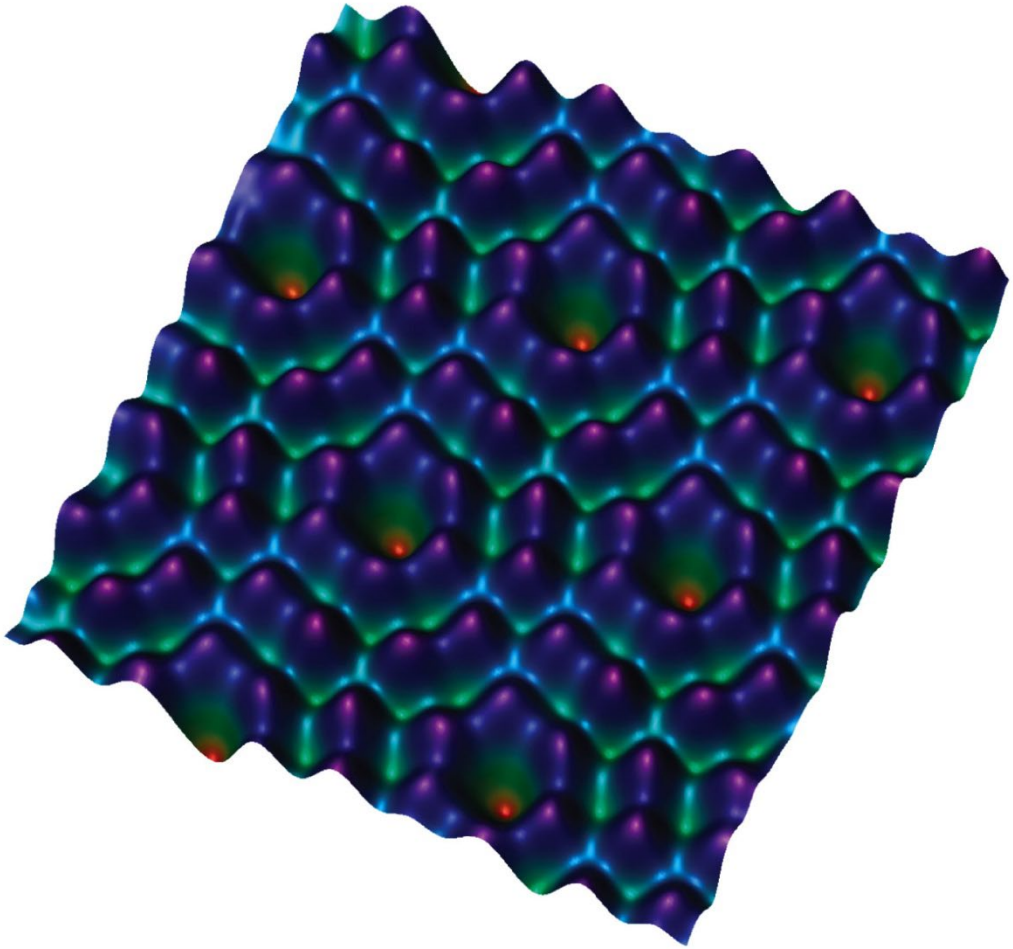
CHEMISTRY

Studying the properties of substances and the reactions that transform substances into other substances.

