted

(a) $\lambda = 5.00 \times 10^{4}$ nm (紅外線)

(b) $\lambda = 5.00 \times 10^{-2}$ nm (x-ray)

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\, J \times s \times 2.998 \times 10^{8}\, m/s}{5.00 \times 10^{4} \times 10^{-9}\, m} = 3.98 \times 10^{-21}\, J$$

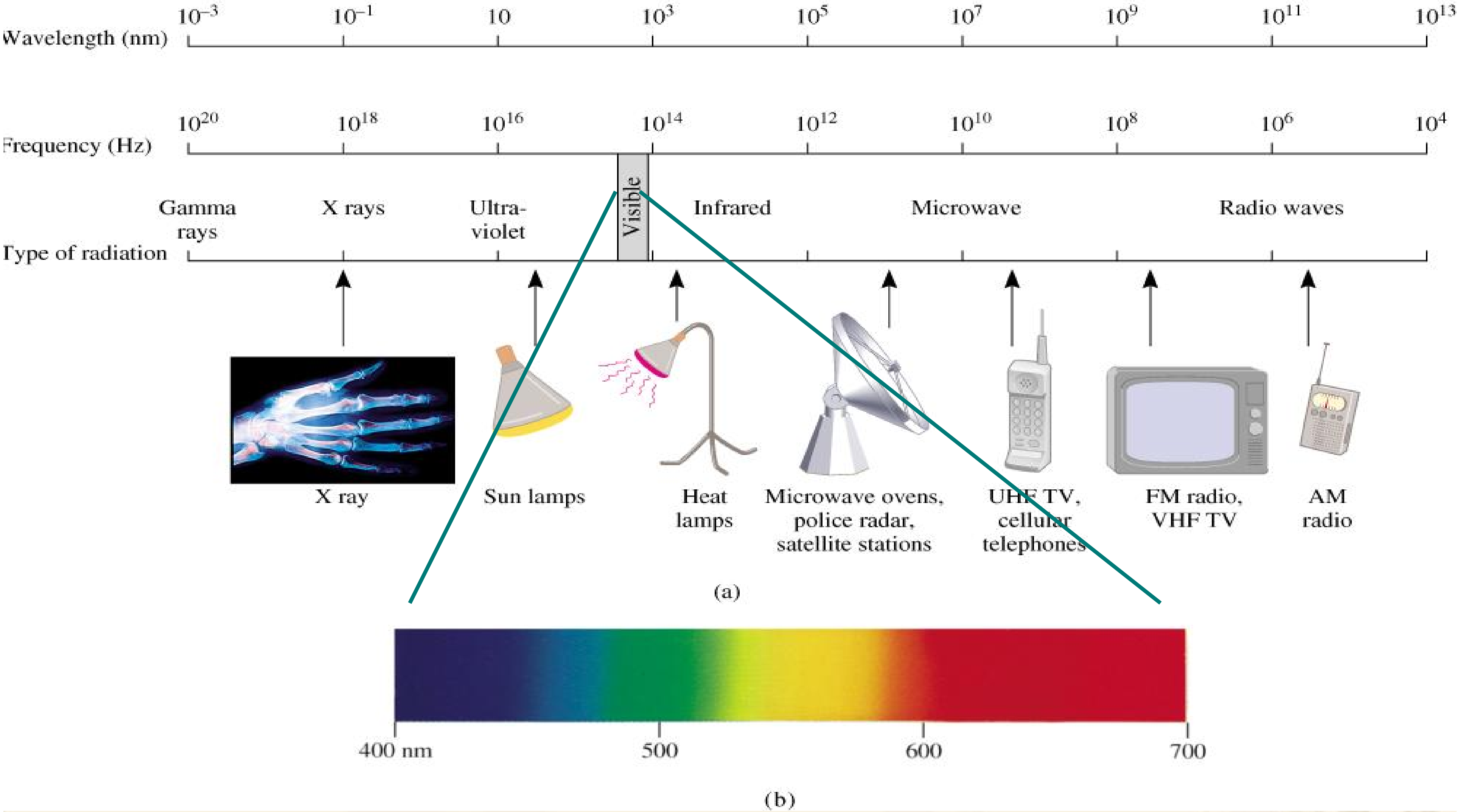
$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\, J \times s \times 2.998 \times 10^{8}\, m/s}{5.00 \times 10^{-2} \times 10^{-9}\, m} = 3.98 \times 10^{-15}\, J$$

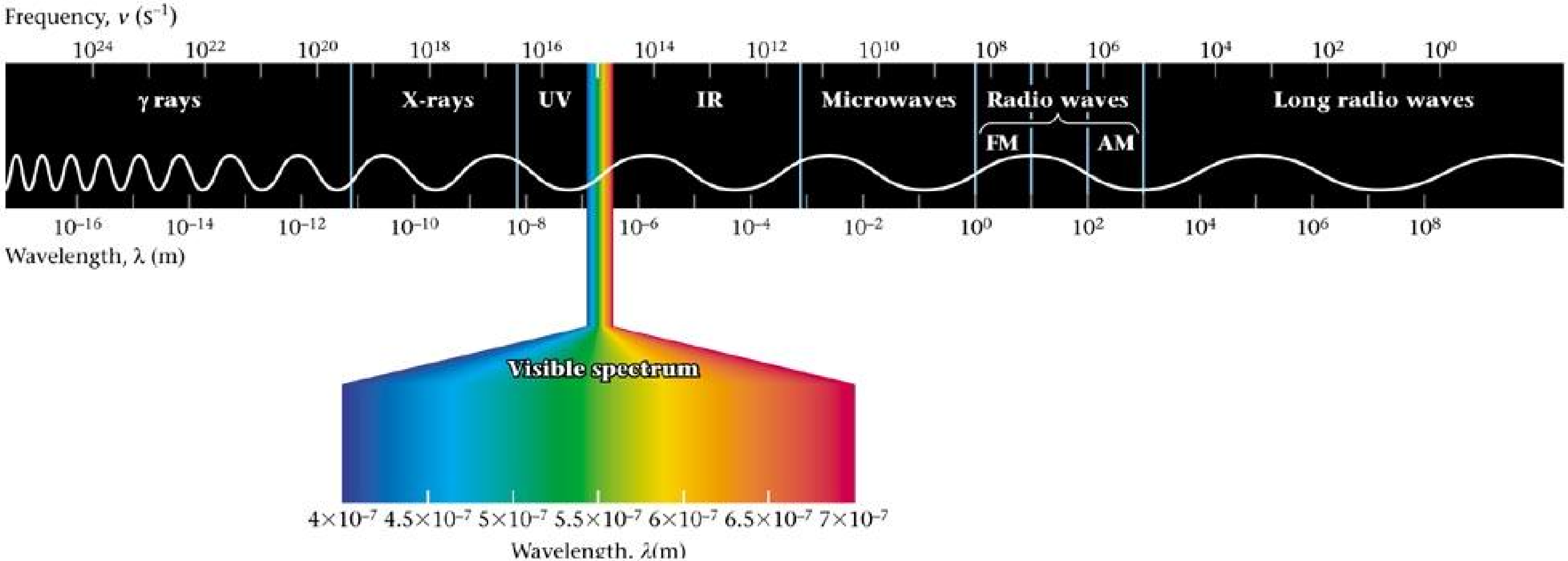
某光子的能量為5.87×10^{-20}J,What is λ?

$$E = hn = \frac{hc}{l}$$

$$l = \frac{hc}{E} = \frac{6.626\times 10^{-34}\,J\times s\times 2.998\times 10^{8}\,m/s}{5.87\times 10^{-20}\,J} = 3.38\times 10^{-6}\,m$$

Fig 6.2 The electromagnetic spectrum.

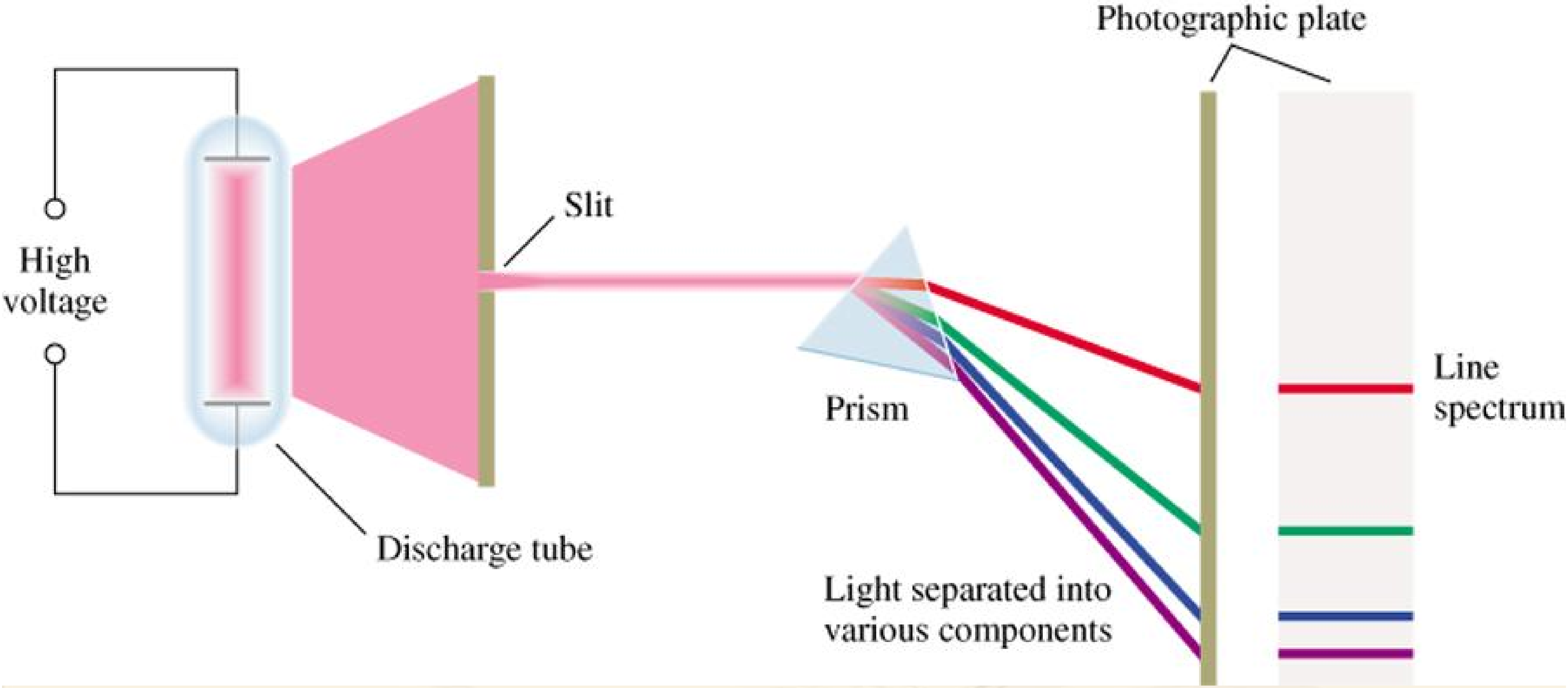




Frequency, ν (s⁻¹)
10²⁴ 10²² 10²⁰ 10¹⁸ 10¹⁶ 10¹⁴ 10¹² 10¹⁰ 10⁸ 10⁶ 10⁴ 10² 10⁰
γ rays
X-rays
UV
IR
Microwaves
Radio waves
FM
AM
Long radio waves
10⁻¹⁶ 10⁻¹⁴ 10⁻¹² 10⁻¹⁰ 10⁻⁸ 10⁻⁶ 10⁻⁴ 10⁻² 10⁰ 10² 10⁴ 10⁶ 10⁸
Wavelength, λ (m)
Visible spectrum
4×10⁻⁷ 4.5×10⁻⁷ 5×10⁻⁷ 5.5×10⁻⁷ 6×10⁻⁷ 6.5×10⁻⁷ 7×10⁻⁷
Wavelength, λ(m)

3.Atomic Spectra(原子光譜)

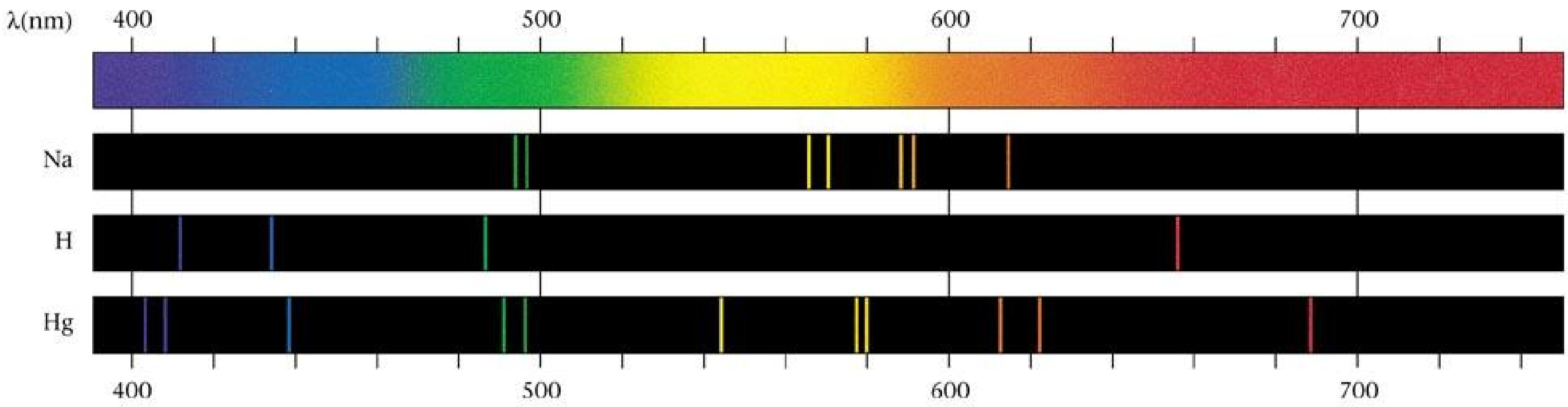
- Sir Isaac Newton showed that visible (white) light from the sum can be broken sown into its various color components by a prism. The Spectrum obtained is continuous ; it contains essentially all wavelengths between 400 and 700 nm.
- 原子發射光譜則是不連續的，僅發生在某些特定的光譜(線光譜 Line Spectra)
- The situation with high-energy atoms of gaseous elements is quite different(Fig6.3)



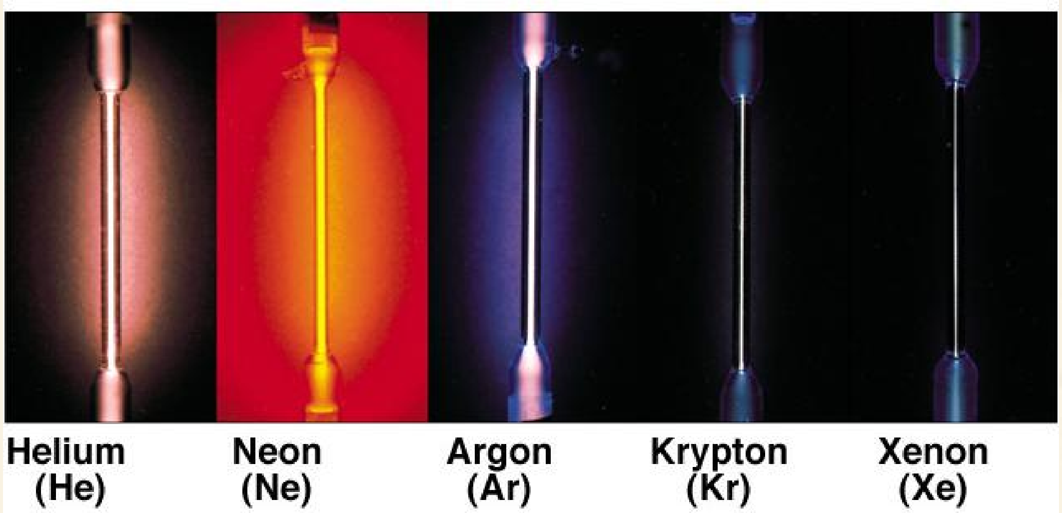
Line Emission Spectrum of Hydrogen Atoms

410.18 434.05 486.13nm 656.28nm

圖6.3 Continuous and Line emission spectra



Chemistry in Action: Discovery of the Noble Gases



Sir William Ramsay

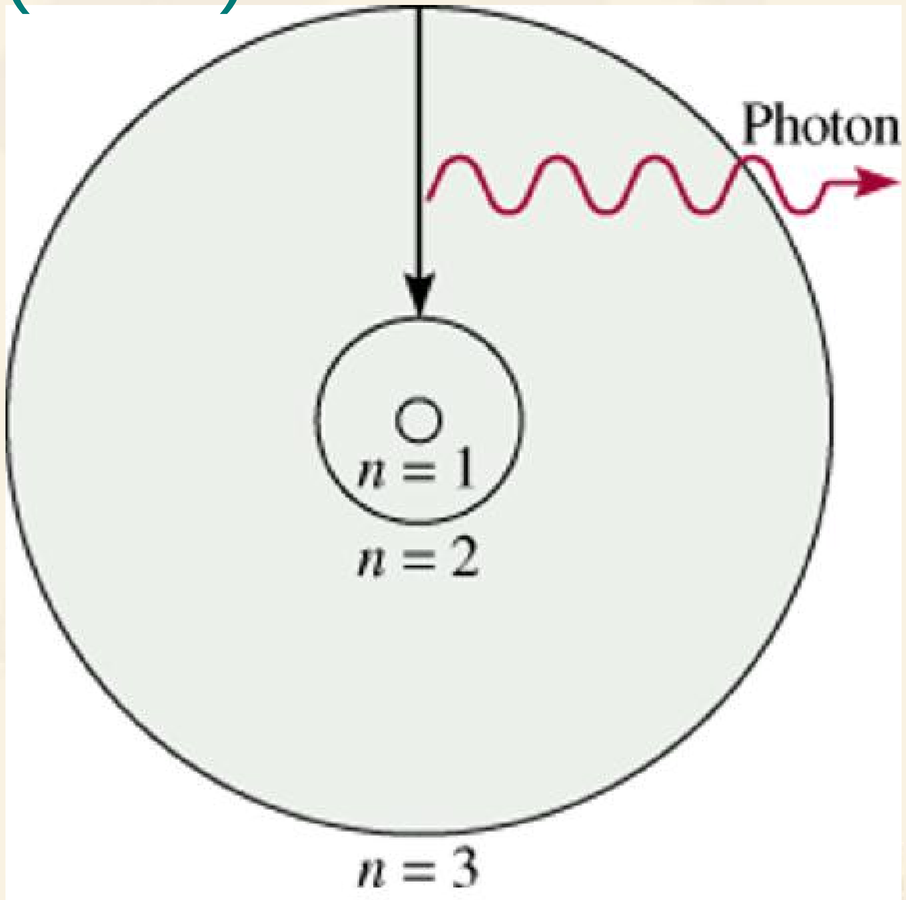
6.2 The Hydrogen atom

Bohr's Model of the Atom (1913)

1. 電子的能量是特定值，被量子化的。
2. 當電子從高能階移向低能階時，光被放射出來。

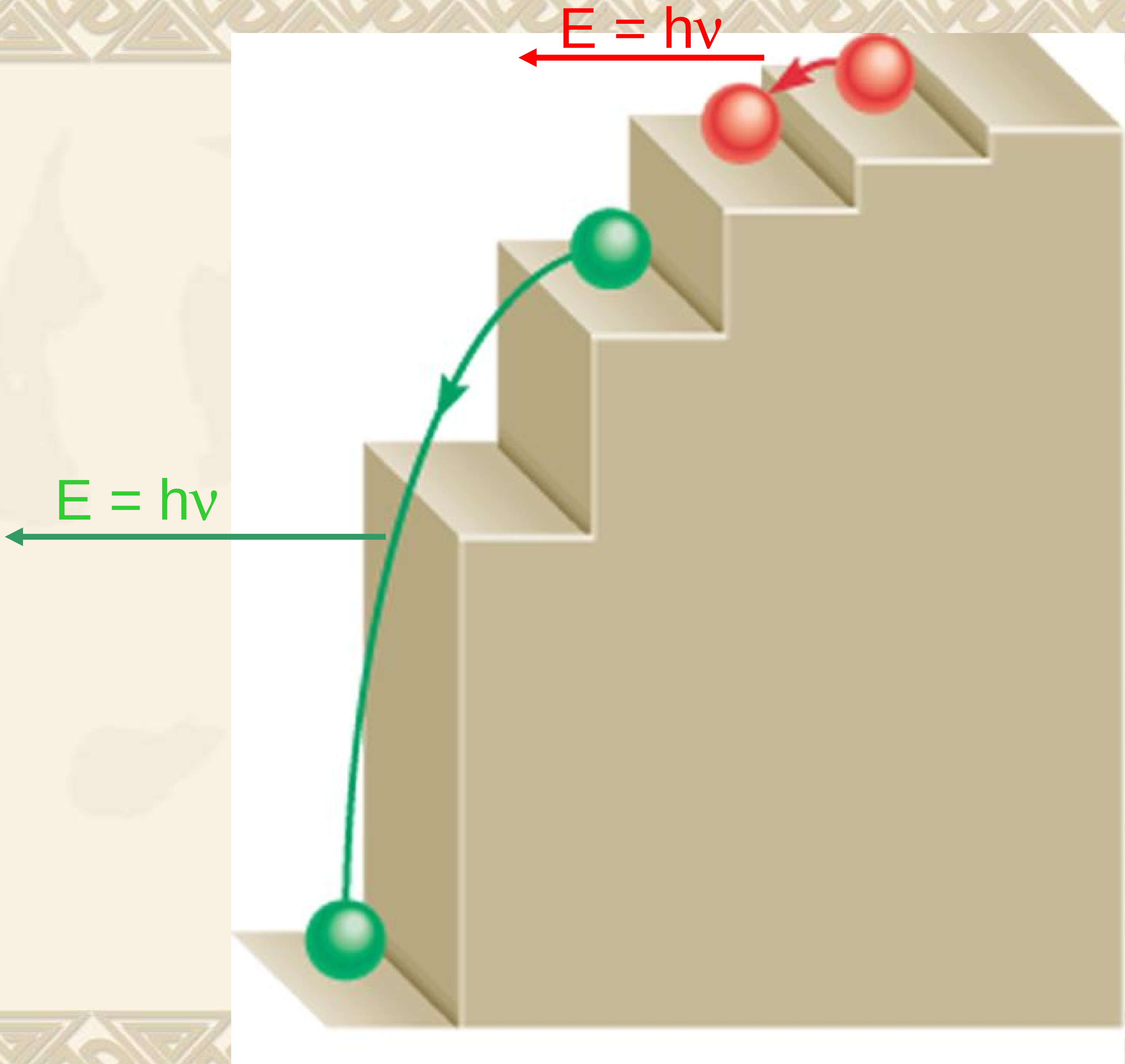
相對量，決定為吸收或發射光譜

$$E_n = -R_H \left(\frac{1}{n^2}\right)$$



n (principal quantum number) = 1,2,3,…

R_H (Rydberg constant) = 2.180×10^{-18} J



E = hν
E = hν

1. Bohr designated zero energy as the point at which the proton and electron are completely separated。

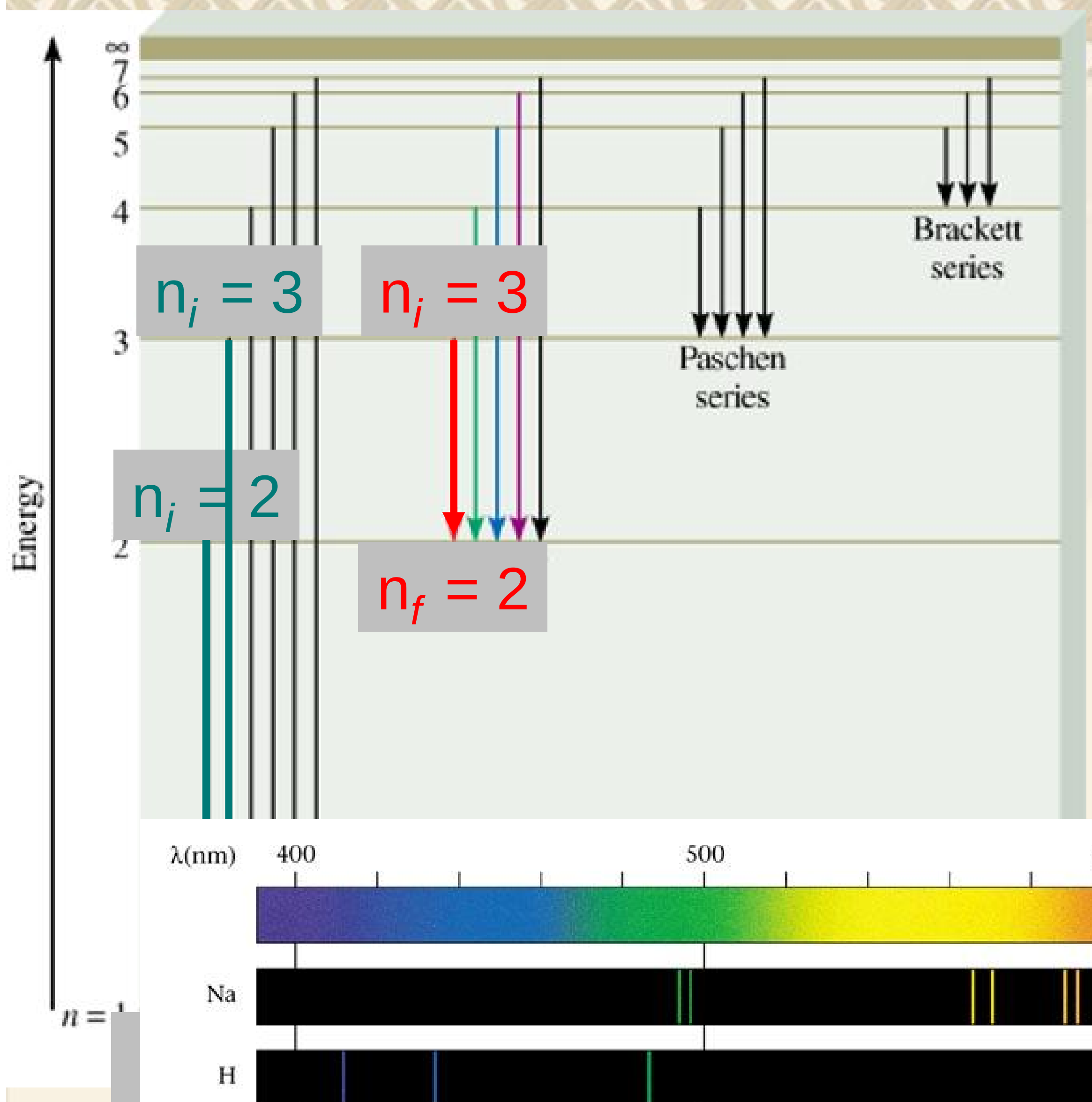
$$E = -\frac{R_H}{n^2}$$

2. The hydrogen electron is in its lowest energy (ground state)，n=1，Electron absorbs enough energy , it moves to a higher, (excited state)。

3. An excited electron gives off energy as a photon of light, it drops back to a lower energy state.

$$\Delta E = hn = E_{hi} - E_{lo}$$

$$hn = -R_H\left[\frac{1}{(n_{hi})^2} - \frac{1}{(n_{lo})^2}\right] \qquad n = \frac{R_H}{h}\left[\frac{1}{(n_{lo})^2} - \frac{1}{(n_{hi})^2}\right]$$

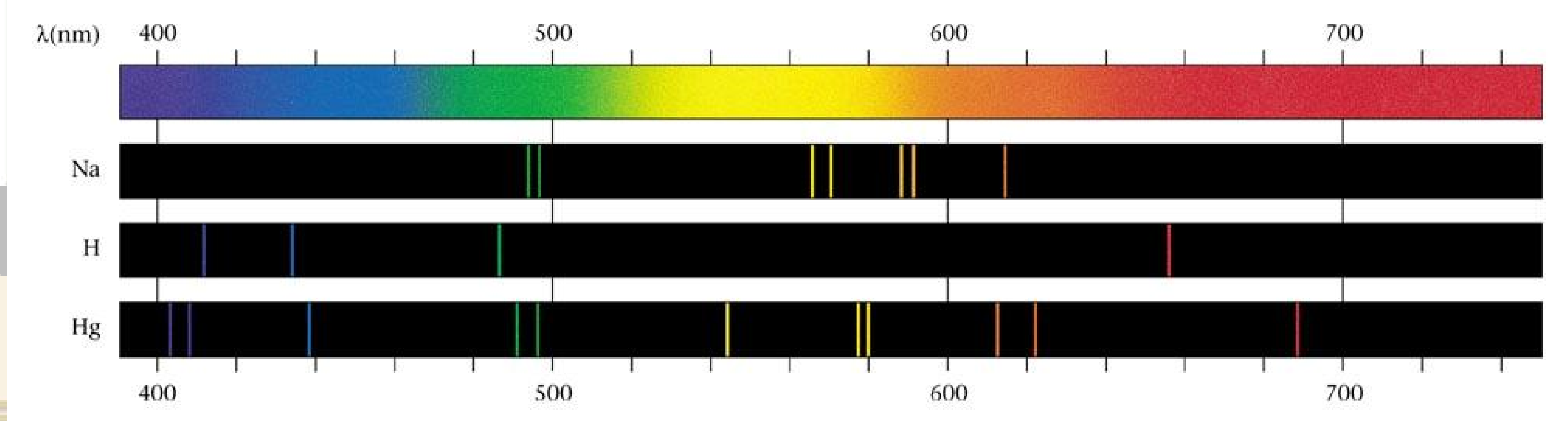


$E_{photon} = \Delta E = E_f - E_i$

$E_f = -R_H \left(\frac{1}{n_f^2} \right)$

$E_i = -R_H \left(\frac{1}{n_i^2} \right)$

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



Ex6.3:Calculate the wavelength in nanometers of the line in the Balmer series that results from the transition n=4至n=2

$$n = \frac{R_H}{h}\left[\frac{1}{(n_{lo})^2} - \frac{1}{(n_{hi})^2}\right] = \frac{2.180\times 10^{-18} J}{6.626\times 10^{-34} J\times s}\left[\frac{1}{2^2} - \frac{1}{4^2}\right] = 6.169\times 10^{14} / s$$

$$l = \frac{c}{n} = \frac{2.998\times 10^{8} m/s}{6.169\times 10^{14} / s} \times \frac{10^{9} nm}{m} = 486.0 nm$$

Calculate the wavelength (in nm) of a photon emitted by a hydrogen atom when its electron drops from the n = 5 state to the n = 3 state.

$$E_{photon} = \Delta E = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$E_{photon} = 2.18 \times 10^{-18}\ \text{J} \times (1/25 - 1/9)$$

$$E_{photon} = \Delta E = -1.55 \times 10^{-19}\ \text{J}$$

$$E_{photon} = h \times c / \lambda$$

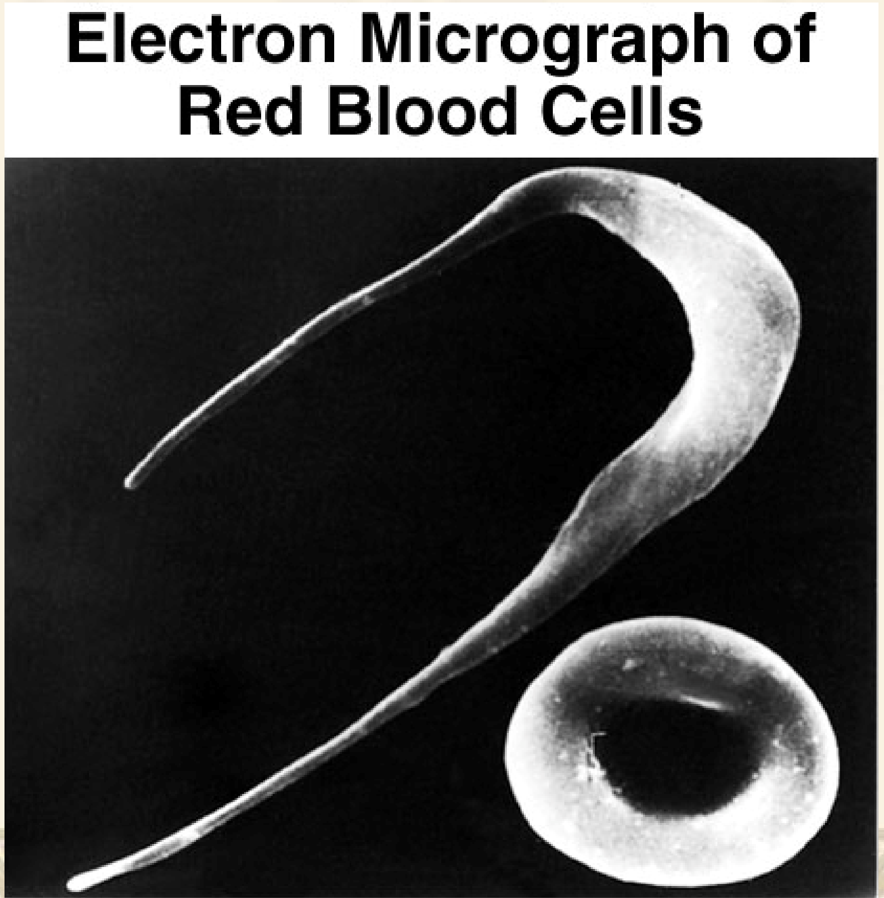
$$\lambda = h \times c / E_{photon}$$

$$\lambda = 6.63 \times 10^{-34}\ (\cancel{\text{J}}\bullet\cancel{\text{s}}) \times 3.00 \times 10^{8}\ (\text{m}/\cancel{\text{s}})/1.55 \times 10^{-19} \cancel{\text{J}}$$

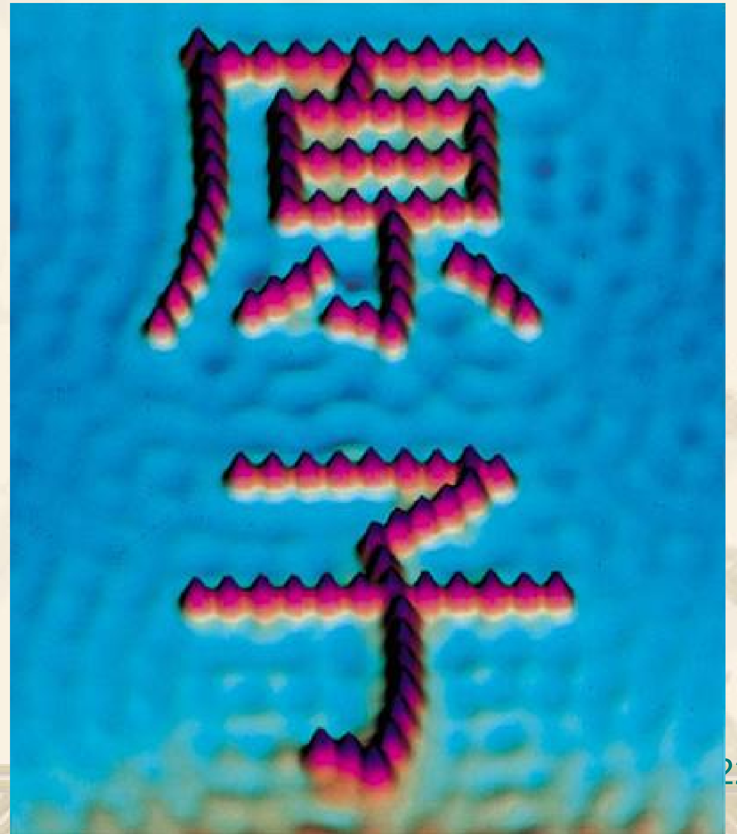
$$\lambda = 1280\ \text{nm}$$

Chemistry in Action: Electron Microscopy

λ_e = 0.004 nm



STM image of iron atoms on copper surface

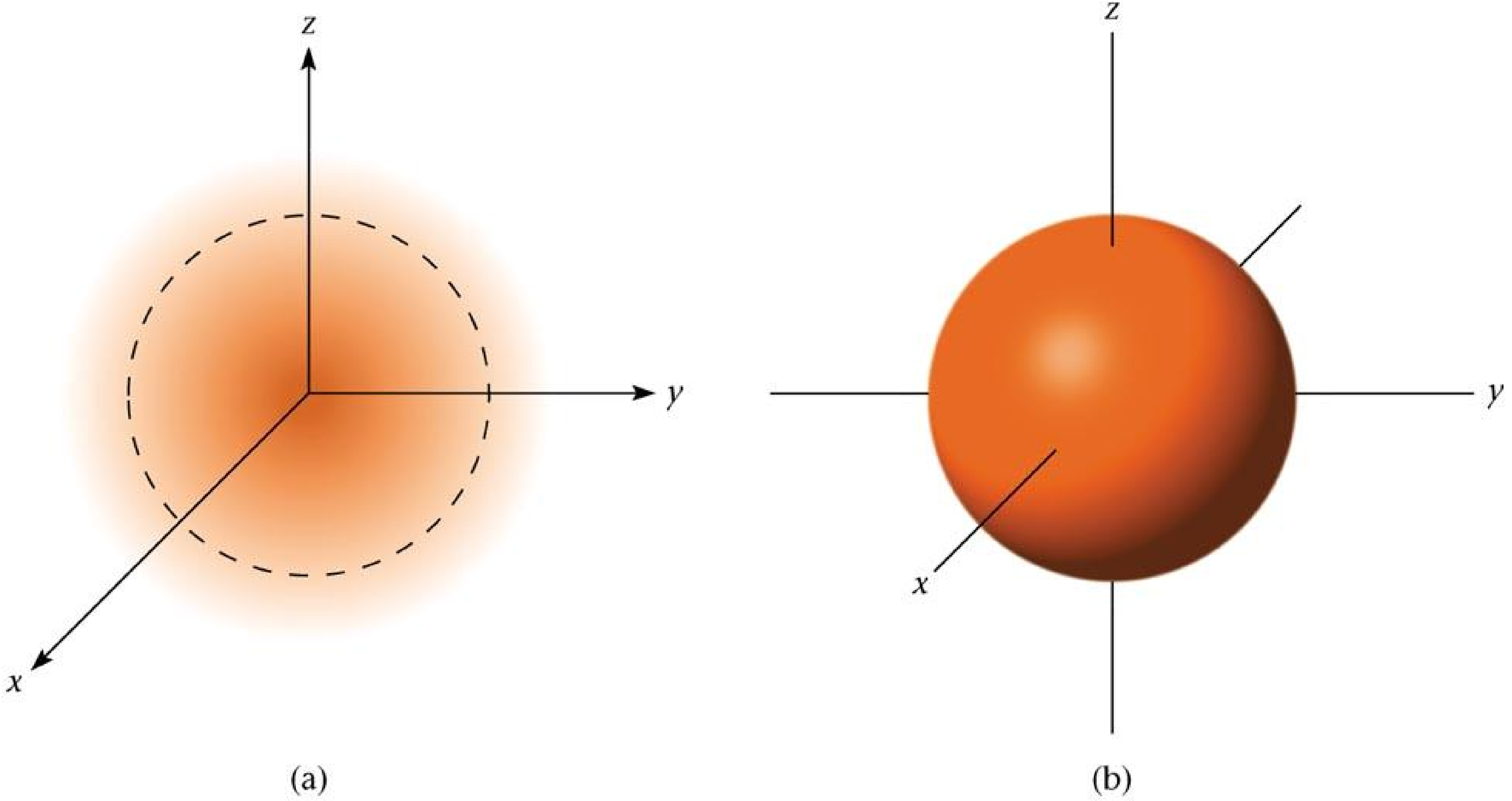


2.Quantum Mechanical Model
量子力學模型

Bohr's theory for the structure of the hydrogen atom was highly successful 0.1 % error. When Bohr's theory is applied to the helium atom have 5%error。

- The Kinetic energy of an electron is inversely related to the volume of the region to which it is confined.(電子的動能和其所侷限的活動範圍的體積成反比。)
- It is impossible to specify the precise position of an electron in an atom at a given instant.
- (在特定的範圍內要正確指出電子在原子中真正的位置是不可能的。)

Fig6-4 Two different ways of showing the electron distribution in the ground state of the hydrogen atom.(兩種不同的方式表示氫原子電子在基態時的分佈)



6.3 Quantum numbers

Schrodinger Wave Equation

Ψ電子波在空間中每一點的振幅

$\Psi = fn(n, \ l, m_l, m_s)$

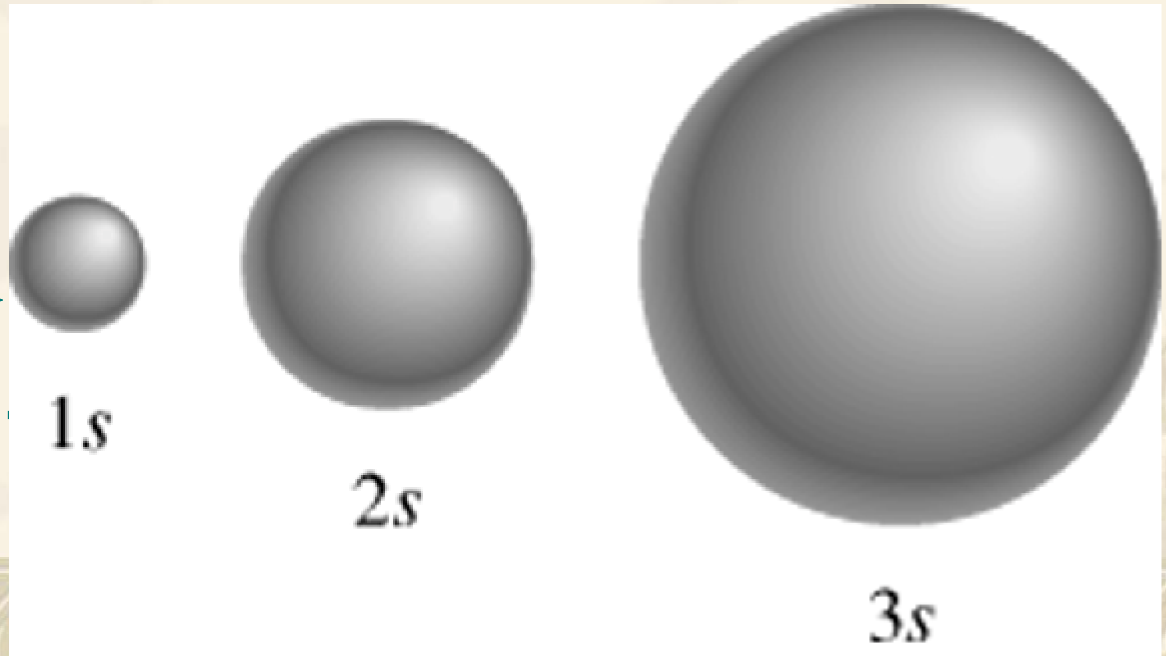
Principal energy levels(

電子與原子核的距離

n=1 → n=2 → n=3 →

1.First Quantum Number ,n ; (Principle quantum number)

- 標明主能階 principal quantum number) n
- n愈大
  - 電子能量愈大
  - 離子原核愈遠
- 為1以上之整數
- n = 1, 2, 3, 4, ...



Second Quantum Number角動量量子數 (angular momentum quantum number) *l*

Schrodinger Wave Equation

$\Psi = fn(n, l, m_l, m_s)$

for a given value of n,

l = 0, 1, 2, 3, … n-1共有n個

n = 1, l = 0
n = 2, l = 0 **or** 1
n = 3, l = 0, 1, **or** 2

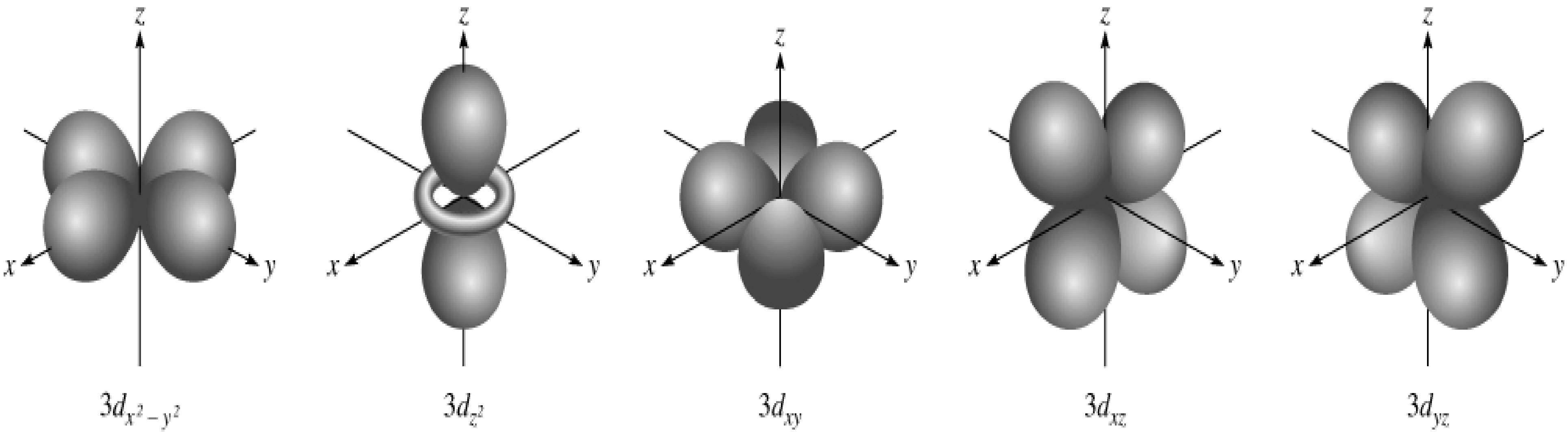
l = 0	s orbital	sharp
l = 1	p orbital	pricipal
l = 2	d orbital	diffuse
l = 3	f orbital	fundamental

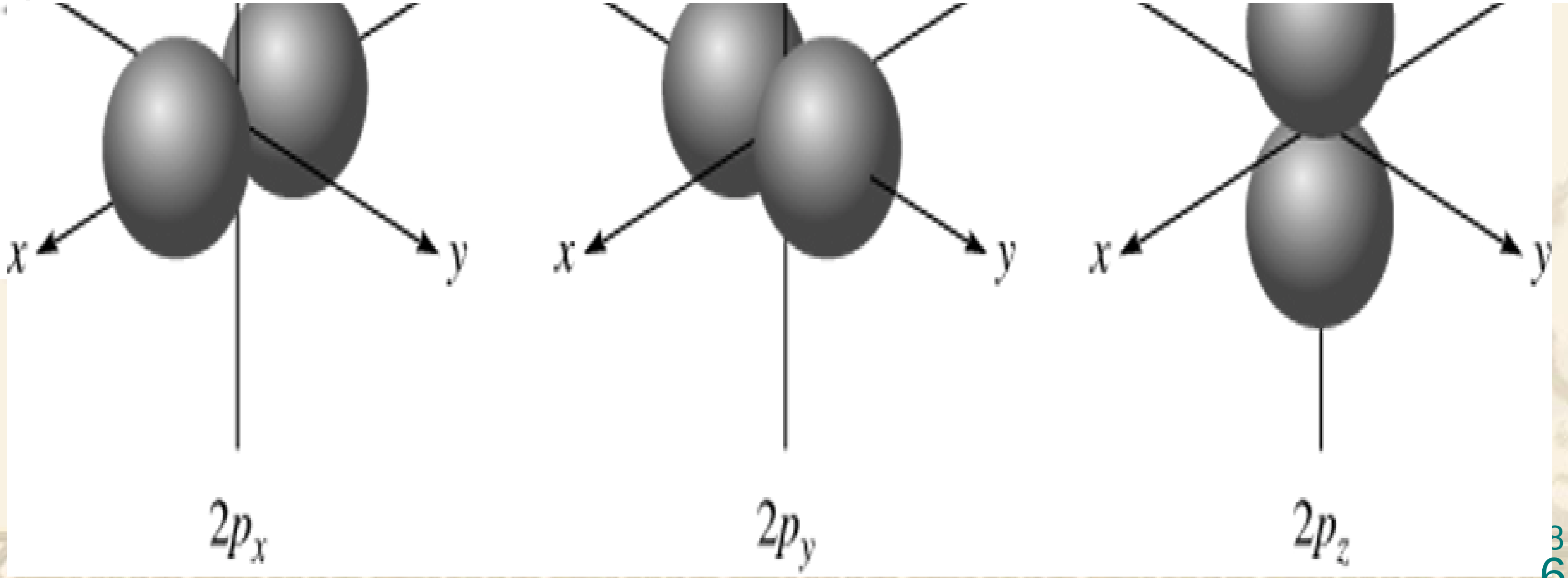
Shape of the “volume” of space that the e^- occupies

ns < np < nd < nf

l = 2 (d orbitals)

l = 0 (s orbitals)





Third Quantum Number 磁量子數 (magnetic quantum number) m_l **(Orbitals)**

Schrodinger Wave Equation

Ψ = fn(n, l, m_l, m_s)

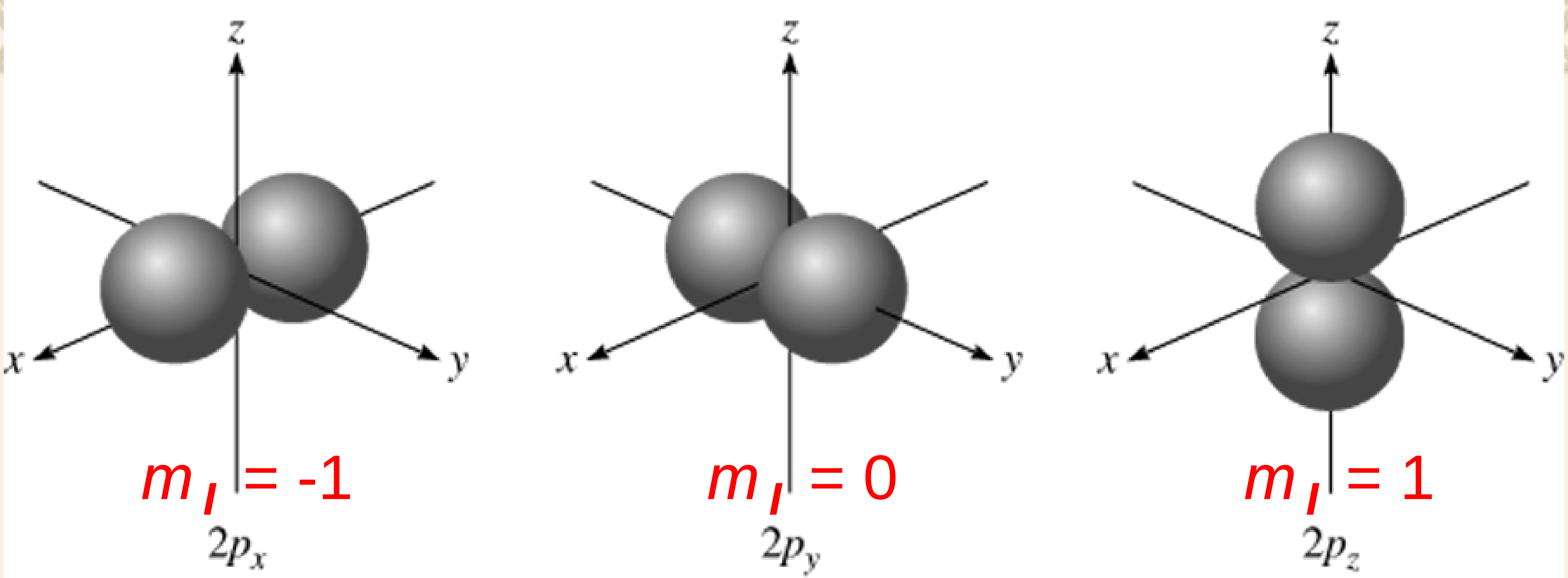
for a given value of l

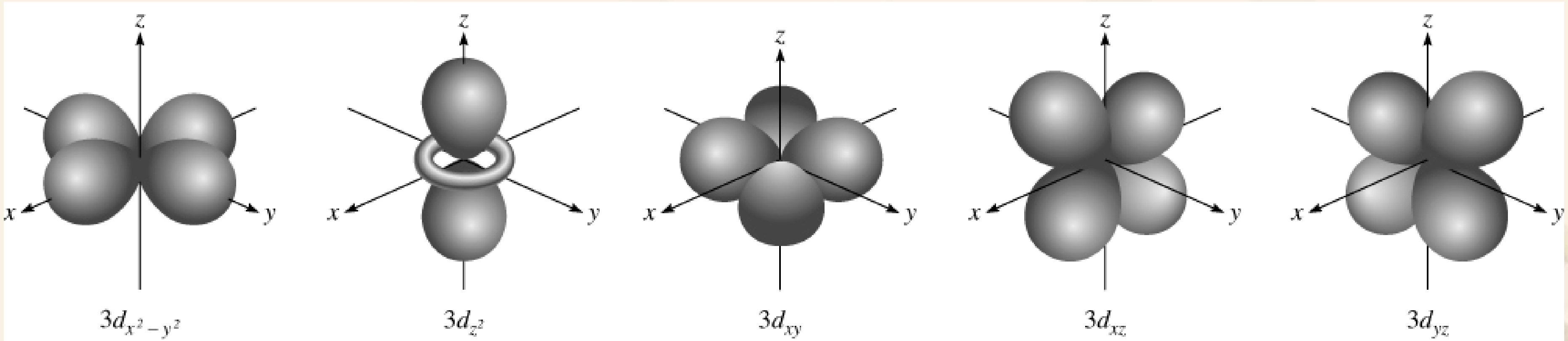
$m_l = -l, \ldots, 0, \ldots +l$

if l = 1 (p orbital), m_l = -1, 0, **or** 1

if l = 2 (d orbital), m_l = -2, -1, 0, 1, **or** 2

orientation of the orbital in space





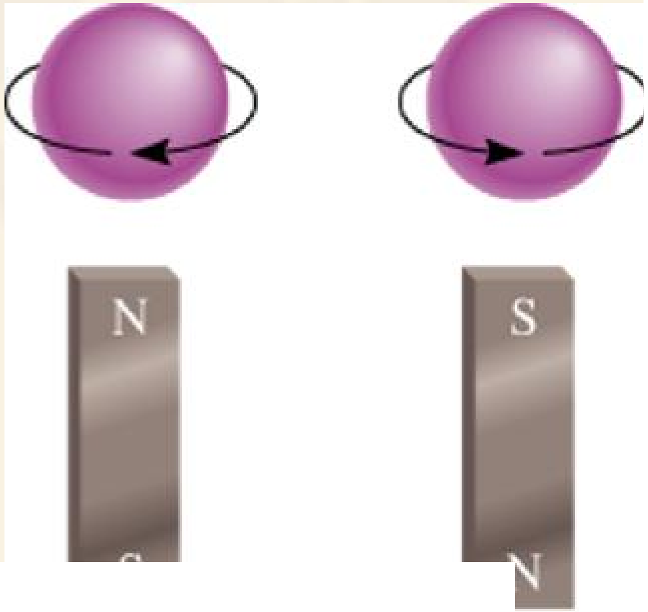
m_l = -2 m_l = -1 m_l = 0 m_l = 1 m_l = 2

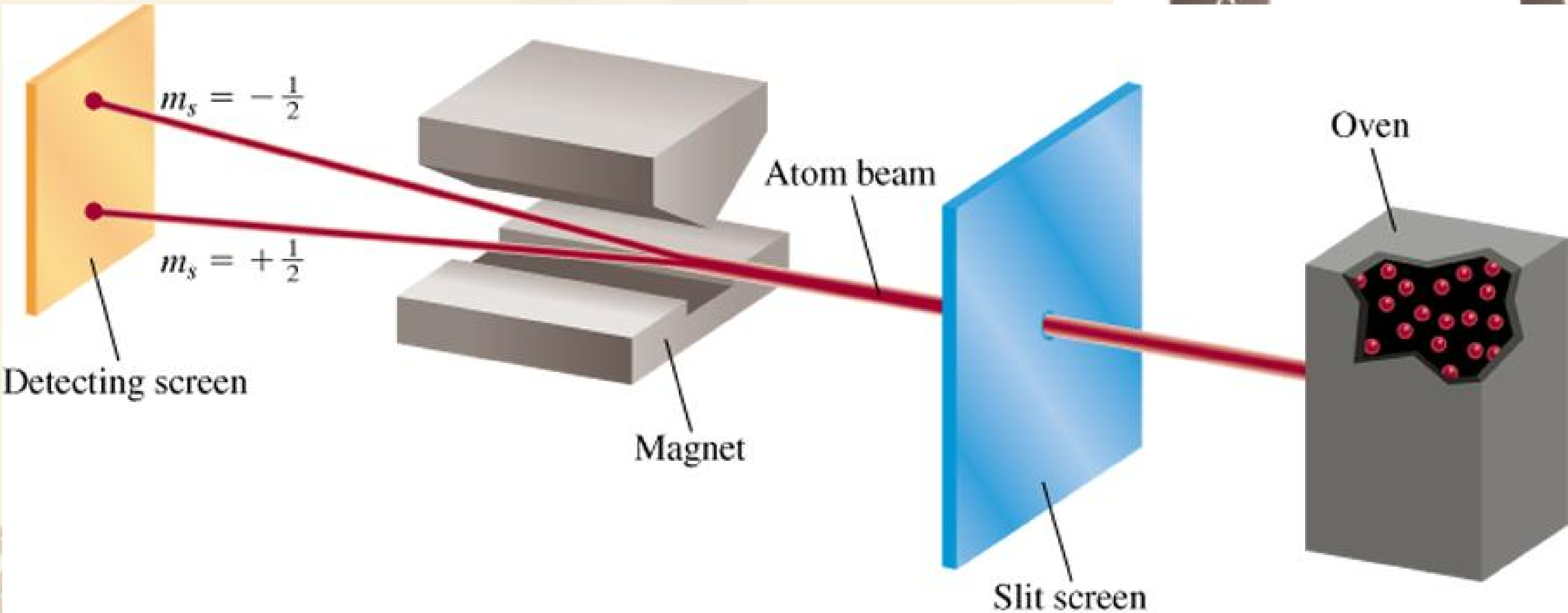
Fourth Quantum Number旋量子數 (spin quantum number) m_s

Schrodinger Wave Equation

$\Psi = fn(n, \ \boldsymbol{l}, m_l, m_s)$ Electron Spin

$m_s = +½$ **or** $-½$





6.3

2.Pauli exclusion principle (庖立不相容原理)

- No two electrons in an atom can have the same set of four quantum numbers.
- (一個原子中的任二個電子不能同時存在兩組完全相同的四種量子數。)
- If two electrons occupy the same orbital, they must gave opposed spins.