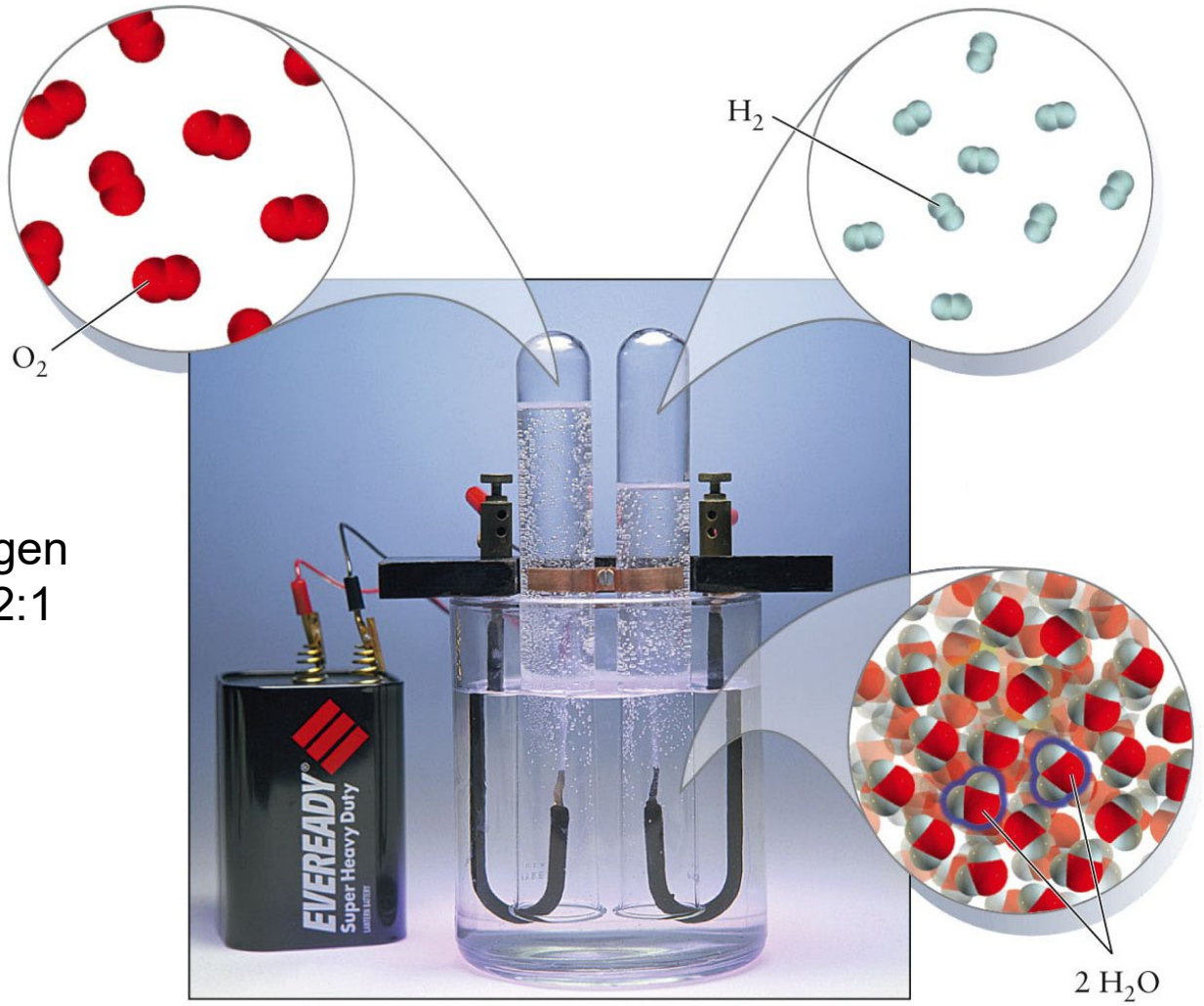
Improving agricultural production, curing many diseases, increasing the efficiency of energy production, and reducing environmental pollution.



Single atom transfer using the scanning tunneling microscope

Alchemists trying to turn base metals to Gold.