Each seat is uniquely identified (E, R12, S8)
Each seat can hold only one individual at a time

Ex6.4: consider the following sets of quantum numbers (n,l,ml,ms) Which ones could not occur? For the valid sets, identify the orbital involved.

(a) (3,1,0,+1/2)

(b) (1,1,0,-1/2)

(c) (2,2,0,+1/2)

(d) (4,3,2,+1/2)

(e) (2,1,0,0)

Ex6.5: (A) What is the capacity for electrons of an S sublevel? A d sublevel ? f sublevel?

(B) What is the total capacity for electrons of the fourth principal level?

SOL:

(a) s sublevel: 1orbital $\times 2e^-$/ orbital=$2e^-$

p sublevel: 3orbital $\times 2e^-$/ orbital=$6e^-$

d sublevel: 5orbital $\times 2e^-$/ orbital=$10e^-$

f sublevel: 7orbital $\times 2e^-$/ orbital=$14e^-$

(b) $2e^-$(4s)+ $6e^-$(4p)+ $10e^-$(4d)+ $14e^-$(4f)=$32e^-$

電子在原子中可能的量子數組

Relation Between Quantum Numbers and Atomic Orbitals

v table.pdf

n	ℓ	m_ℓ	Number of Orbitals	Atomic Orbital Designations
1	0	0	1	$1s$
2	0	0	1	$2s$
	1	−1, 0, 1	3	$2p_x$, $2p_y$, $2p_z$
3	0	0	1	$3s$
	1	−1, 0, 1	3	$3p_x$, $3p_y$, $3p_z$
	2	−2, −1, 0, 1, 2	5	$3d_{xy}$, $3d_{yz}$, $3d_{xz}$, $3d_{x^2-y^2}$, $3d_{z^2}$
⋮	⋮	⋮	⋮	⋮

主層、次層與軌域的容納量

- 量子數n的每一主層包含了n個次層。共$2n^2$個電子。
- 量子數 l 的每一次層包含了總數2 l +1個軌域；共有2(2 l +1)個電子。
  - 一個s次層(l =0)包含1個軌域
  - 一個p次層(l =1)包含3個軌域
  - 一個d次層(l =2)包含5個軌域
  - 一個f次層(l =3)包含7個軌域
- 任何一個軌域最多僅能容納2個電子，且旋轉的方向必須是相反的。

Schrodinger Wave Equation

$\Psi = \text{fn}(n, l, m_l, m_s)$

Shell – electrons with the same value of *n*

Subshell – electrons with the same values of *n* **and** *l*

Orbital – electrons with the same values of *n, l,* **and** m_l

How many electrons can an orbital hold?

If *n, l,* and m_l are fixed, then m_s = ½ or - ½

$\Psi = (n, l, m_l, \frac{1}{2})$ or $\Psi = (n, l, m_l, -\frac{1}{2})$

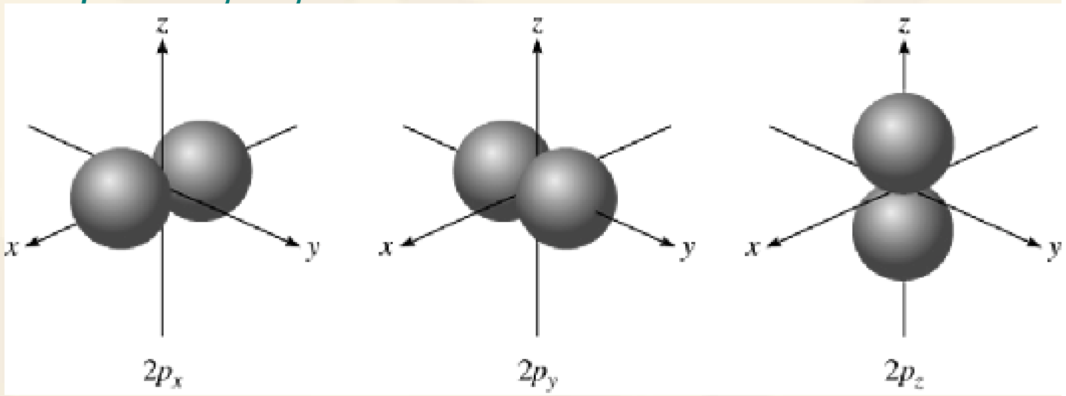
An orbital can hold 2 electrons

How many 2p orbitals are there in an atom?

n=2 ↓ 2p ↑ *l* = 1

If *l* = 1, then m_l = -1, 0, or +1

3 orbitals



How many electrons can be placed in the 3d subshell?

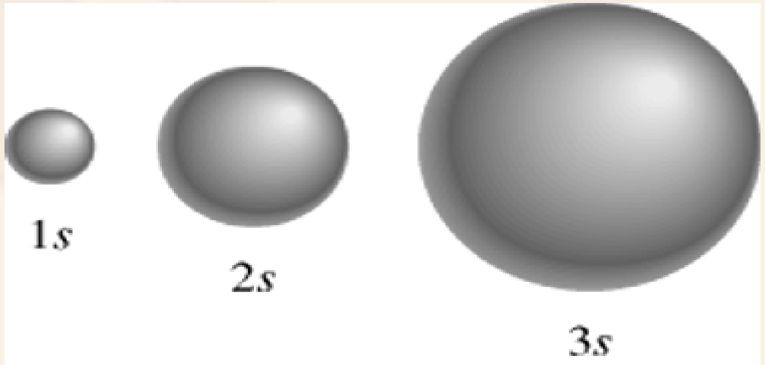
n=3 ↓ 3d ↑ *l* = 2

If *l* = 2, then m_l = -2, -1, 0, +1, or +2

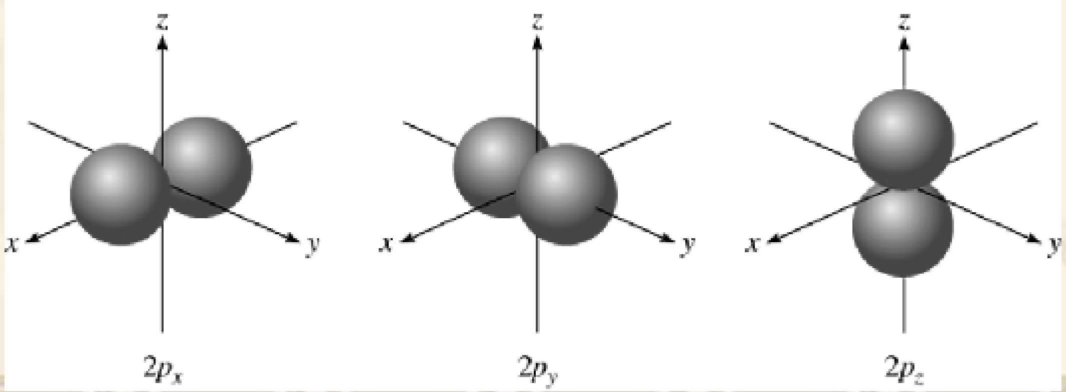
5 orbitals which can hold a total of 10 e^-

6.4 Atom orbitals ;Shapes and sizes

They differ from one another only in size .As n increases, the radius of the orbital becomes larger.



A P orbital consists of two lobes along an axis (x,y,z) , there is zero probability of finding an electron at the origin , at the nucleus or the atom.



6.5 Electron configurations in Atoms

Shows the number of electrons, indicated by a superscript, in each sublevel. **電子組態** 用以描述原子中電子的排列情形，將每一層的電子數呈現在該次層的右上角。

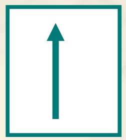
在軌域或次層的電子數

$1s^1$

主量子數 ***n***　　　　角動量量子數 ***l***

Orbital diagram

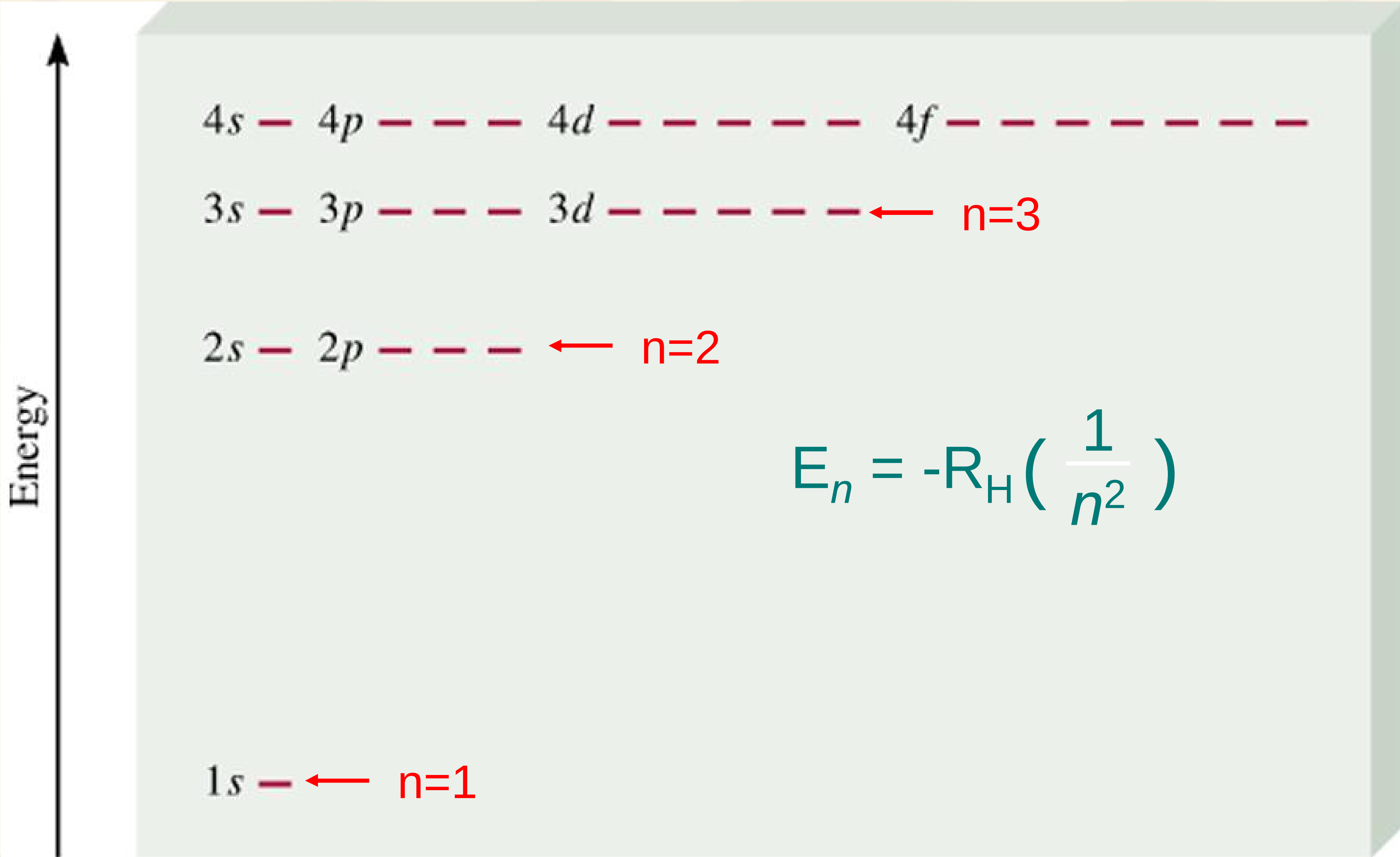
H



$1s^1$

Single electron orbital energy level

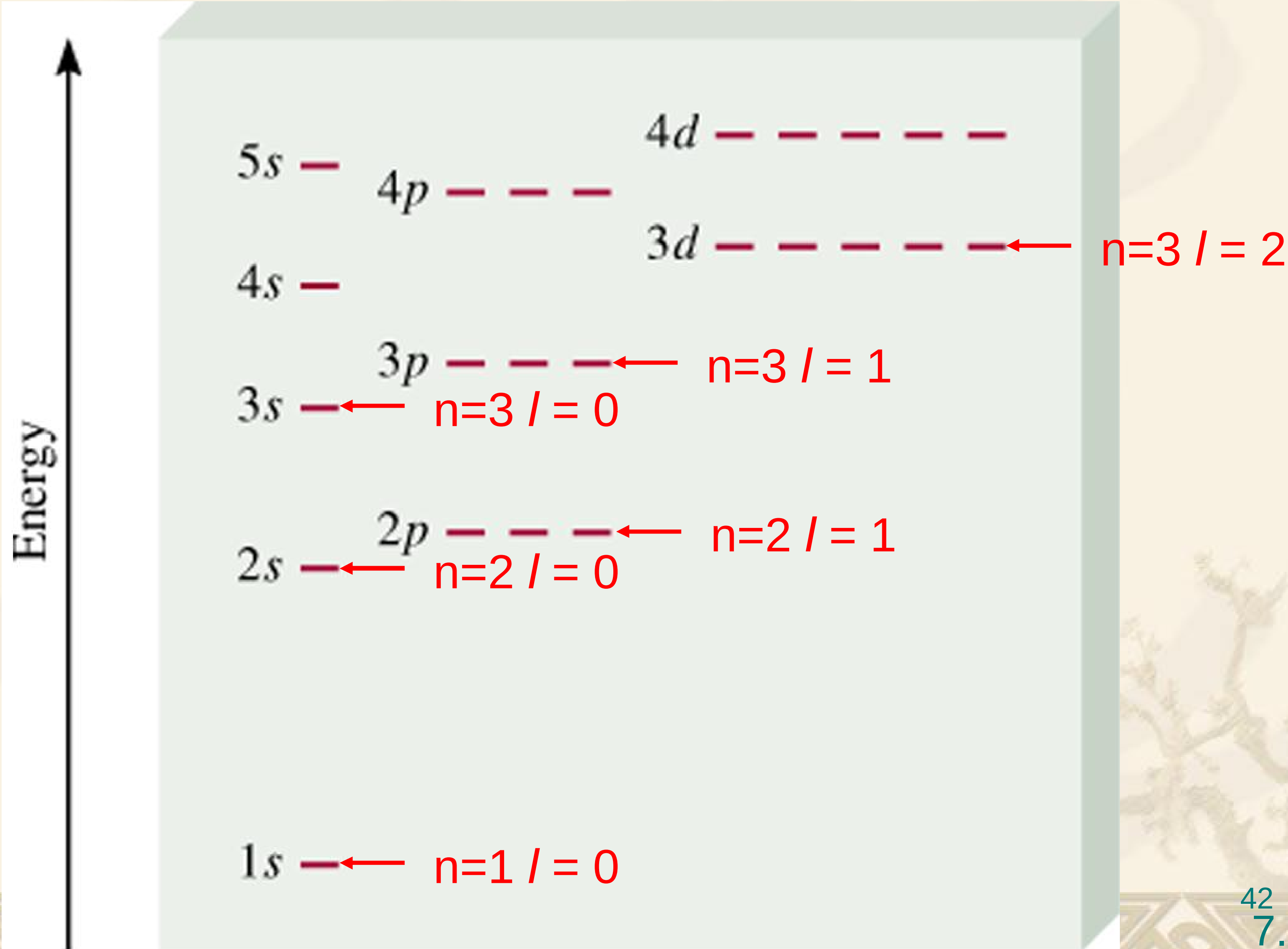
能階由主量子數***n***決定



$$E_n = -R_H\left(\frac{1}{n^2}\right)$$

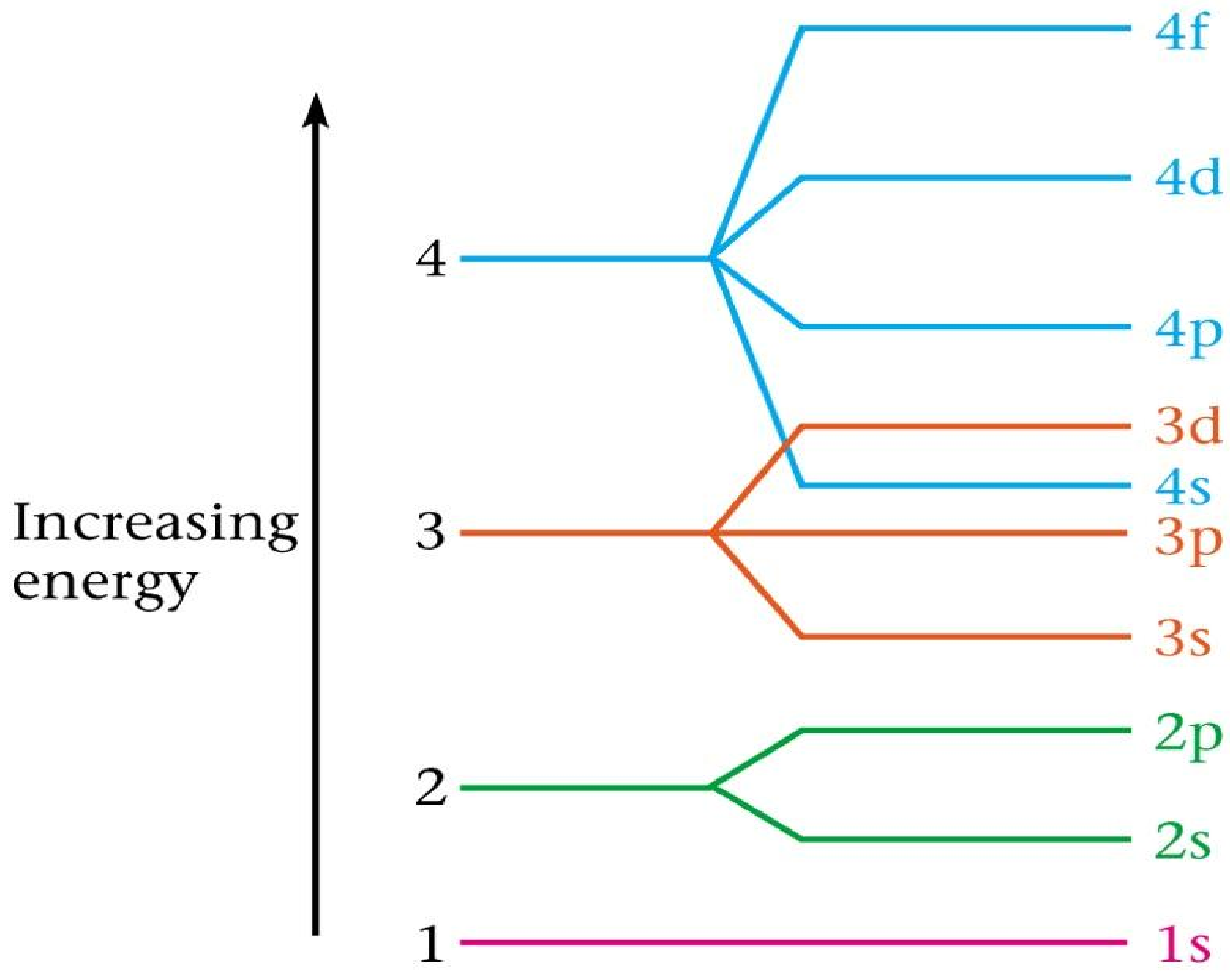
多電子原子的軌域能階

能階由***n*** 及 ***l*** 決定

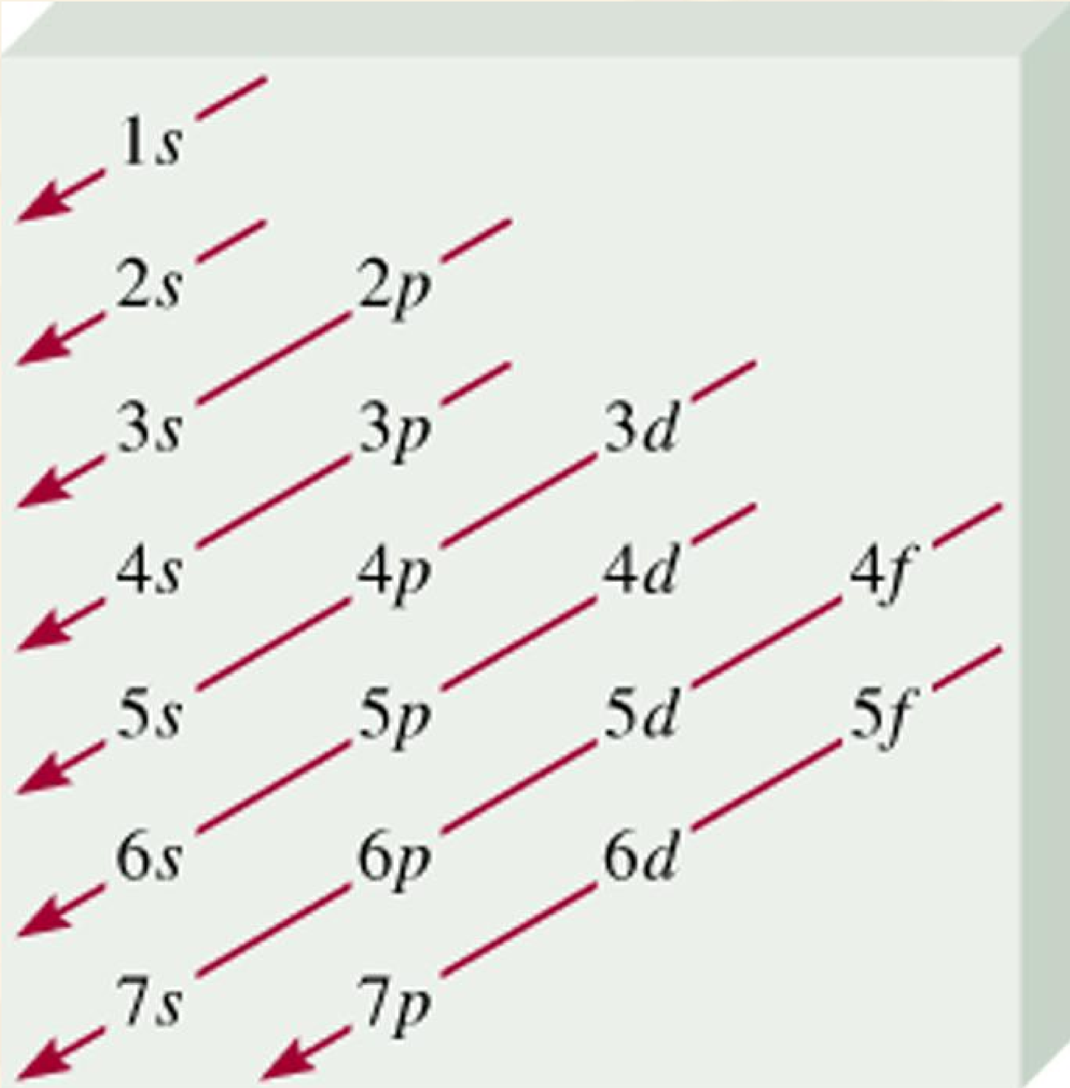


7.7

Fig 6.8Electron energy sublevels in the order of increasing energy.



Order of orbitals (filling) in multi-electron atom



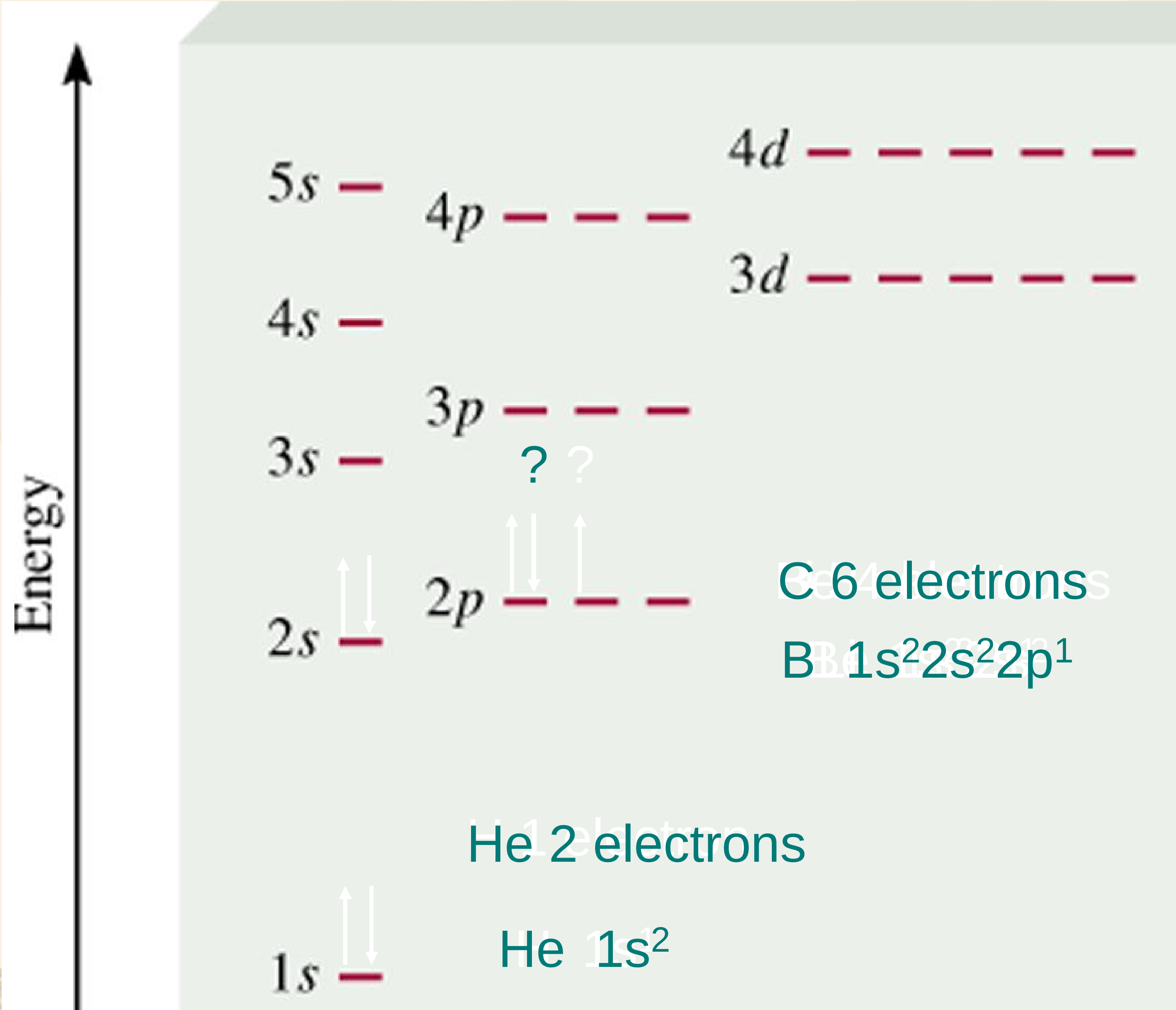
1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s

6.4

原子基態的電子組態遵循原則

- 構築原理
  - 電子進入軌域的順序由低能階開始
- 庖立不相容原理
  - 不個軌域內最多只能容納兩個電子，且在同一軌域內的兩個電子自旋方向必相反。
- 韓德法則(Hund's rule)
  - 整個電子要填入同能階的同型軌域(如2Px, 2Py, 2Pz)時，必須先以相同自旋方式填入不同方位的軌域而不成對，等各軌域均有一個電子時，才能填入自旋方式相反的電子進入而成對。

"Fill up" electrons in lowest energy orbitals (***Aufbau principle***)



? ?

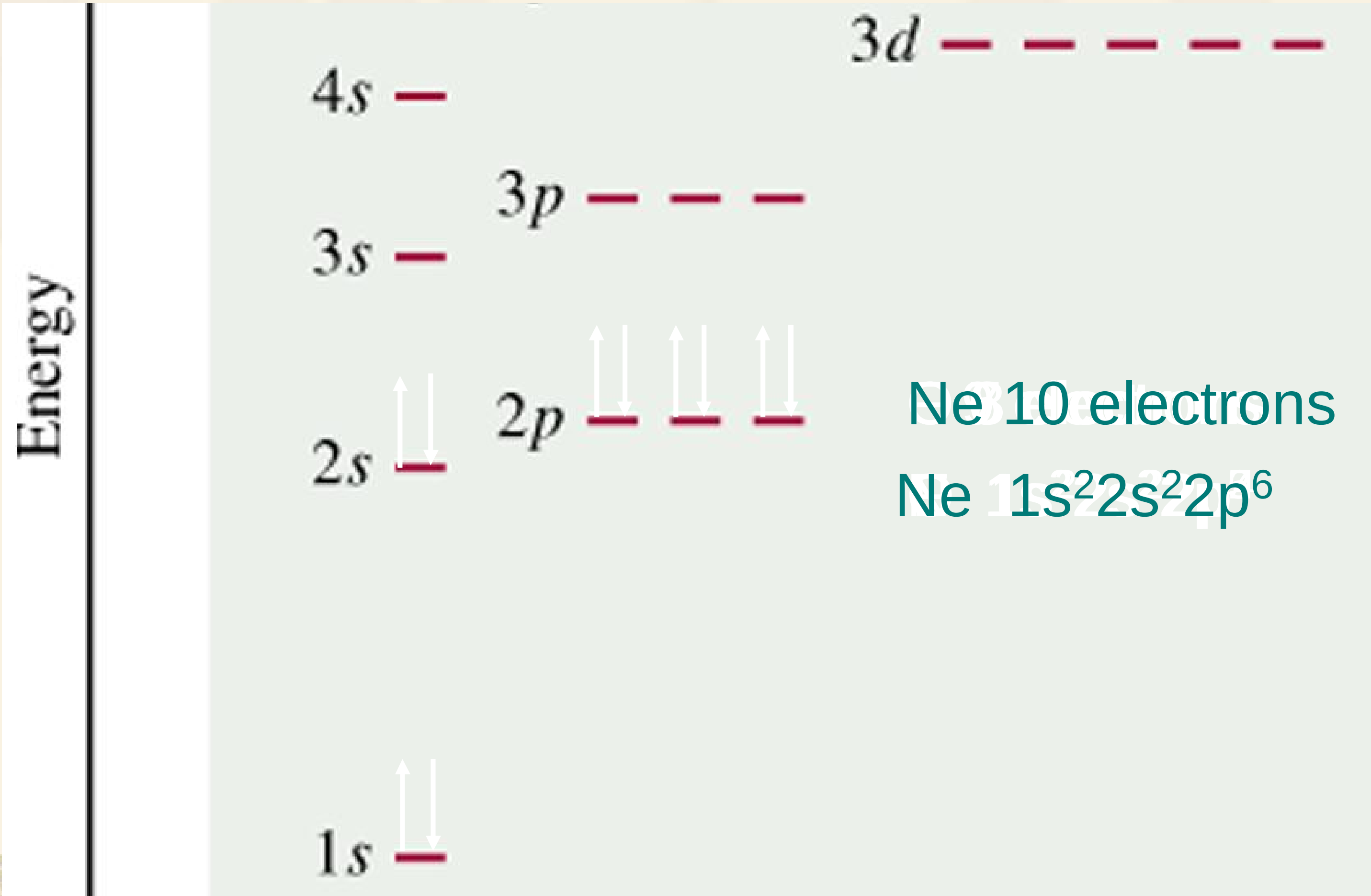
C 6 electrons

B $1s^2 2s^2 2p^1$

He 2 electrons

He $1s^2$

The most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins (***Hund's rule***).



Ne 10 electrons

Ne $1s^2 2s^2 2p^6$

Ex6.6:Find the electron configurations of the sulfur (S) and (Ni) atoms?

S 16 electrons

1s < 2s < 2p < 3s < 3p < 4s

$1s^2 2s^2 2p^6 3s^2 3p^4$ 2 + 2 + 6 + 2 + 4 = 16 electrons

abbreviate $[Ne]3s^2 3p^4$ $[Ne]\ 1s^2 2s^2 2p^6$

Ni 28 electrons

1s < 2s < 2p < 3s < 3p < 4s < 3d

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$ 2+2+6+2+2+6+2+8 = 28 electrons

abbreviate $[Ar]4s^2 3d^8$ $[Ar]\ 1s^2 2s^2 2p^6 3s^2 3p^6$

What is the electron configuration of Mg?

Mg 12 electrons

1s < 2s < 2p < 3s < 3p < 4s

$1s^2 2s^2 2p^6 3s^2$ 2 + 2 + 6 + 2 = 12 electrons

Abbreviated as $[Ne]3s^2$ $[Ne]$ $1s^2 2s^2 2p^6$

What are the possible quantum numbers for the last (outermost) electron in Cl?

Cl 17 electrons 1s < 2s < 2p < 3s < 3p < 4s

$1s^2 2s^2 2p^6 3s^2 3p^5$ 2 + 2 + 6 + 2 + 5 = 17 electrons

Last electron added to 3p orbital

$n = 3$ $l = 1$ $m_l = -1, 0, \text{or} +1$ $m_s = ½ \text{ or } -½$

Ex6.7:Find the iodine atom. write

(a) The electron configurations (b) the abbreviated electron configuration.

(a) I 53 electrons

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^5$

2 + 2 + 6 + 2 + 6 + 2 + 10 + 6 + 2 + 10 + 5 = 53 electrons

[Kr] $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$

(b) Abbreviate electron configuration [Kr]$5s^2 4d^{10} 5p^5$

Filling of Sublevels and the Periodic Table

- The atoms of elements in a group of the periodic table have the same distribution of electrons in the outermost principal energy level.

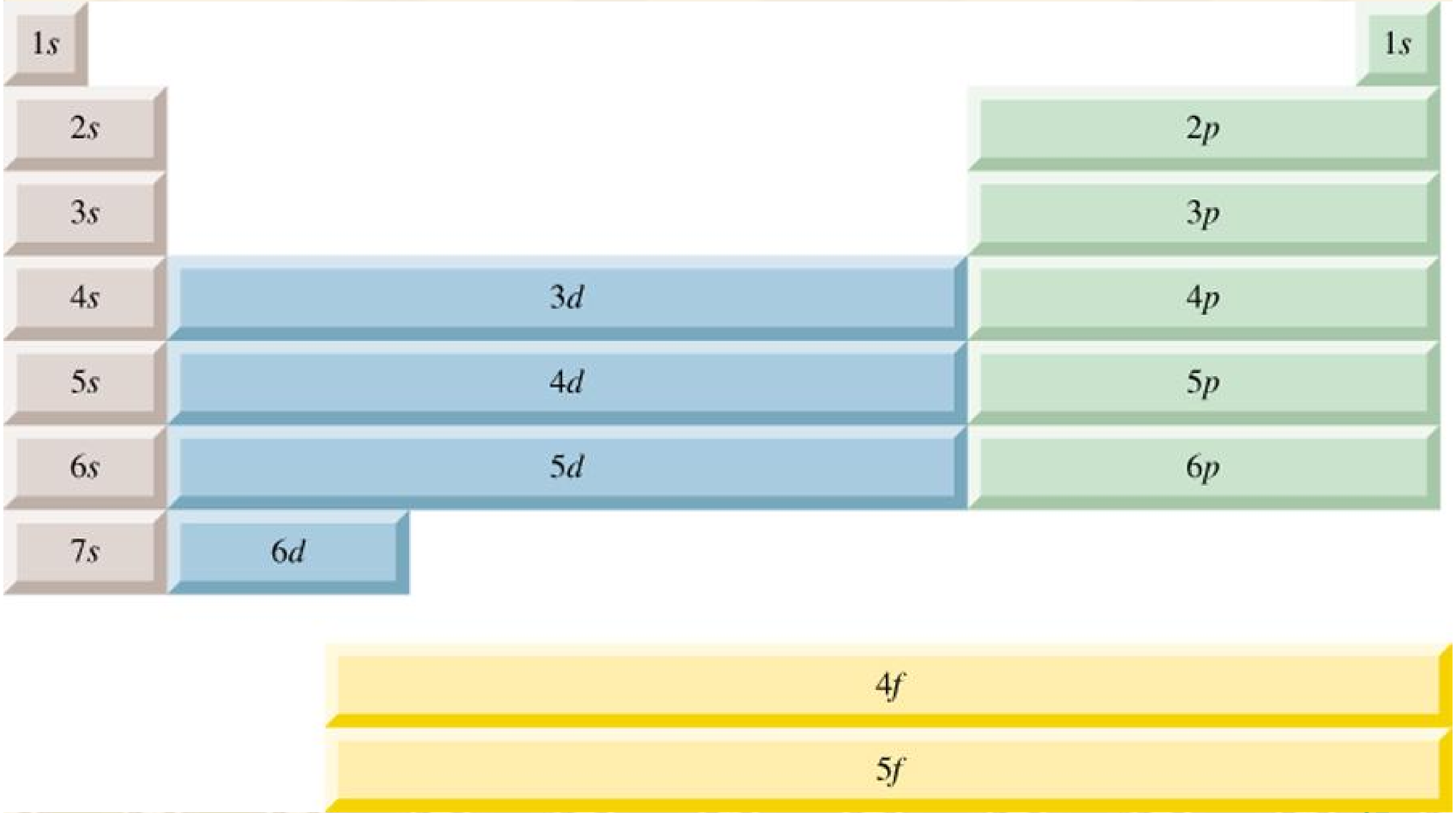
(1) The elements in groups 1 and 2 are filling an s sublevel.

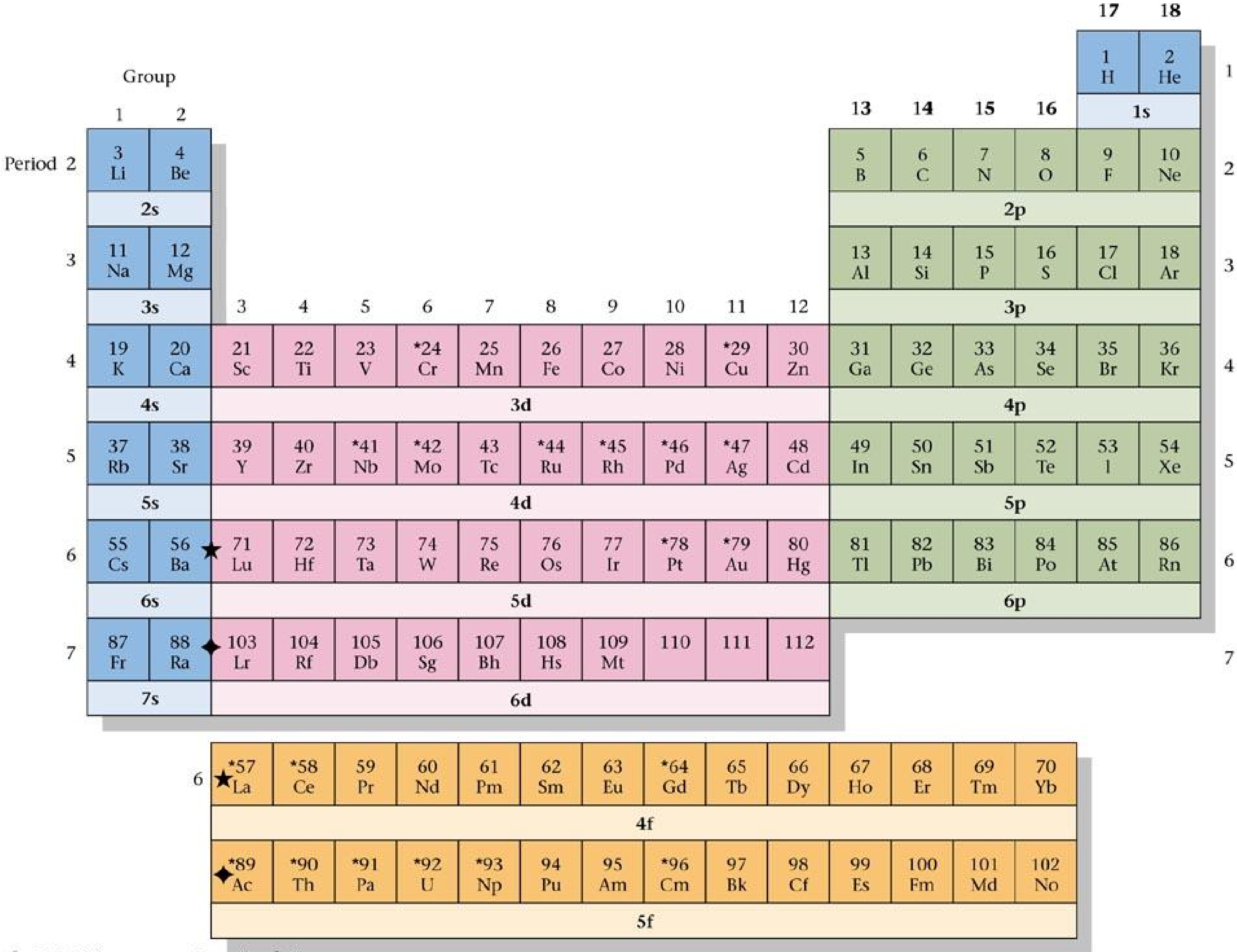
(2) The elements in groups 13 through 18 fill p sublevels.

(3) The transition metals, in the center of the periodic table , fill d sublevels.

(4) The two sets of 14 elements listed separately at the bottom of the table are filling f sublevels with a principal quantum number two less than the period number.

Outermost sub shell being filled with electrons




Group
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
Period
1 H 2 He
1s
3 Li 4 Be
2s
5 B 6 C 7 N 8 O 9 F 10 Ne
2p
11 Na 12 Mg
3s
13 Al 14 Si 15 P 16 S 17 Cl 18 Ar
3p
19 K 20 Ca
4s
21 Sc 22 Ti 23 V *24 Cr 25 Mn 26 Fe 27 Co 28 Ni *29 Cu 30 Zn
3d
31 Ga 32 Ge 33 As 34 Se 35 Br 36 Kr
4p
37 Rb 38 Sr
5s
39 Y 40 Zr *41 Nb *42 Mo 43 Tc *44 Ru *45 Rh *46 Pd *47 Ag 48 Cd
4d
49 In 50 Sn 51 Sb 52 Te 53 I 54 Xe
5p
55 Cs 56 Ba
6s
71 Lu 72 Hf 73 Ta 74 W 75 Re 76 Os 77 Ir *78 Pt *79 Au 80 Hg
5d
81 Tl 82 Pb 83 Bi 84 Po 85 At 86 Rn
6p
87 Fr 88 Ra
7s
103 Lr 104 Rf 105 Db 106 Sg 107 Bh 108 Hs 109 Mt 110 111 112
6d
*57 La *58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu *64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb
4f
*89 Ac *90 Th *91 Pa *92 U *93 Np 94 Pu 95 Am *96 Cm 97 Bk 98 Cf 99 Es 100 Fm 101 Md 102 No
5f

特例

- 3d and4s orbitals have very similar energies. it has been suggested that there is a slight increase in stability with a half- filled (Cr) or completely filled (cu)3d sublevel.
- 因此半滿或全滿的3d次層可稍微的提高穩定度。

Cu 29 electrons

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p

~~$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$~~ **error**

2 + 2 + 6 + 2 + 6 + 2 + 9 = 29 electrons

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

Abbreviated electron configuration $[Ar]4s^1 3d^{10}$

Cr 24 electrons

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p

~~$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$~~ **error**

2 + 2 + 6 + 2 + 6 + 2 + 4 = 24 electrons

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

Abbreviated electron configuration $[Ar]4s^1 3d^5$

6.6 Orbital diagrams of atoms

- It is useful to go a step further and show how electrons are distribute among orbitals.
- Orbital diagrams each orbital is represented by ( ),and electrons are shown by arrows written(↑) ,or (↓) ,depending on spin.

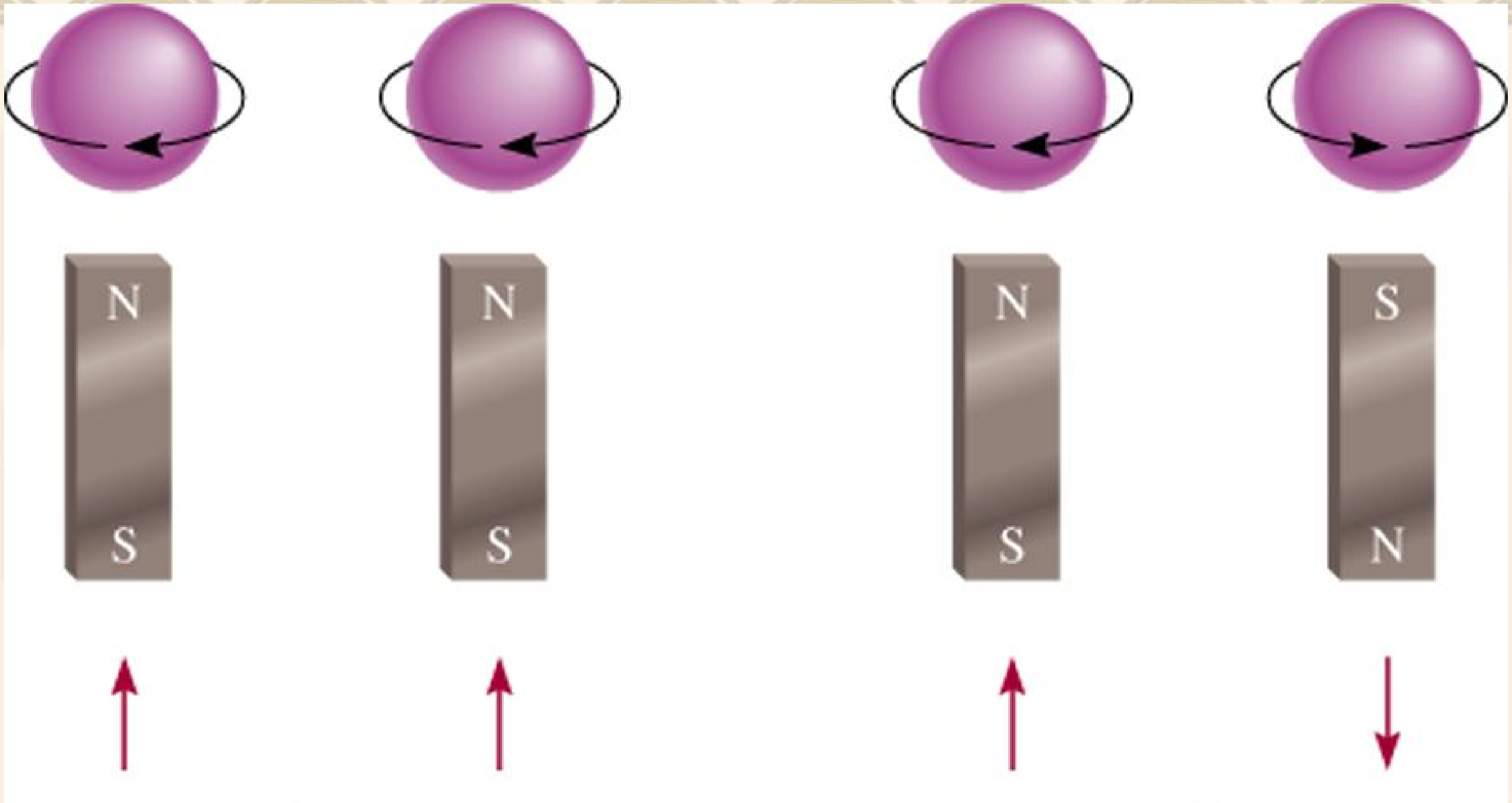
Atom	Orbital diagram 1s	2s	2p			Electron configuration
B	↑↓	↑↓	↑			$1s^2 2s^2 2p^1$
C	↑↓	↑↓	↑	↑		$1s^2 2s^2 2p^2$
N	↑↓	↑↓	↑	↑	↑	$1s^2 2s^2 2p^3$
O	↑↓	↑↓	↑↓	↑	↑	$1s^2 2s^2 2p^4$
F	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p^5$
Ne	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2 2s^2 2p^6$

Hund’s rule 韓德法則

- When several orbitals of equal energy are available, as in a given sublevel, electrons enter singly with parallel spin.
- Hund’s rule is based on experiment.

Notice

- 1.In all filled orbitals , the two electrons have opposed spins.
- 2. In accordance with Hund’s rule , within a given sublevel there are as many half filled orbitals as possible.



順磁*Paramagnetic*

unparied electrons

↑ ↑ _

2p

逆磁Diamagnetic

all electrons paired

↑↓ ↑↓ ↑↓

2p

- Paramagnetic順磁
  - 當電子自旋相為↑↑或↓↓時，則兩電子的淨磁場會加強而呈順磁。即可被磁鐵吸引的物質

- Diamagnetic逆磁
  - 若電子自旋配對為↑↓或↓↑時，則電子的磁效應會相互抵消而呈逆磁。指會受到磁場些微排斥的物質。

Ex6.8:Construct orbital diagrams fro atoms of sulfur and iron atom

S 16 electrons $1s^2 2s^2 2p^6 3s^2 3p^4$

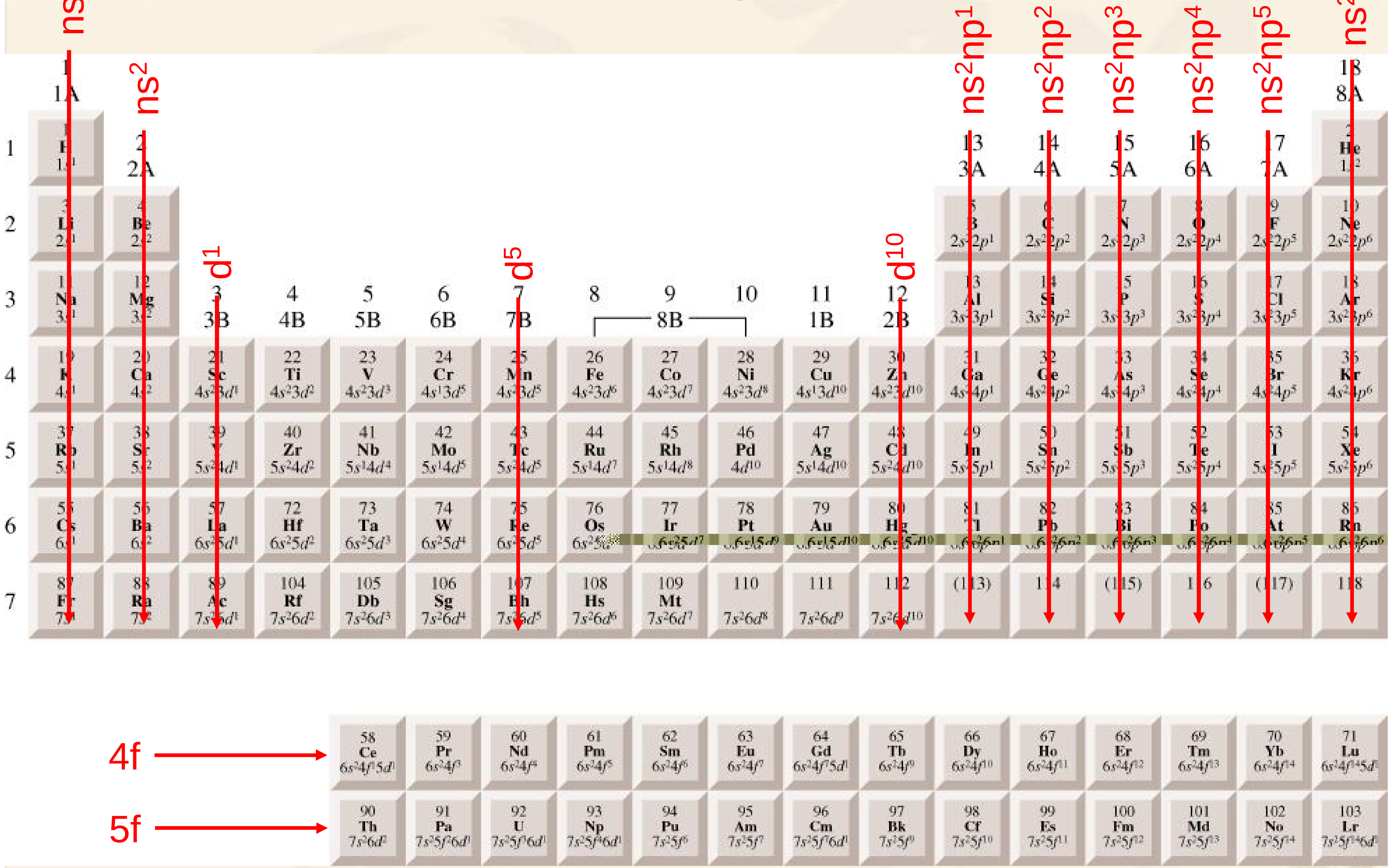
	1s	2s	2p	3s	3p
$_{16}S$	(↑↓)	(↑↓)	(↑↓)(↑↓)(↑↓)	(↑↓)	(↑↓)(↑)(↑)

Fe 26 electrons $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

	1s	2s	2p	3s	3p
$_{26}Fe$	(↑↓)	(↑↓)	(↑↓)(↑↓)(↑↓)	(↑↓)	(↑↓)(↑↓)(↑↓)

4s	3d
(↑↓)	(↑↓)(↑)(↑)(↑)(↑)

Ground State Electron Configurations of the Elements



6.7 Electron arrangements in Monatomic ions

- When a monatomic ion is formed from an atom, electrons are added to or removed from sublevels in the highest principal energy level.

1.Ions with Noble-Gas Structures

- Elements close to a noble gas in the periodic table form ions that have the same number of electrons as the noble- gas atom.
- ${}_{7}N(1s^2 2s^2 2p^3) + 3e^- \rightarrow {}_{7}N^{3-}(1s^2 2s^2 2p^6)$
- ${}_{8}O(1s^2 2s^2 2p^4) + 2e^- \rightarrow {}_{8}O^{2-}(1s^2 2s^2 2p^6)$
- ${}_{9}F(1s^2 2s^2 2p^5) + e^- \rightarrow {}_{9}F^-(1s^2 2s^2 2p^6)$
- ${}_{11}Na(1s^2 2s^2 2p^6 3s^1) \rightarrow {}_{11}Na^+(1s^2 2s^2 2p^6) + e^-$
- ${}_{12}Mg(1s^2 2s^2 2p^6 3s^2) \rightarrow {}_{12}Mg^{+2}(1s^2 2s^2 2p^6) + 2e^-$
- ${}_{13}Al(1s^2 2s^2 2p^6 3s^2 3p^1) \rightarrow {}_{13}Al^{+3}(1s^2 2s^2 2p^6) + 3e^-$

Na^+: [Ne]　　Al^{3+}: [Ne]　　F^-: $1s^2 2s^2 2p^6$ or [Ne]

O^{2-}: $1s^2 2s^2 2p^6$ or [Ne]　　N^{3-}: $1s^2 2s^2 2p^6$ or [Ne]

Na^+, Al^{3+}, F^-, O^{2-}, and N^{3-}與 Ne為等電子(***isoelectronic***)

What neutral atom is isoelectronic with H^- ?