Macroscopic and Nanoscopic Models



Hydrogen and oxygen gas evolution in a 2:1 ratio from water by passing an electric current

UNIT II

CHEMICAL BONDING AND MOLECULAR STRUCTURE

CHAPTER 3
Chemical Bonding: The Classical Description

CHAPTER 4
Introduction to Quantum Mechanics

CHAPTER 5
Quantum Mechanics and Atomic Structure

CHAPTER 6
Quantum Mechanics and Molecular Structure

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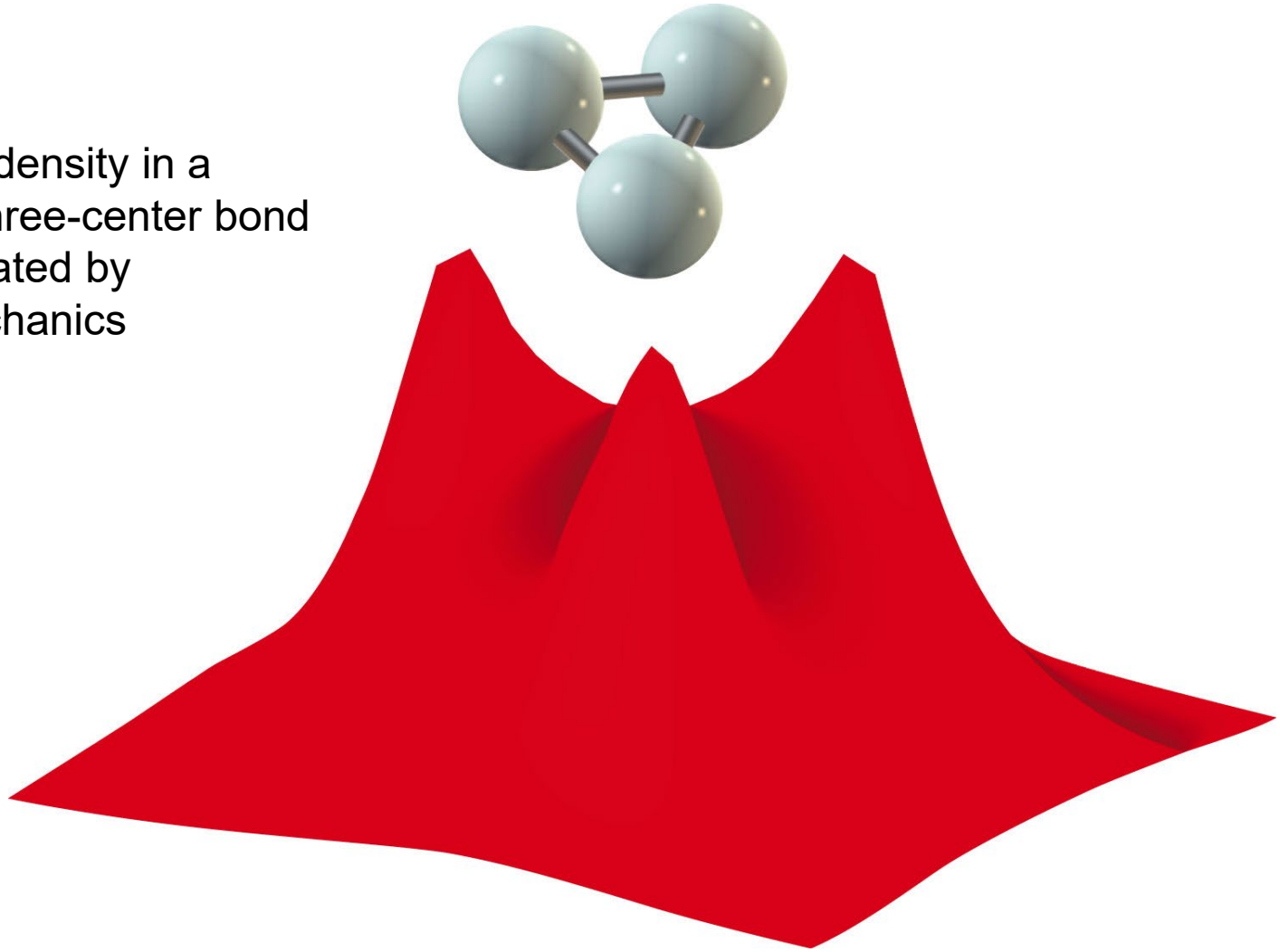
The electron density in a delocalized three-center bond for H_3^+ calculated by quantum mechanics



3

CHAPTER

CHEMICAL BONDING: THE CLASSICAL DESCRIPTION

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3.1 REPRESENTATIONS OF MOLECULES

- A **molecule**: a collection of atoms bonded together, with the elements in fixed proportions and with a well-defined 3D structure.