H^-: $1s^2$　　same electron configuration as He

Electron Configurations ***of Cations of Transition Metals***

When a cat ion is formed from an atom of a transition metal, electrons are always removed first from the *ns* orbital and then from the (*n* – 1)*d* orbital's.

Fe: $[Ar]4s^2 3d^6$

Fe^{2+}: $[Ar]4s^0 3d^6$ or $[Ar]3d^6$

Fe^{3+}: $[Ar]4s^0 3d^5$ or $[Ar]3d^5$

Mn: $[Ar]4s^2 3d^5$

Mn^{2+}: $[Ar]4s^0 3d^5$ or $[Ar]3d^5$

Electron Configurations of Cations and Anions Of Representative Elements

Na [Ne]$3s^1$ → Na^+ [Ne]

Ca [Ar]$4s^2$ → Ca^{2+} [Ar]

Al [Ne]$3s^2 3p^1$ → Al^{3+} [Ne]

Atoms lose electrons so that cation has a noble-gas outer electron configuration.

H $1s^1$ → H^- $1s^2$ or [He]

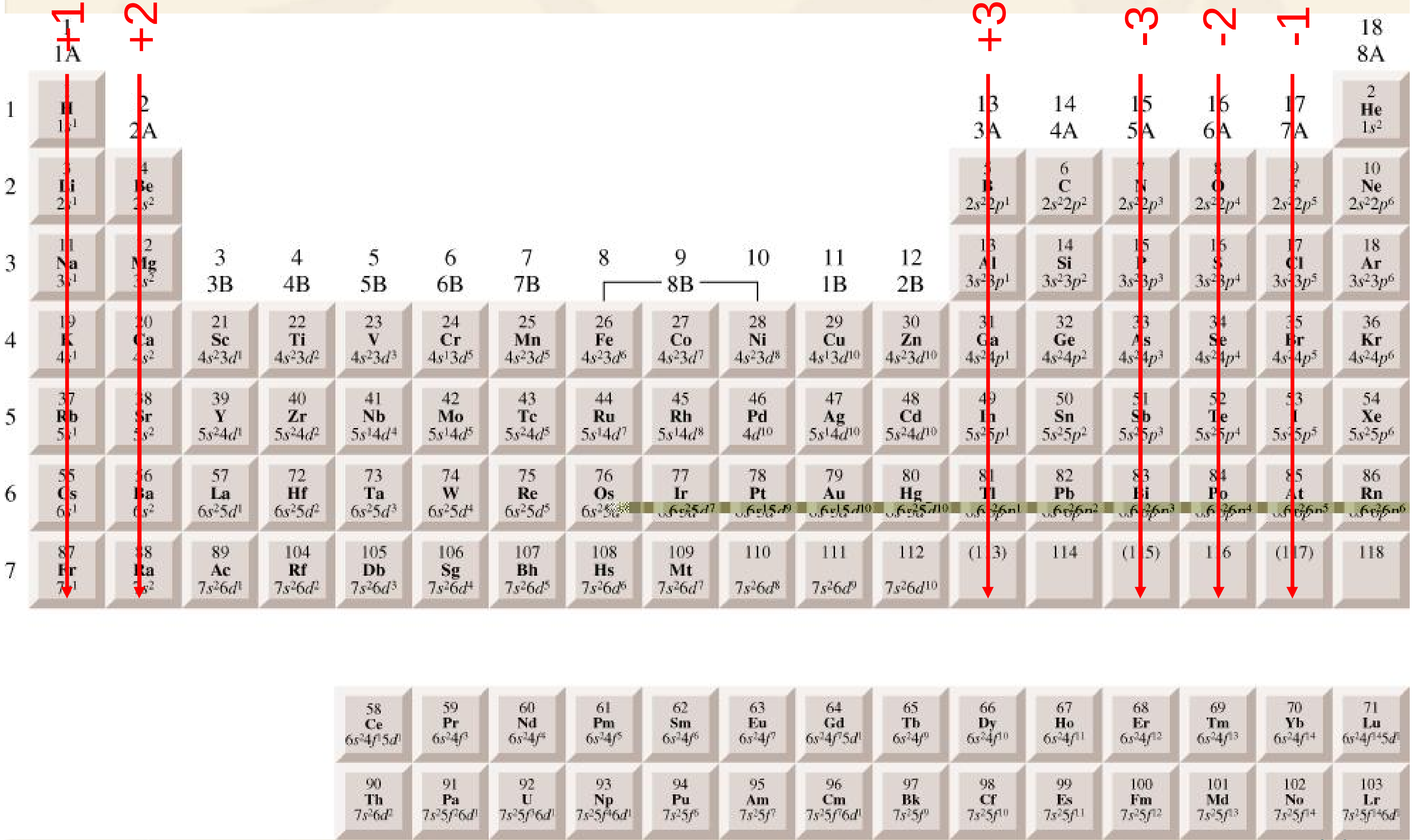
F $1s^2 2s^2 2p^5$ → F^- $1s^2 2s^2 2p^6$ or [Ne]

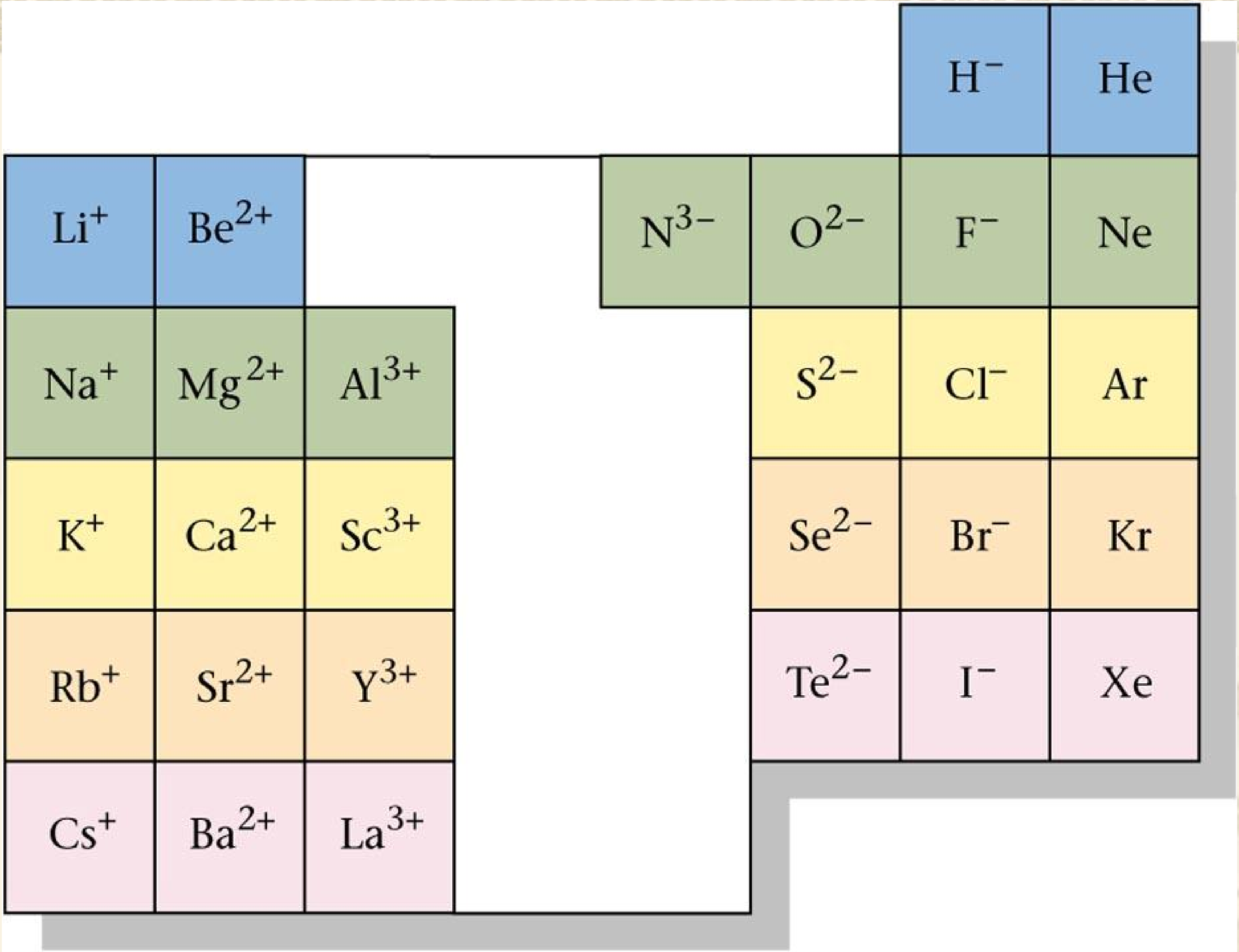
O $1s^2 2s^2 2p^4$ → O^{2-} $1s^2 2s^2 2p^6$ or [Ne]

N $1s^2 2s^2 2p^3$ → N^{3-} $1s^2 2s^2 2p^6$ or [Ne]

Atoms gain electrons so that anion has a noble-gas outer electron configuration.

Cations and Anions Of Representative Elements




H⁻
He
Li⁺
Be²⁺
N³⁻
O²⁻
F⁻
Ne
Na⁺
Mg²⁺
Al³⁺
S²⁻
Cl⁻
Ar
K⁺
Ca²⁺
Sc³⁺
Se²⁻
Br⁻
Kr
Rb⁺
Sr²⁺
Y³⁺
Te²⁻
I⁻
Xe
Cs⁺
Ba²⁺
La³⁺

Example 6.9 Give the electron configuration of

(a) $_{30}Zn^{+2}$

$_{30}Zn$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

$_{30}Zn^{+2}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^{10}$

(b) $_{34}Se^{-2}$

$_{34}Se$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$

$_{34}Se^{-2}$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$

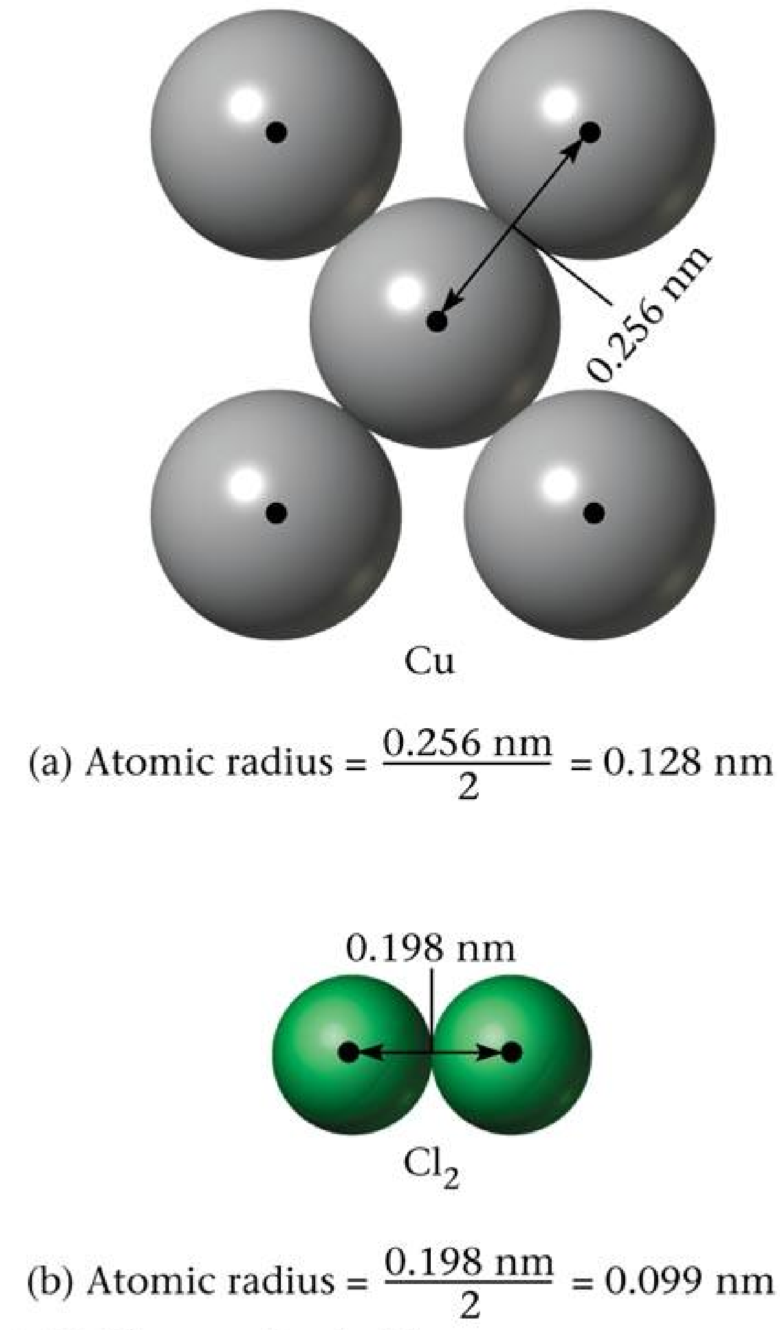
6.8 Periodic tends in the properties of atoms 原子之週期性趨勢

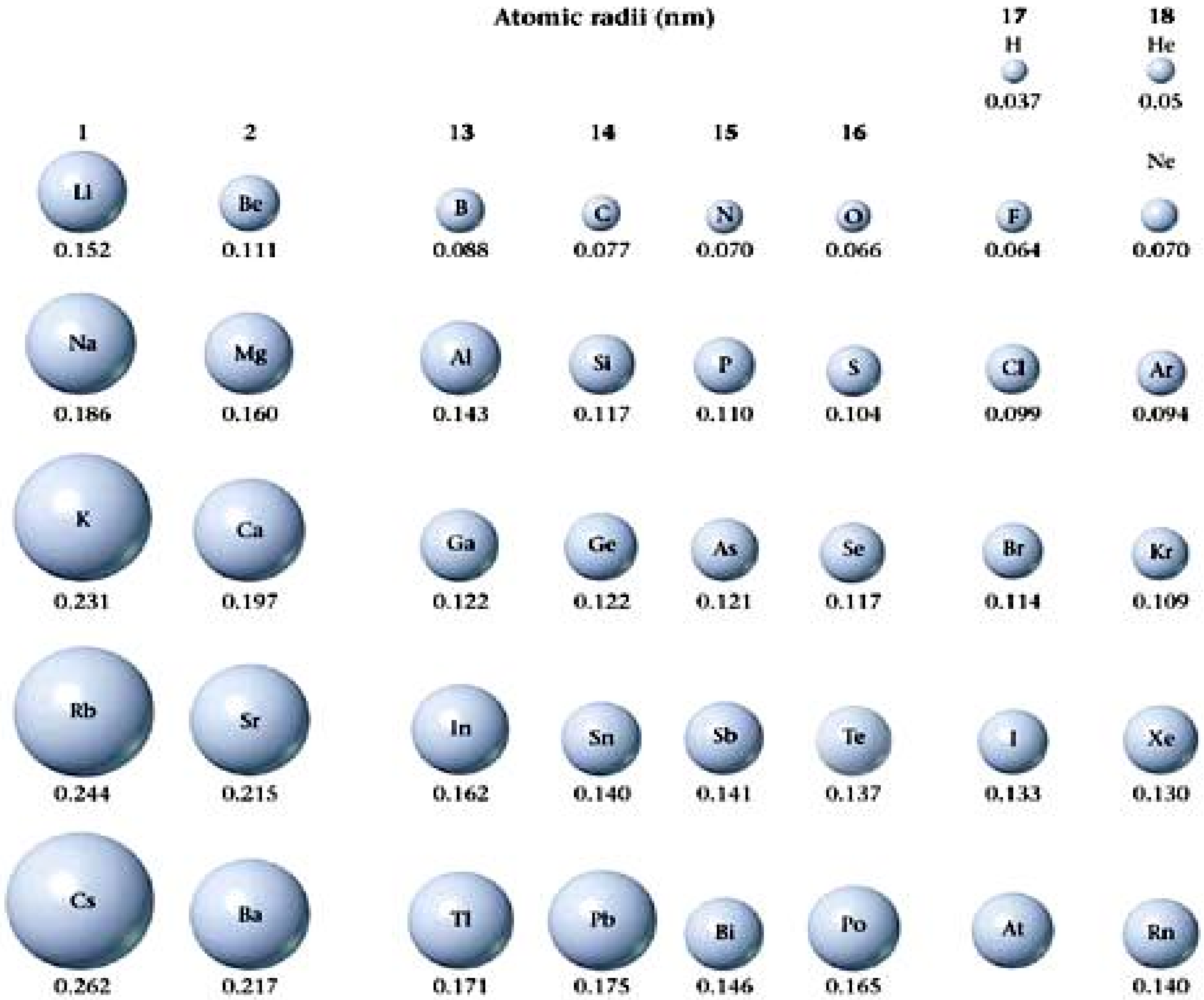
- The chemical and physical properties of elements are a periodic function of atomic number.
- 元素的物理化學性質與原子序週期性有關。
- Elements within a given vertical group resemble one another chemically because chemical properties repeat themselves at regular intervals of 2,8,18,32.

atomic radius

The atomic radius is taken to be one half the distance of closest approach between atoms in an elemental substance.

1. Decrease across a period from left to right in the periodic table.
2. Increase down a group in the periodic table.

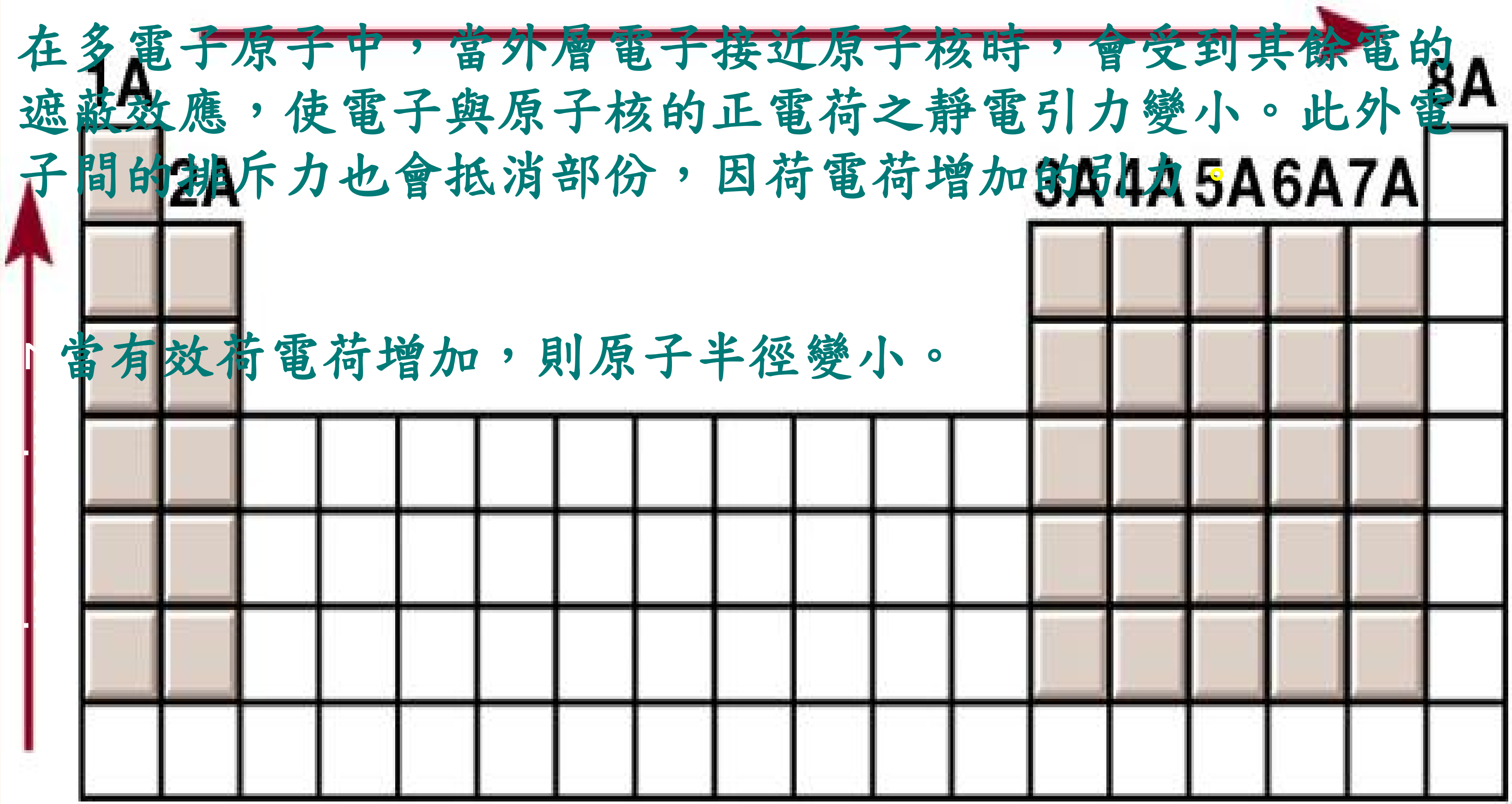


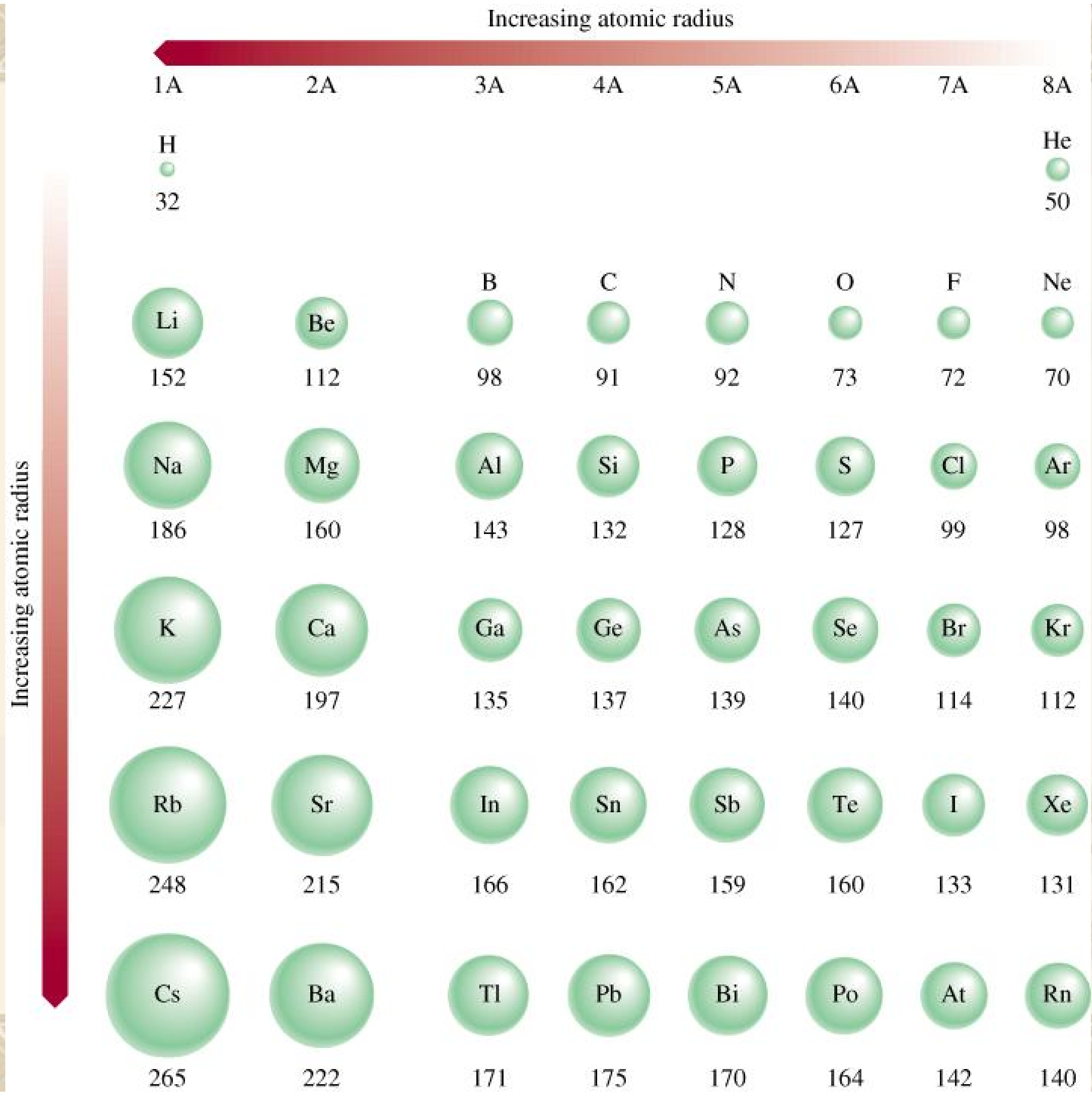

Atomic radii (nm)
17
H
0.037
18
He
0.05
1
2
13
14
15
16
Ne
Li
0.152
Be
0.111
B
0.088
C
0.077
N
0.070
O
0.066
F
0.064
0.070
Na
0.186
Mg
0.160
Al
0.143
Si
0.117
P
0.110
S
0.104
Cl
0.099
Ar
0.094
K
0.231
Ca
0.197
Ga
0.122
Ge
0.122
As
0.121
Se
0.117
Br
0.114
Kr
0.109
Rb
0.244
Sr
0.215
In
0.162
Sn
0.140
Sb
0.141
Te
0.137
I
0.133
Xe
0.130
Cs
0.262
Ba
0.217
Tl
0.171
Pb
0.175
Bi
0.146
Po
0.165
At
Rn
0.140

Effective Nuclear Charge (Z_{eff})

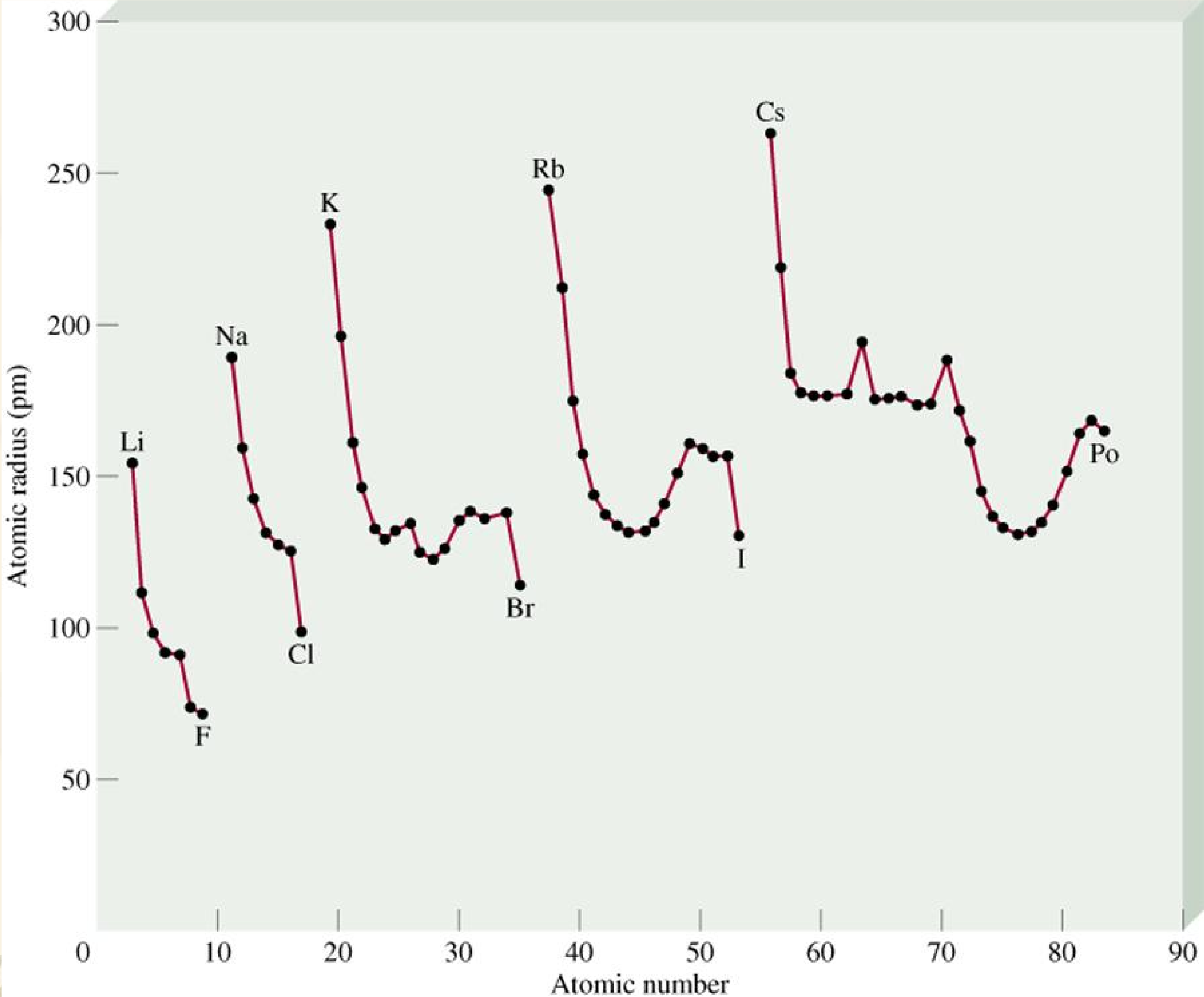
在多電子原子中，當外層電子接近原子核時，會受到其餘電的遮蔽效應，使電子與原子核的正電荷之靜電引力變小。此外電子間的排斥力也會抵消部份，因荷電荷增加的引力。

當有效荷電荷增加，則原子半徑變小。




Increasing atomic radius
1A 2A 3A 4A 5A 6A 7A 8A
H 32
He 50
Li 152
Be 112
B 98
C 91
N 92
O 73
F 72
Ne 70
Na 186
Mg 160
Al 143
Si 132
P 128
S 127
Cl 99
Ar 98
K 227
Ca 197
Ga 135
Ge 137
As 139
Se 140
Br 114
Kr 112
Rb 248
Sr 215
In 166
Sn 162
Sb 159
Te 160
I 133
Xe 131
Cs 265
Ba 222
Tl 171
Pb 175
Bi 170
Po 164
At 142
Rn 140
Increasing atomic radius

Atomic Radii

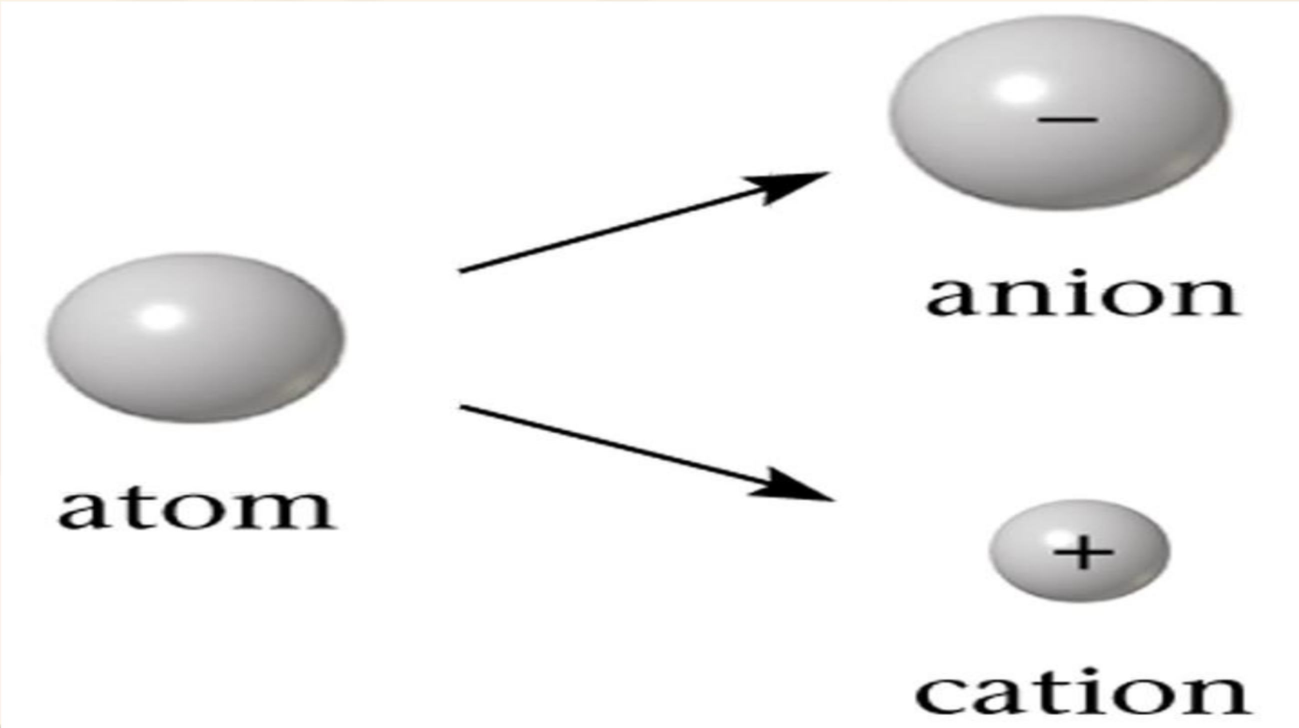


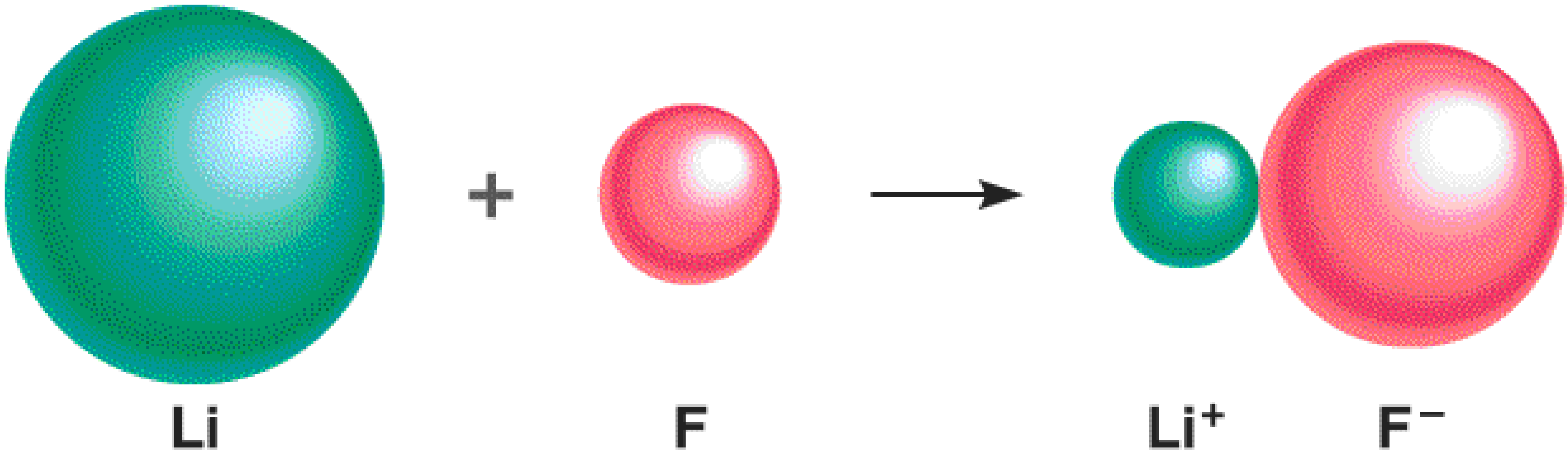
6.7

Ionic Radius

Positive ions are smaller than the metal atoms from which they are formed.

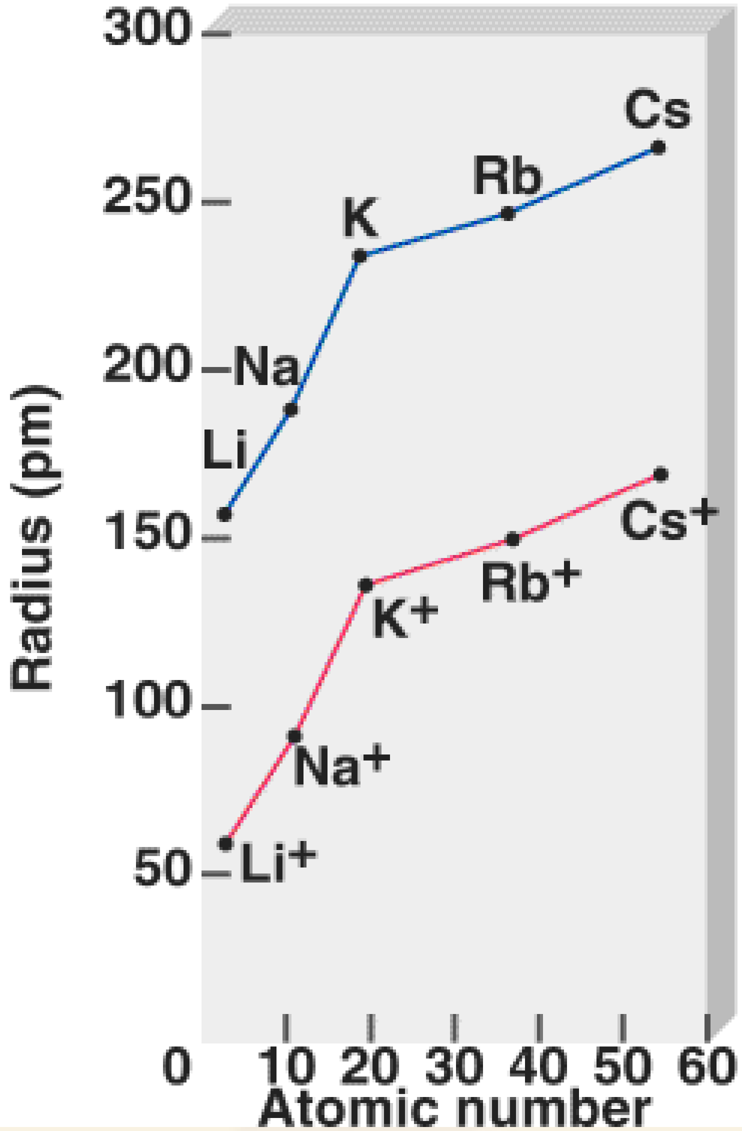
Negative ions are larger than the nonmetal atoms from which they are formed.

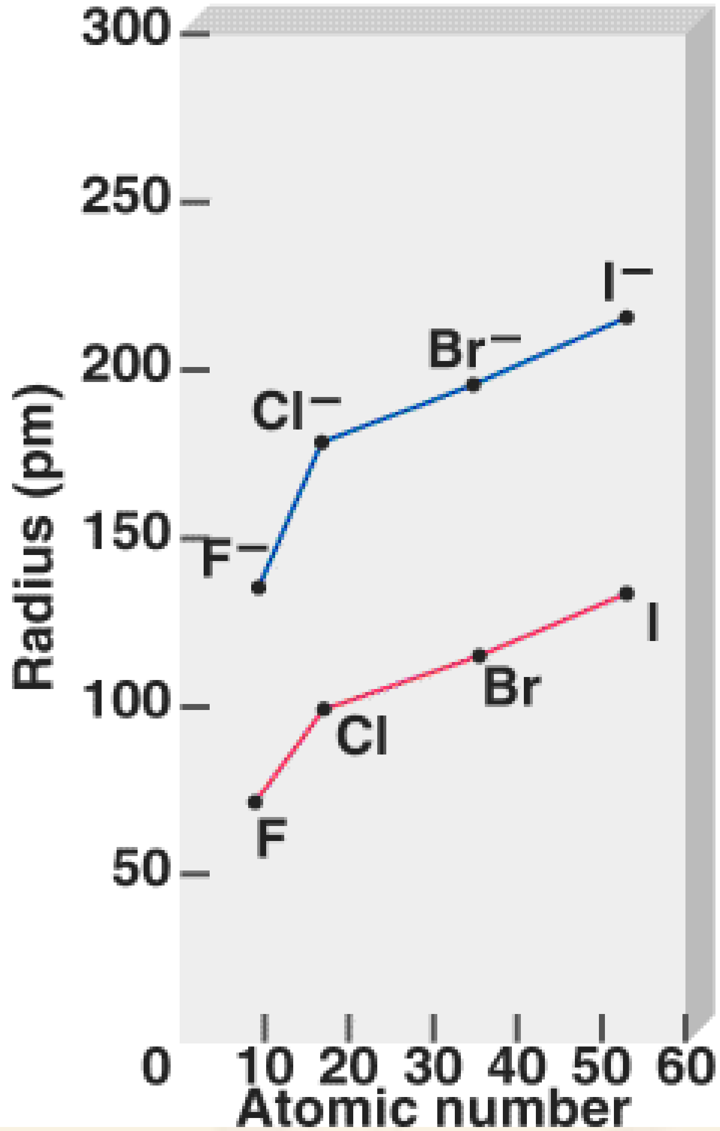




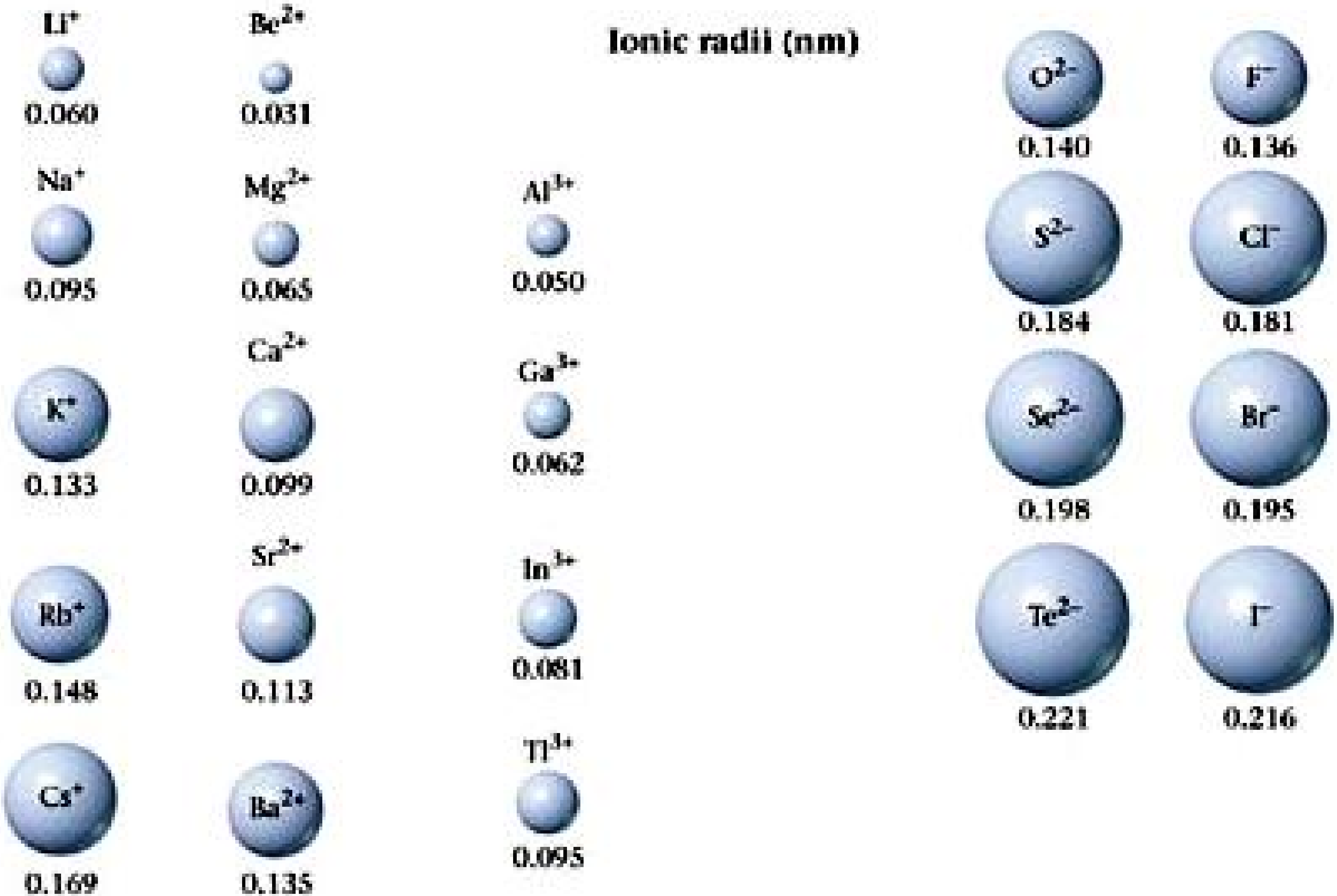
Cation is always **smaller** than atom from which it is formed.
Anion is always **larger** than atom from which it is formed.

Comparison of Atomic Radii with Ionic Radii

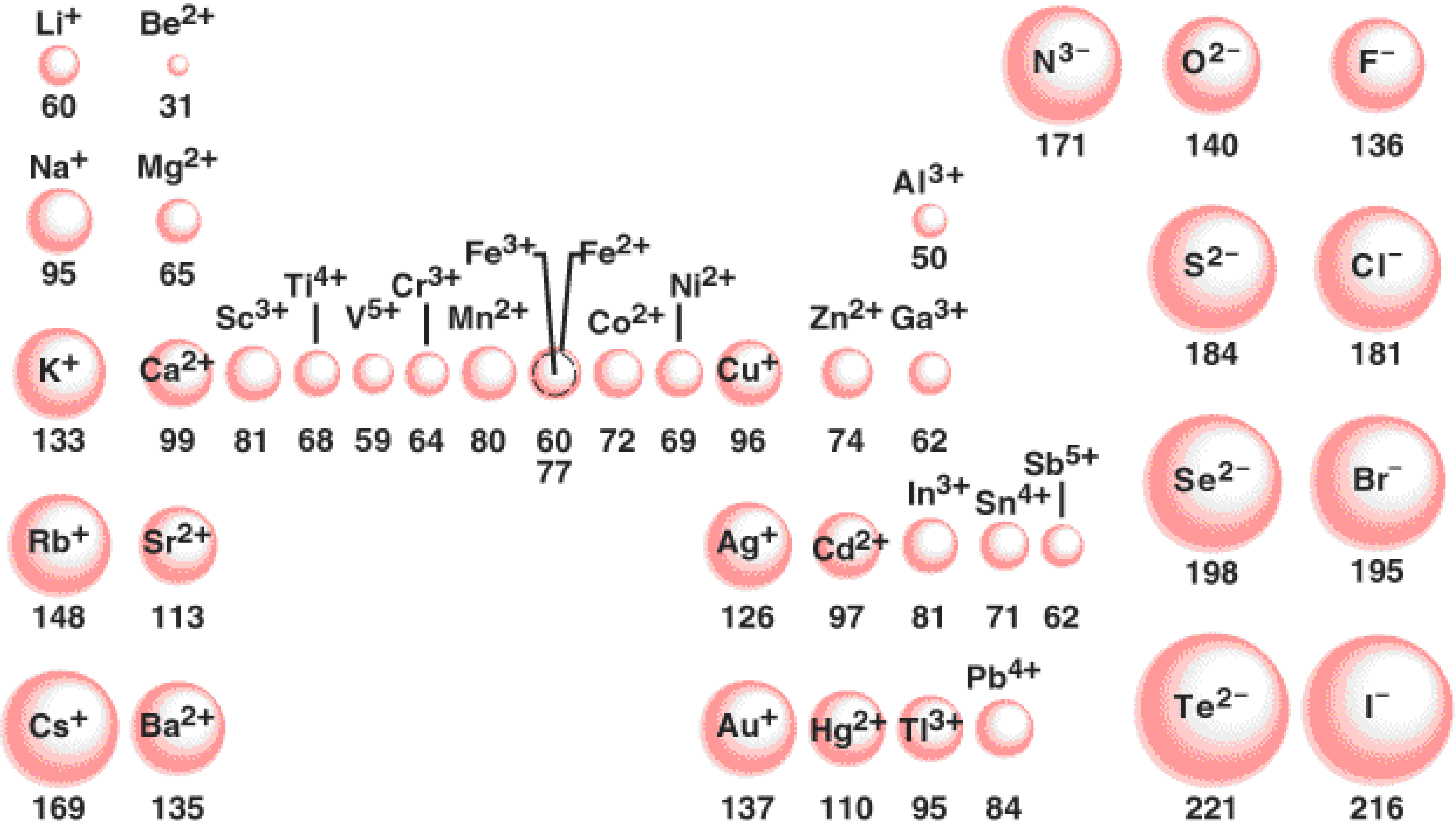




6.7


Ionic radii (nm)
Li+
0.060
Be2+
0.031
Na+
0.095
Mg2+
0.065
Al3+
0.050
K+
0.133
Ca2+
0.099
Ga3+
0.062
Rb+
0.148
Sr2+
0.113
In3+
0.081
Cs+
0.169
Ba2+
0.135
Tl3+
0.095
O2-
0.140
F-
0.136
S2-
0.184
Cl-
0.181
Se2-
0.198
Br-
0.195
Te2-
0.221
I-
0.216

Ionic Radii

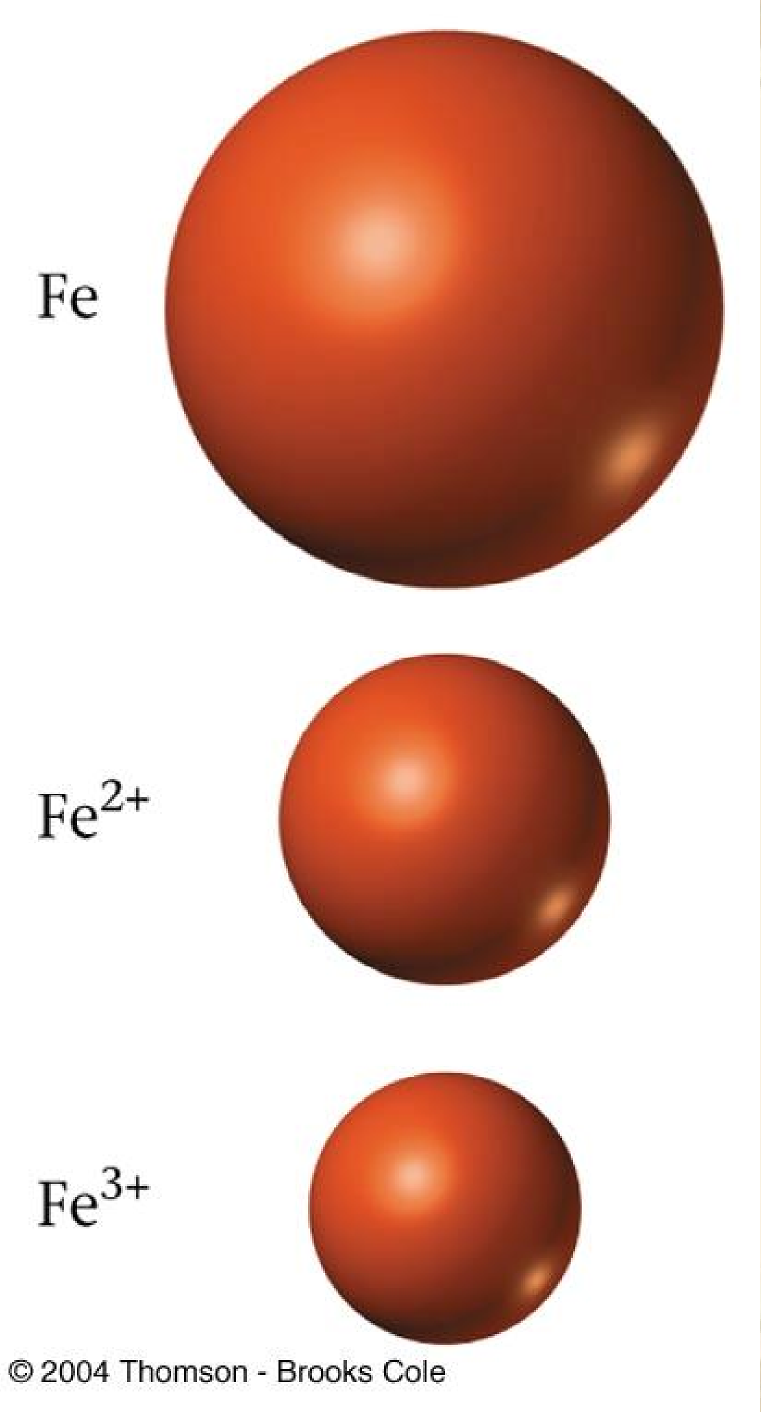

Li+ 60
Be2+ 31
Na+ 95
Mg2+ 65
K+ 133
Ca2+ 99
Sc3+ 81
Ti4+ 68
V5+ 59
Cr3+ 64
Mn2+ 80
Fe3+ 60
Fe2+ 77
Co2+ 72
Ni2+ 69
Cu+ 96
Zn2+ 74
Al3+ 50
Ga3+ 62
Rb+ 148
Sr2+ 113
Ag+ 126
Cd2+ 97
In3+ 81
Sn4+ 71
Sb5+ 62
Cs+ 169
Ba2+ 135
Au+ 137
Hg2+ 110
Tl3+ 95
Pb4+ 84
N3− 171
O2− 140
F− 136
S2− 184
Cl− 181
Se2− 198
Br− 195
Te2− 221
I− 216

- 同一原子形成陽離子時，隨著其失去電子愈多，則其半徑愈小。

  Fe > Fe^{+2} > Fe^{+3}

- 同一原子形成陰離子時，隨著其獲得電子愈多，則其半徑愈大。

  S^{-2} > S



Example 6.10 Using only the periodic table, arrange each of the following sets of atoms and ions in order of increasing size.