- Determination of a molecular formula

1) Empirical formula: the set of smallest integers that represents the ratios of the numbers of atoms in a compound.

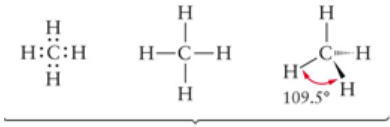
2) Measuring the molar mass of the compound under study from its gas-law behavior or by mass spectrometry.

3) Taking the ratio of that molar mass to the molar mass of the empirical formula, and obtaining the molecular formula as a simple integral multiple of the empirical formula.

i.e.) empirical formula CH_2O ->
glucose $C_6H_{12}O_6$, acetic acid $C_2H_4O_2$, or formaldehyde CH_2O

Molecular Representations

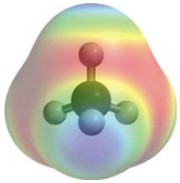
- **Simple 2D drawings from molecular formula: ex) methane CH_4**



- **Lewis models**: defining each bond as a pair of electrons localized between two particular atoms and represents structural formulas using Lewis dot diagrams.

- **Ball-and-stick models**: the balls represent the atoms and the sticks represent the bonds between them.

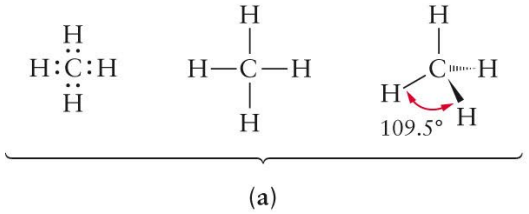
- **Space-filling models**: showing the atoms with specific sizes that physically contact each other in molecules



- **Electrostatic potential energy diagram (elpot diagram)**: displaying the electrostatic potential energy that a small positive "test charge" would experience at every position on the electron density surface that defines the space-filling model.

Lewis dot | line | line angle | ball and stick | space filling | Electrostatic potential energy

CH_4



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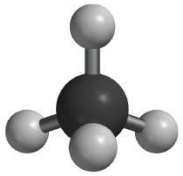
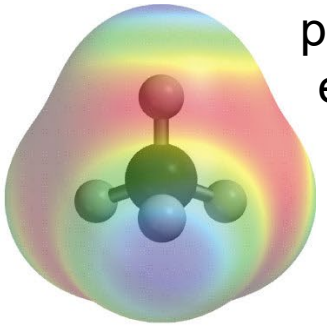


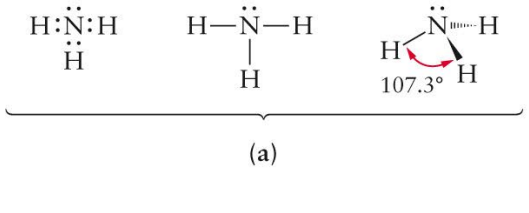
(b)

(c)



(d)

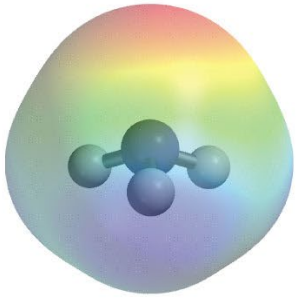
NH_3



(a)

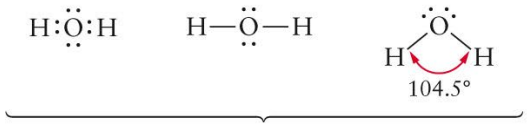
(b)

(c)

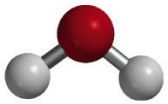


(d)

H_2O

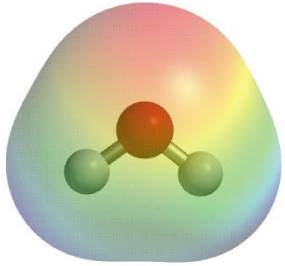


(a)