(a) Mg, Al, Ca **Ca > Mg > Al**

Mg, Al, 為同週期$_{12}$**Mg,** $_{13}$**Al**，故原子半徑**Mg > Al**

Mg, Ca, 為同族$_{12}$**Mg,** $_{20}$**Ca**，故原子半徑**Ca > Mg**

(b) S, Cl, S^{-2} S^{-2} **> S > Cl**

S, Cl, 為同週期$_{16}$**S,** $_{17}$**Cl**，故原子半徑**S > Cl**

S, S^{-2}**,** 陰離子半徑較原子大，故原子半徑S^{-2} **> S**

(c) Fe, Fe^{+2}**,** Fe^{+3}

$$Fe^{3+} \angle Fe^{2+} \angle Fe$$

ionization energy

- It is a measure of how difficult it is to remove an electron from a gaseous atom
- Energy must always be absorbed to bring about ionization, so ionization energies are always positive quantites.須吸收能量才足以產生離子態，因此游離能均為正值。
- $M(g) \rightarrow M^{+}(g) + e^{-}$ ΔE_1=first ionization energy
- $M^{+}(g) \rightarrow M^{+2}(g) + e^{-}$ ΔE_2=Second ionization energy

  $\Delta E_1 < \Delta E_2 \ldots$
- Increases across the periodic table from left to right.
- Decreses moving down the periodic table

General Trend in First Ionization Energies

Increasing First Ionization Energy (left to right →)

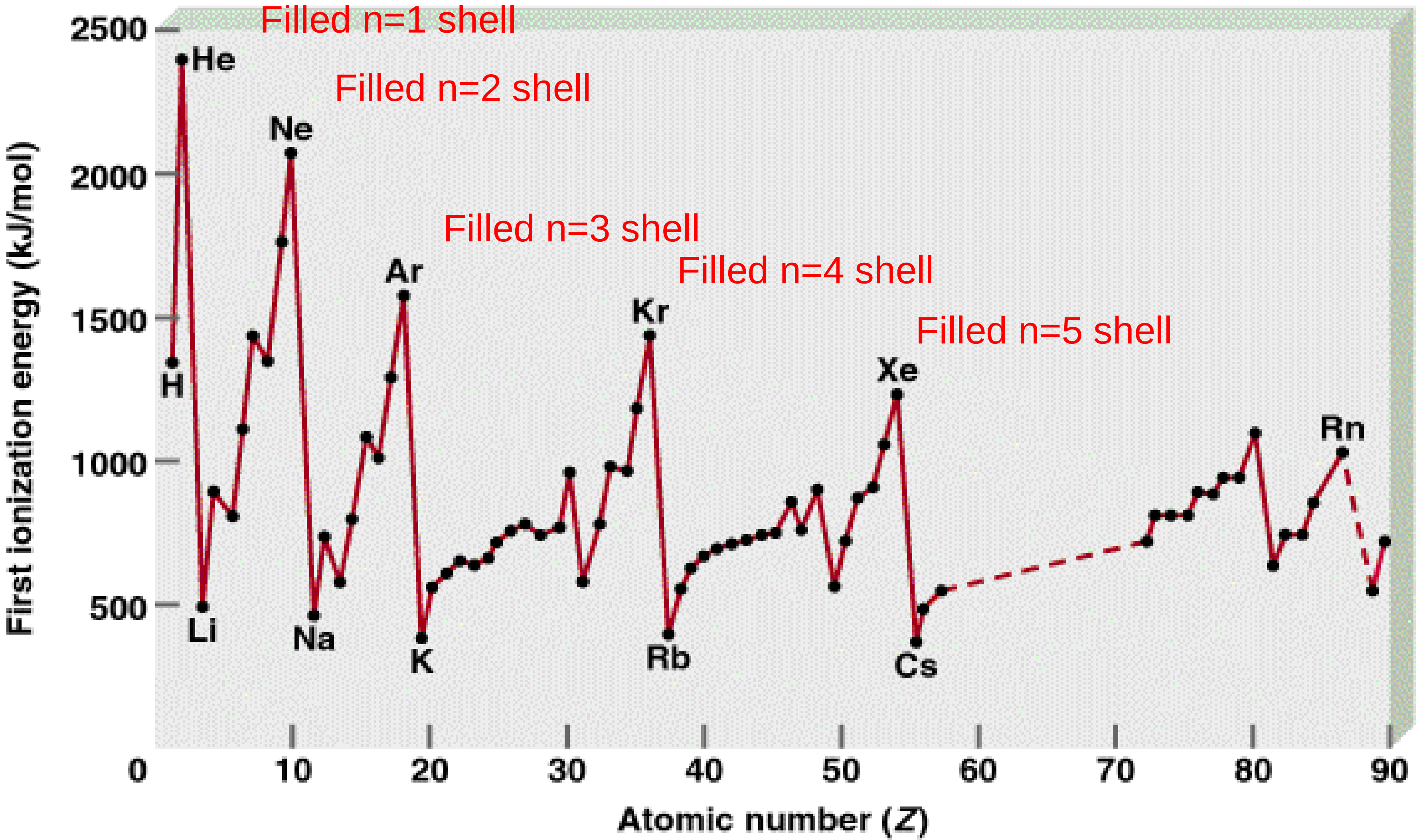
Increasing First Ionization Energy (bottom to top ↑)

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112	(113)	114	(115)	116	(117)	118
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

The Ionization Energies (kJ/mol) of the First 20 Elements

Z	Element	First	Second	Third	Fourth	Fifth	Sixth
1	H	1,312					
2	He	2,373	5,251				
3	Li	520	7,300	11,815			
4	Be	899	1,757	14,850	21,005		
5	B	801	2,430	3,660	25,000	32,820	
6	C	1,086	2,350	4,620	6,220	38,000	47,261
7	N	1,400	2,860	4,580	7,500	9,400	53,000
8	O	1,314	3,390	5,300	7,470	11,000	13,000
9	F	1,680	3,370	6,050	8,400	11,000	15,200
10	Ne	2,080	3,950	6,120	9,370	12,200	15,000
11	Na	495.9	4,560	6,900	9,540	13,400	16,600
12	Mg	738.1	1,450	7,730	10,500	13,600	18,000
13	Al	577.9	1,820	2,750	11,600	14,800	18,400
14	Si	786.3	1,580	3,230	4,360	16,000	20,000
15	P	1,012	1,904	2,910	4,960	6,240	21,000
16	S	999.5	2,250	3,360	4,660	6,990	8,500
17	Cl	1,251	2,297	3,820	5,160	6,540	9,300
18	Ar	1,521	2,666	3,900	5,770	7,240	8,800
19	K	418.7	3,052	4,410	5,900	8,000	9,600
20	Ca	589.5	1,145	4,900	6,500	8,100	11,000

Variation of the First Ionization Energy with Atomic Number



同週期中游離能隨原子序增加而增加

例外

同族中游離能隨主量子數增加而減少

1	2	13	14	15	16	17	18
						H 1312	He 2372
Li 520	Be 900	B 801	C 1086	N 1402	O 1314	F 1681	Ne 2081
Na 496	Mg 738	Al 578	Si 786	P 1012	S 1000	Cl 1251	Ar 1520
K 419	Ca 590	Ga 579	Ge 762	As 944	Se 941	Br 1140	Kr 1351
Rb 403	Sr 550	In 558	Sn 709	Sb 832	Te 869	I 1009	Xe 1170
Cs 376	Ba 503	Tl 589	Pb 716	Bi 703	Po 812	At	Rn 1037

Example 6.11: Consider the three elements C ,N, and Si. Using only the periodic table, predict which of the three elements has (a) the largest atomic radius; the smallest atomic radius. (b) the largest ionization energy ; the smallest ionization energy.

Sol:

(a) C is larger than N but smaller than Si. Silicon must be the largest atom and nitrogen the smallest.

(b) C has a smaller ionization energy than N but a larger ionization energy than Si.

週期表預測下列三個元素B, C及Al之

(a) 何者具最大及最小原子半徑 Al > B > C

B, C, 為同週期$_5$B, $_6$C，故原子半徑B > C

B, Al, 為同族$_5$B, $_{13}$Al，故原子半徑Al > B

(b) 何者具有最大及最小游離能 C > B > Al

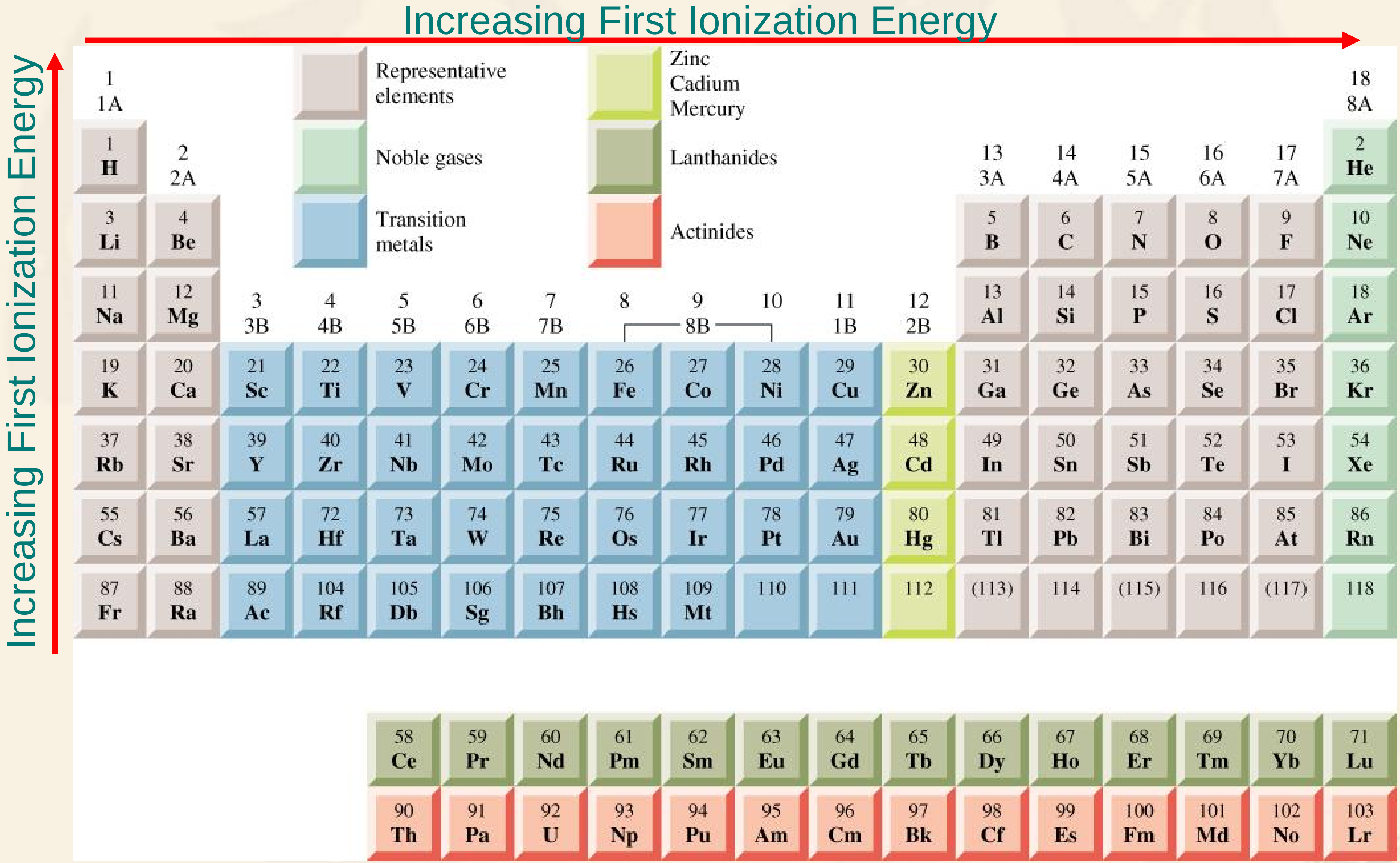
B, C, 為同週期$_5$B, $_6$C，故游離能C > B

B, Al, 為同族$_5$B, $_{13}$Al，故游離能B > Al

electronegativity

- 由Linus Pouling提出，為相對觀念。
- Atom is a measure of its tendency to lose electrons, the larger the ionization energy ,the more difficult is to remove an electron. 。
- 陰電性值
- 同一週期由左而右增加，同一族由上而下變小。

General Trend in Electronegativity



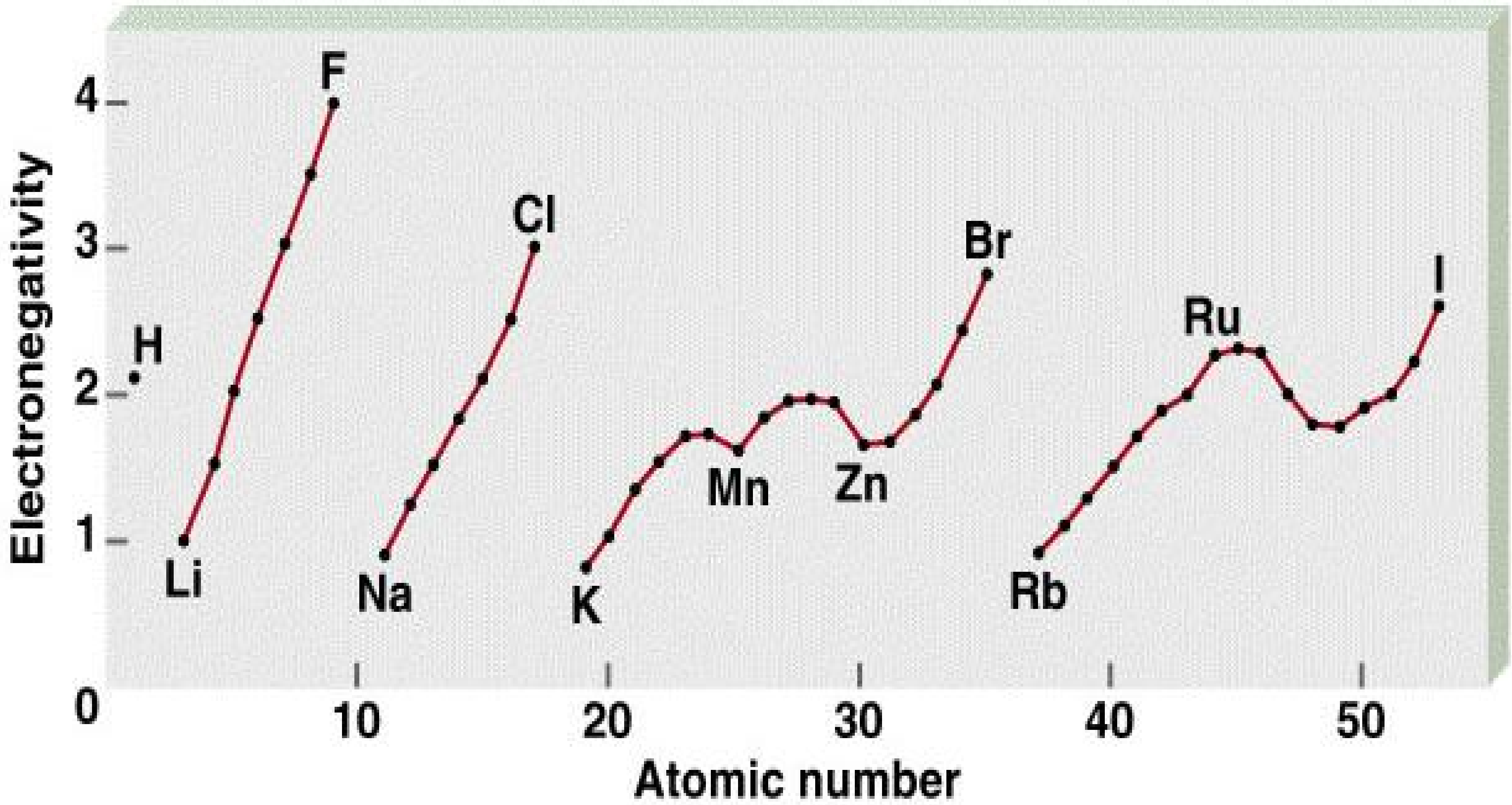
Electronegativities of Common Elements

Increasing electronegativity →

↑ Increasing electronegativity

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
H 2.1																	
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	
Cs 0.7	Ba 0.9	La-Lu 1.0-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	
Fr 0.7	Ra 0.9																

Variation of Electronegativity with Atomic Number



Classification of bonds by difference in electronegativity

Difference	Bond Type
0	Covalent
≥ 2	Ionic
0 < and <2	Polar Covalent

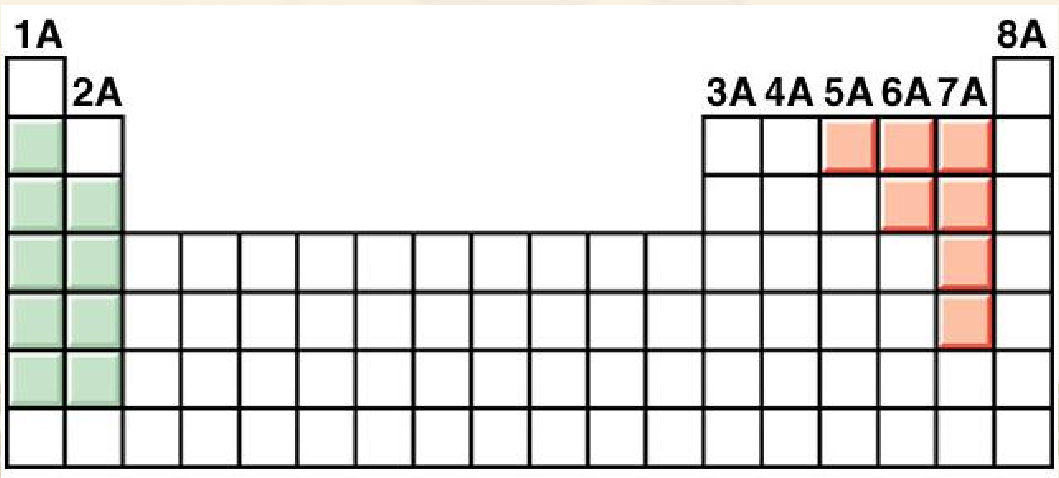
Increasing difference in electronegativity →

Covalent → Polar Covalent → Ionic

share e^- → partial transfer of e^- → transfer e^-

Classify the following bonds as ionic, polar covalent, or covalent: The bond in CsCl; the bond in H_2S; and the NN bond in H_2NNH_2.

Cs – 0.7	Cl – 3.0	3.0 – 0.7 = 2.3	Ionic
H – 2.1	S – 2.5	2.5 – 2.1 = 0.4	Polar Covalent
N – 3.0	N – 3.0	3.0 – 3.0 = 0	Covalent



Electron affinity is the negative of the energy change that occurs when an electron is accepted by an atom in the gaseous state to form an anion.

$X_{(g)} + e^- \longrightarrow X^-_{(g)}$

$F_{(g)} + e^- \longrightarrow X^-_{(g)}$ $\Delta H = -328$ kJ/mol EA = +328 kJ/mol

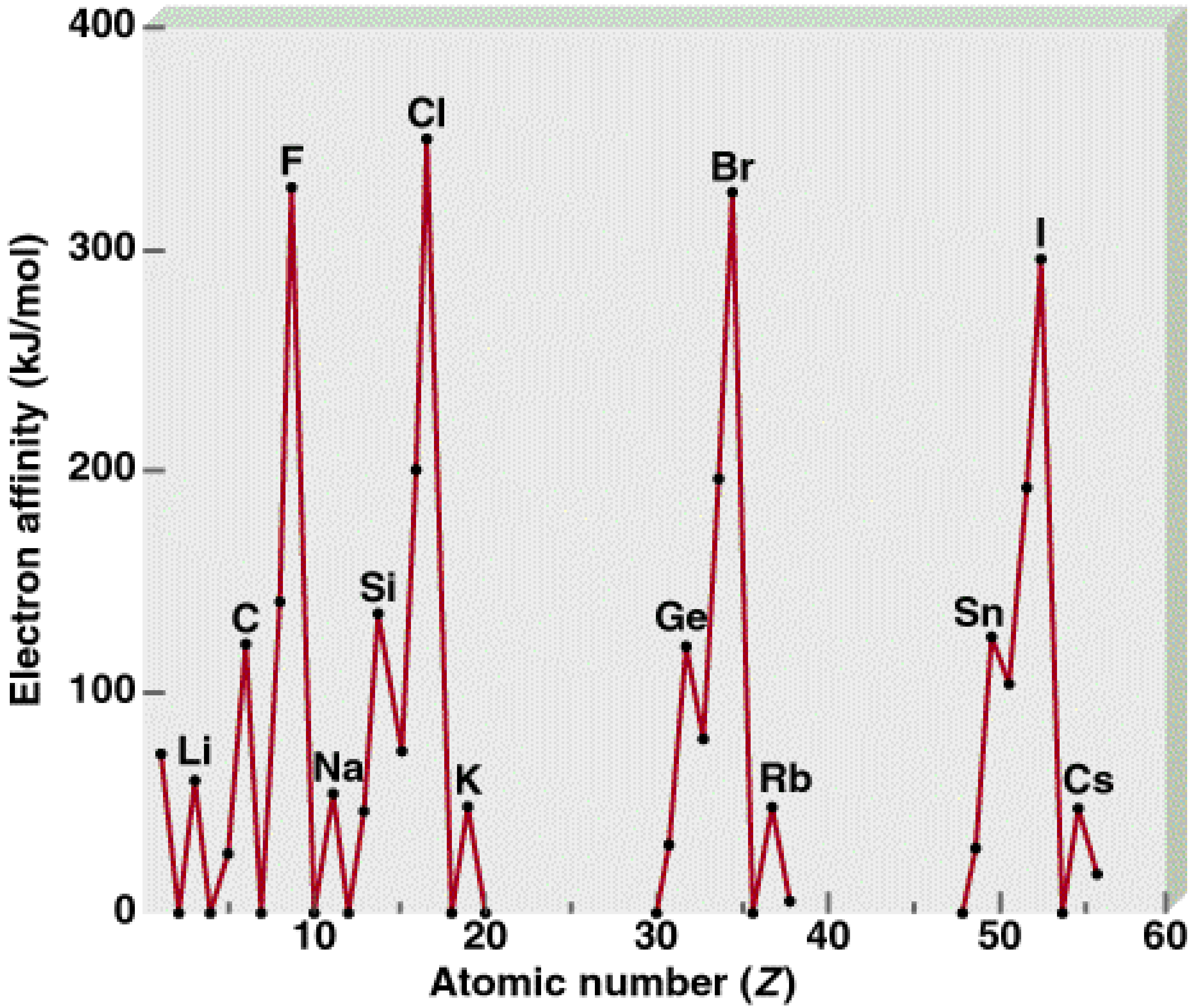
$O_{(g)} + e^- \longrightarrow O^-_{(g)}$ $\Delta H = -141$ kJ/mol EA = +141 kJ/mol

Electron Affinities (kJ/mol) of Some Representative Elements and the Noble Gases*

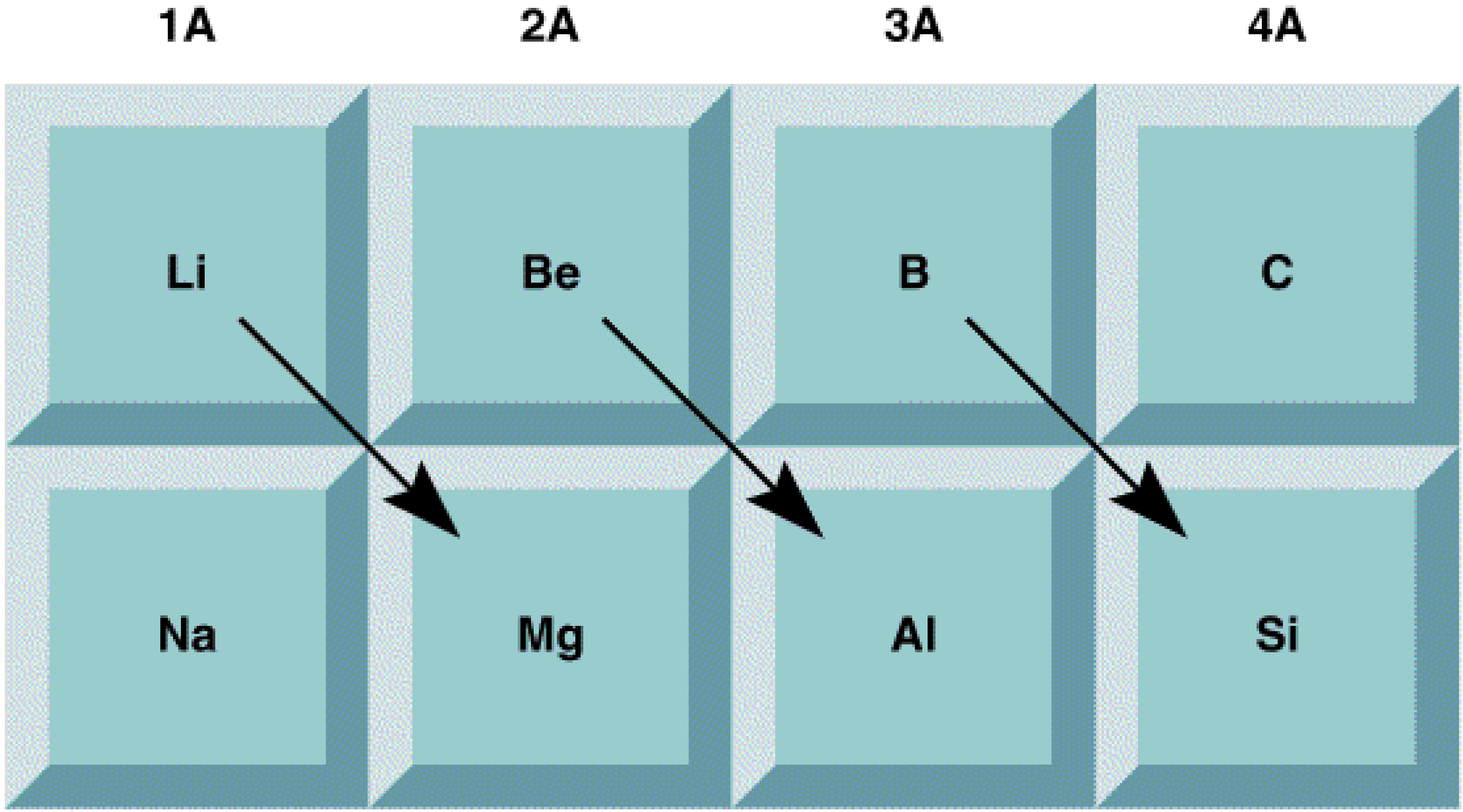
1A	2A	3A	4A	5A	6A	7A	8A
H							He
73							< 0
Li	Be	B	C	N	O	F	Ne
60	≤ 0	27	122	0	141	328	< 0
Na	Mg	Al	Si	P	S	Cl	Ar
53	≤ 0	44	134	72	200	349	< 0
K	Ca	Ga	Ge	As	Se	Br	Kr
48	2.4	29	118	77	195	325	< 0
Rb	Sr	In	Sn	Sb	Te	I	Xe
47	4.7	29	121	101	190	295	< 0
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
45	14	30	110	110	?	?	< 0

* The electron affinities of the noble gases, Be, and Mg have not been determined experimentally, but are believed to be close to zero or negative.

Electron Affinity Versus Atomic Number



Diagonal Relationships in the Periodic Table

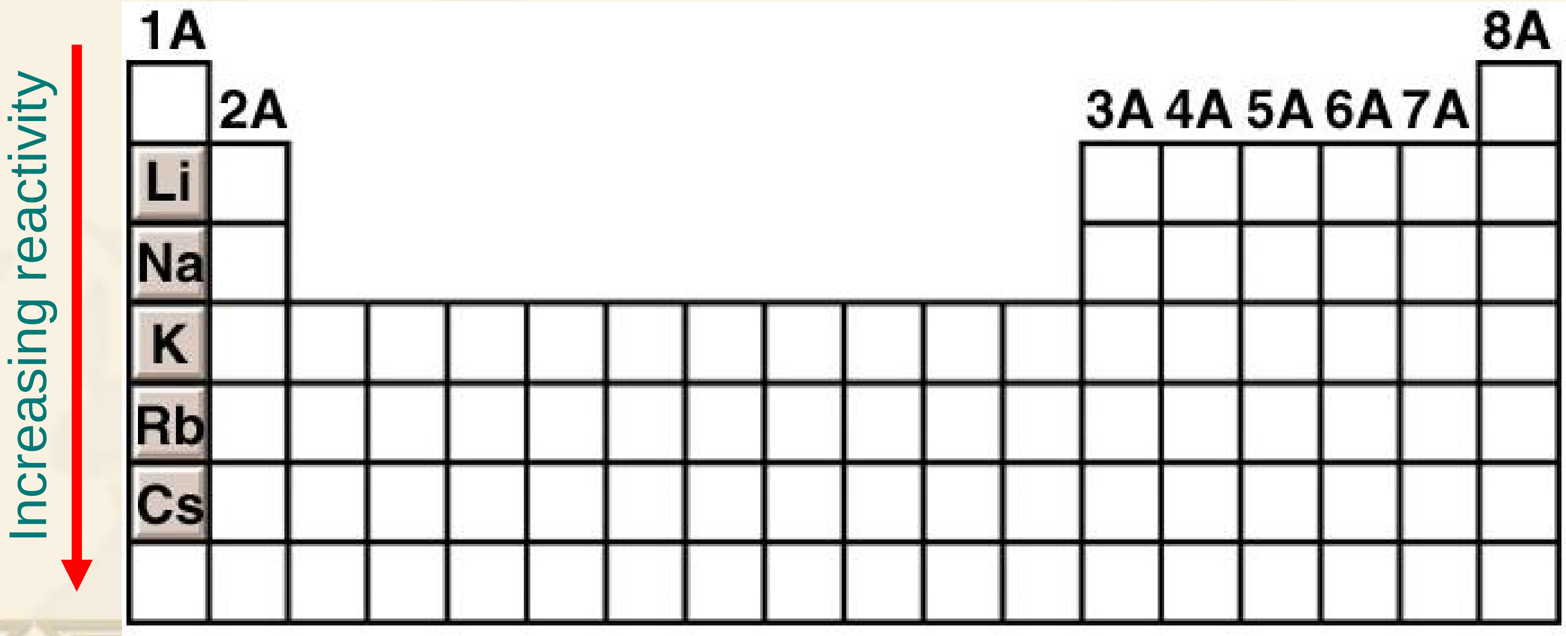


Group 1A Elements (ns^1, $n \geq 2$)

$$M \longrightarrow M^{+1} + 1e^-$$

$$2M_{(s)} + 2H_2O_{(l)} \longrightarrow 2MOH_{(aq)} + H_{2(g)}$$

$$4M_{(s)} + O_{2(g)} \longrightarrow 2M_2O_{(s)}$$



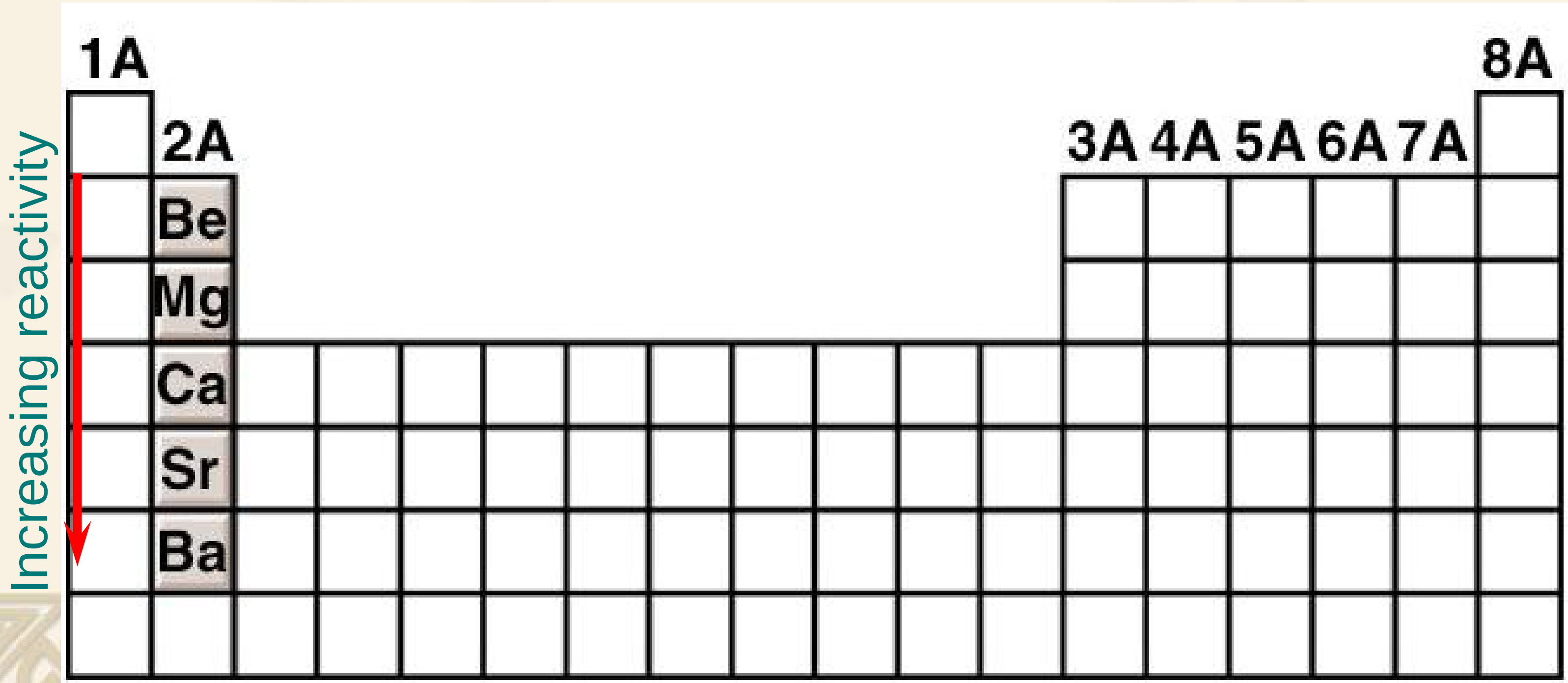
Group 2A Elements (ns^2, $n \geq 2$)

$$M \longrightarrow M^{+2} + 2e^-$$

$$Be_{(s)} + 2H_2O_{(l)} \longrightarrow \text{No Reaction}$$

$$Mg_{(s)} + 2H_2O_{(g)} \longrightarrow Mg(OH)_{2(aq)} + H_{2(g)}$$

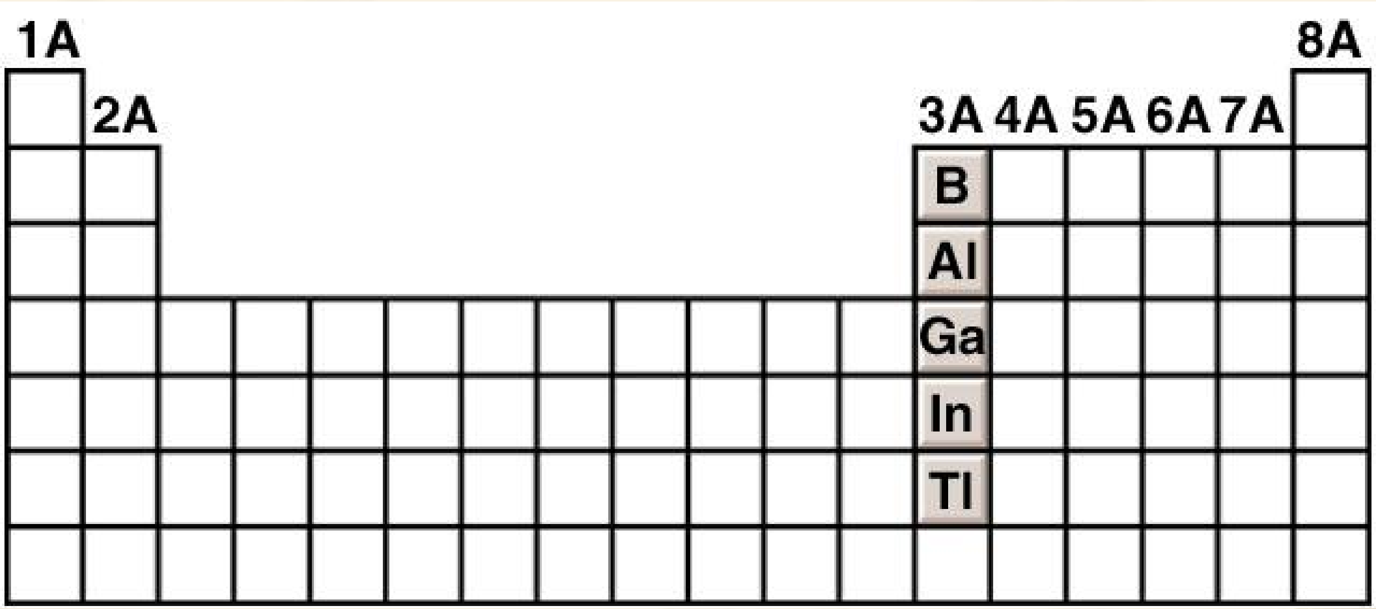
$$M_{(s)} + 2H_2O_{(l)} \longrightarrow M(OH)_{2(aq)} + H_{2(g)} \quad M = \text{Ca, Sr, or Ba}$$



Group 3A Elements (ns^2np^1, $n \geq 2$)

$$4Al_{(s)} + 3O_{2(g)} \longrightarrow 2Al_2O_{3(s)}$$

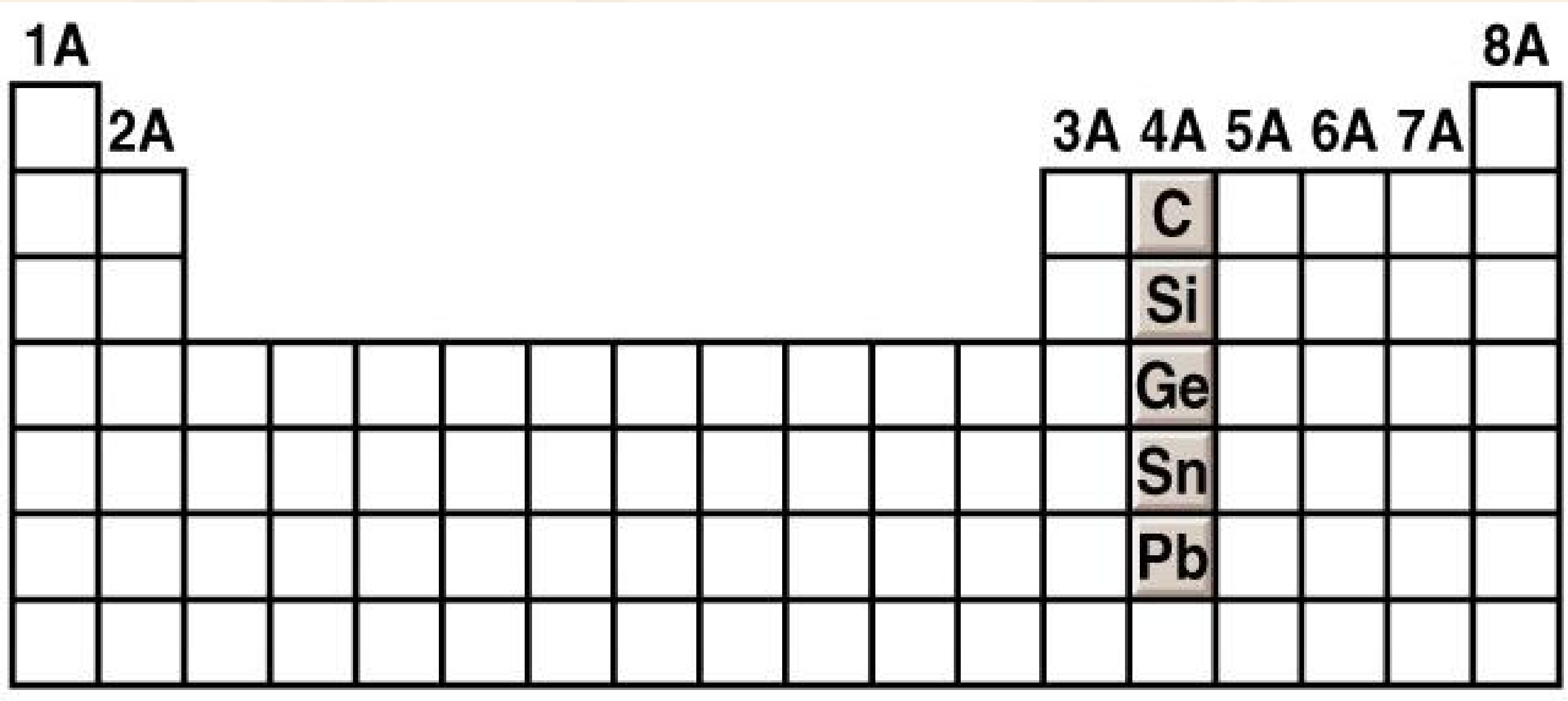
$$2Al_{(s)} + 6H^+_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3H_{2(g)}$$



Group 4A Elements (ns^2np^2, $n \geq 2$)

$$Sn_{(s)} + 2H^+_{(aq)} \longrightarrow Sn^{2+}_{(aq)} + H_{2\ (g)}$$

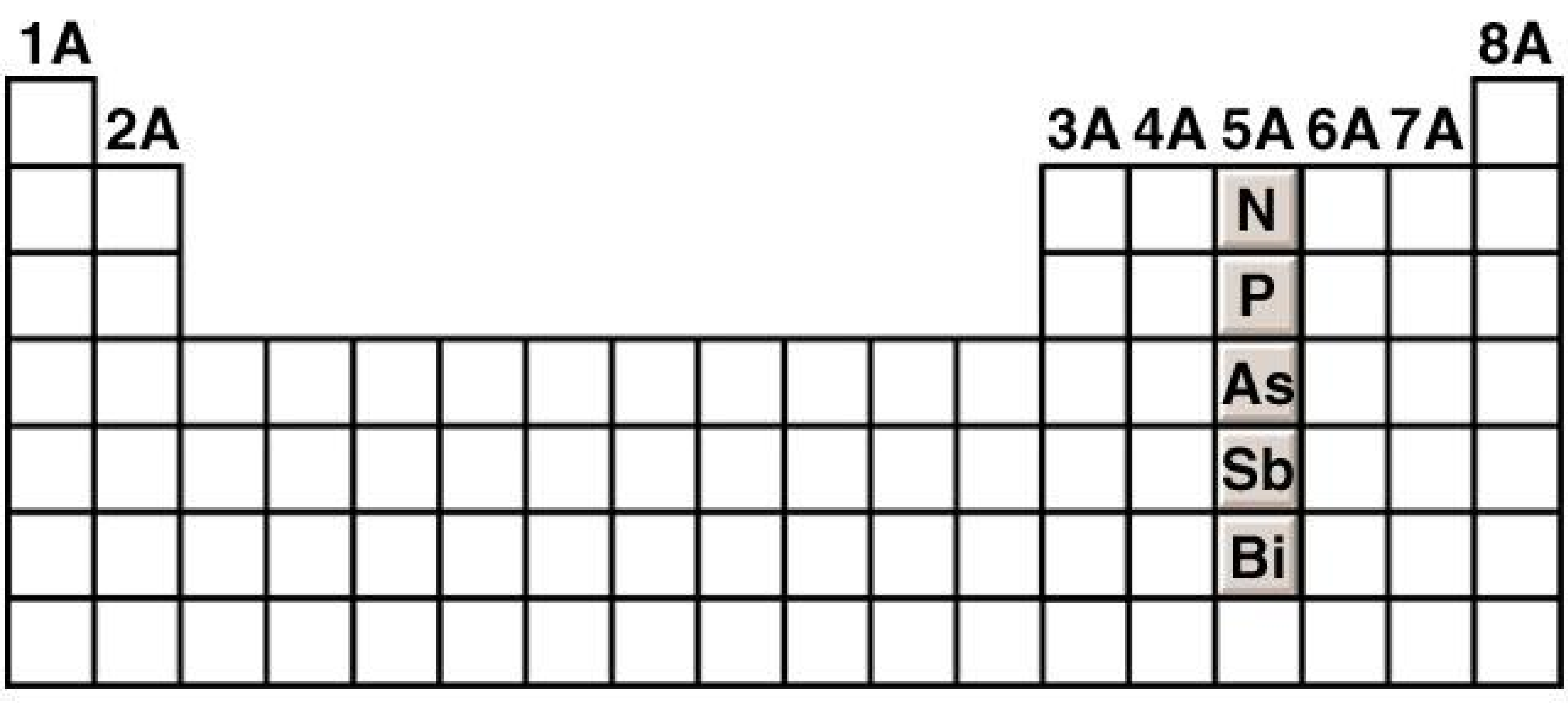
$$Pb_{(s)} + 2H^+_{(aq)} \longrightarrow Pb^{2+}_{(aq)} + H_{2\ (g)}$$



Group 5A Elements (ns^2np^3, $n \geq 2$)

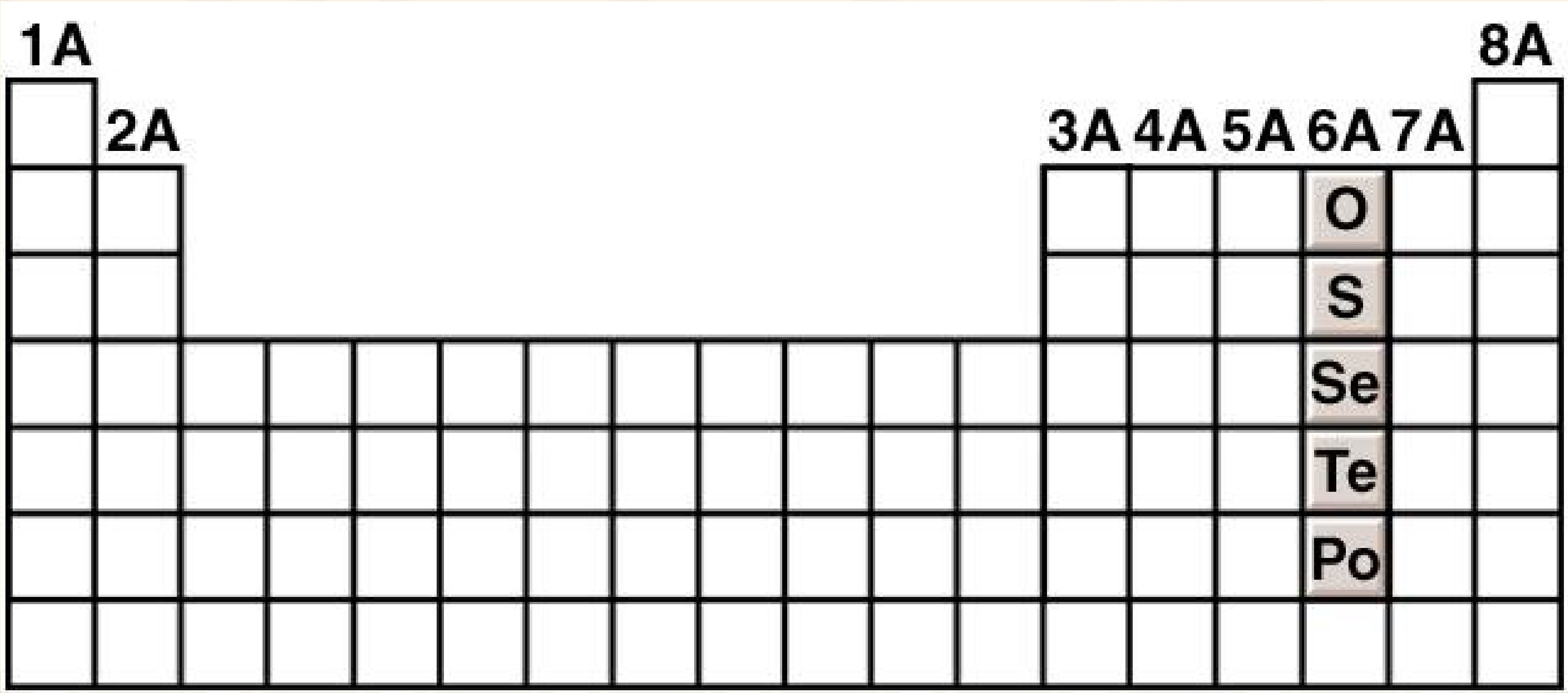
$$N_2O_{5(s)} + H_2O_{(l)} \longrightarrow 2HNO_{3(aq)}$$

$$P_4O_{10(s)} + 6H_2O_{(l)} \longrightarrow 4H_3PO_{4(aq)}$$



Group 6A Elements (ns^2np^4, n ≥ 2)

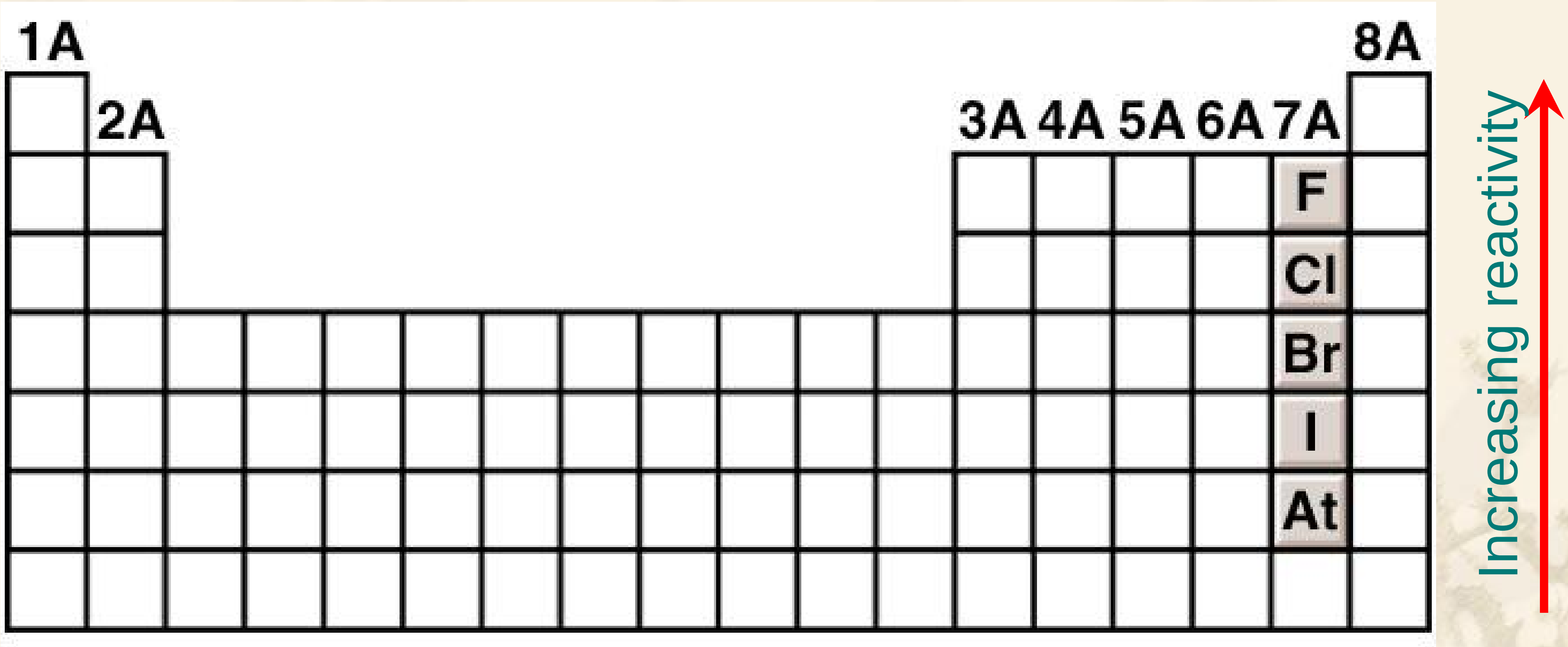
$$SO_{3(g)} + H_2O_{(l)} \longrightarrow H_2SO_{4(aq)}$$



Group 7A Elements (ns^2np^5, $n \geq 2$)

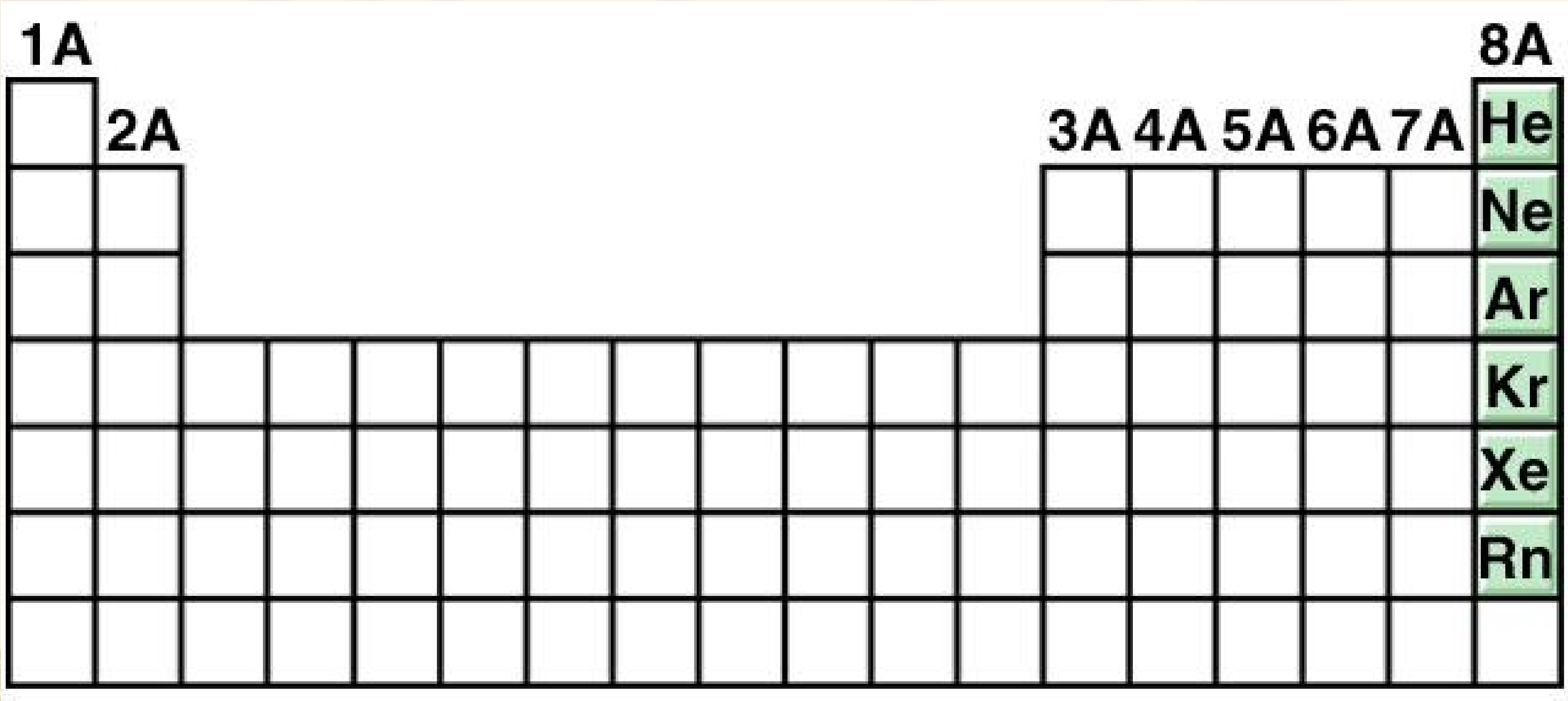
$$X + 1e^- \longrightarrow X^{-1}$$

$$X_{2(g)} + H_{2(g)} \longrightarrow 2HX_{(g)}$$

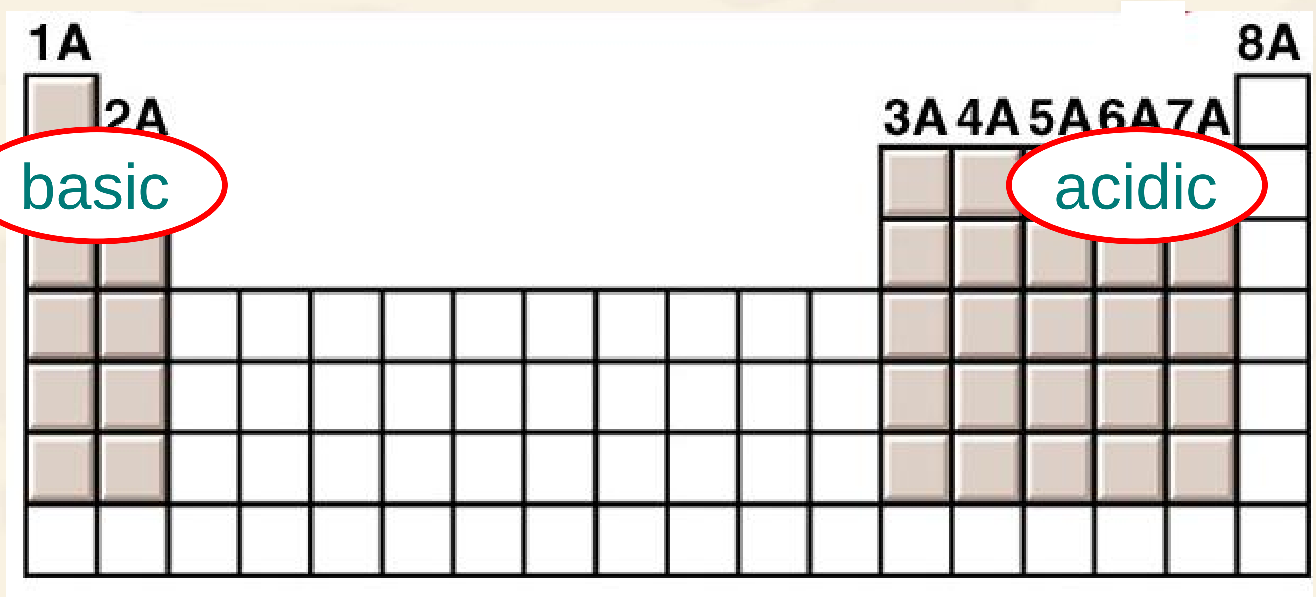


Group 8A Elements (ns^2np^6, $n \geq 2$)

Completely filled *ns* and *np* subshells.
Highest ionization energy of all elements.
No tendency to accept extra electrons.



Properties of Oxides Across a Period



Some Properties of Oxides of the Third-Period Elements

	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
Type of compound	← Ionic →			← Molecular →			
Structure	← Extensive three-dimensional →				← Discrete molecular units →		
Melting point (°C)	1275	2800	2045	1610	580	16.8	−91.5
Boiling point (°C)	?	3600	2980	2230	?	44.8	82
Acid-base nature	Basic	Basic	Amphoteric	← Acidic →			