(b)

(c)



(d)

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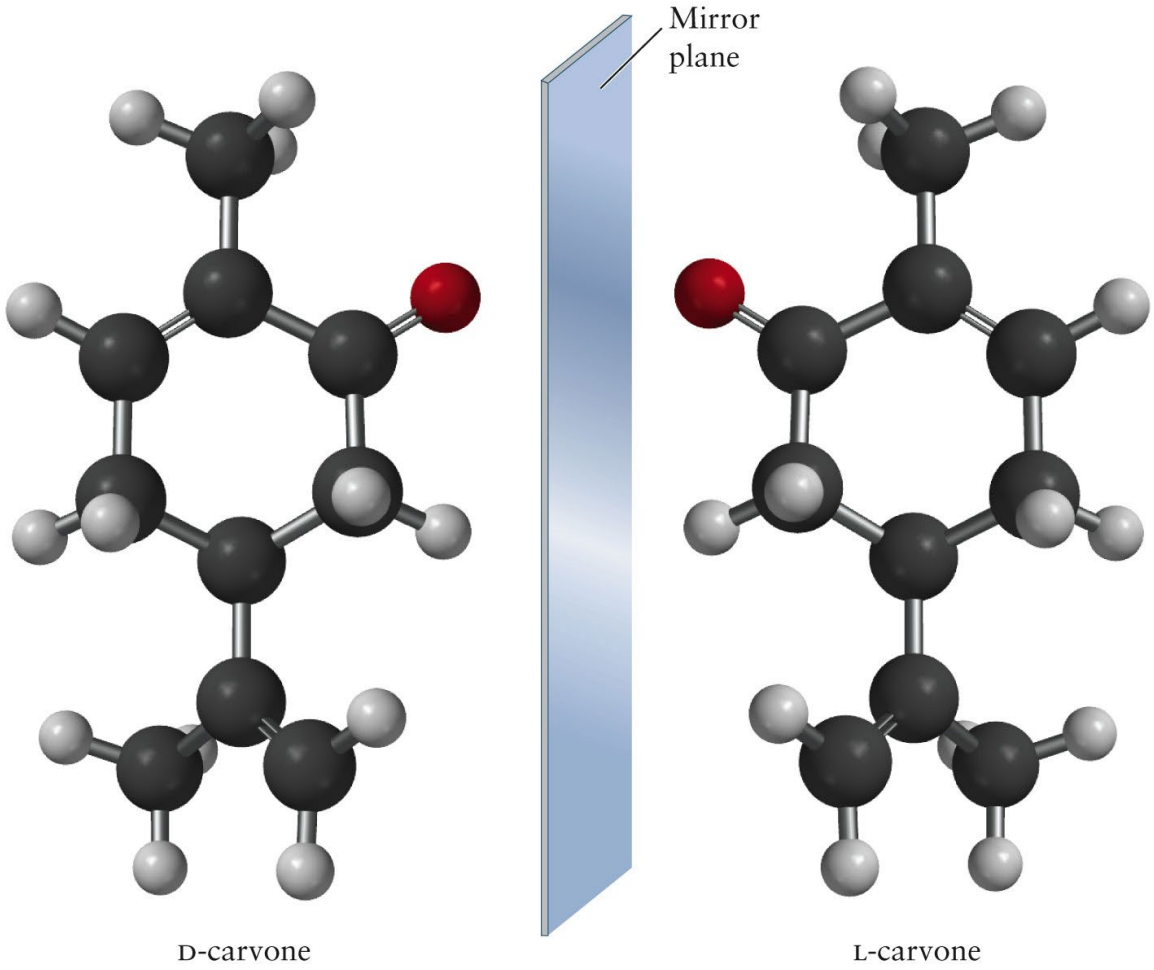
Isomers

Different compounds having the same molecular formula but different molecular structures and therefore different properties

Optical isomers: their mirror images are not superimposable.

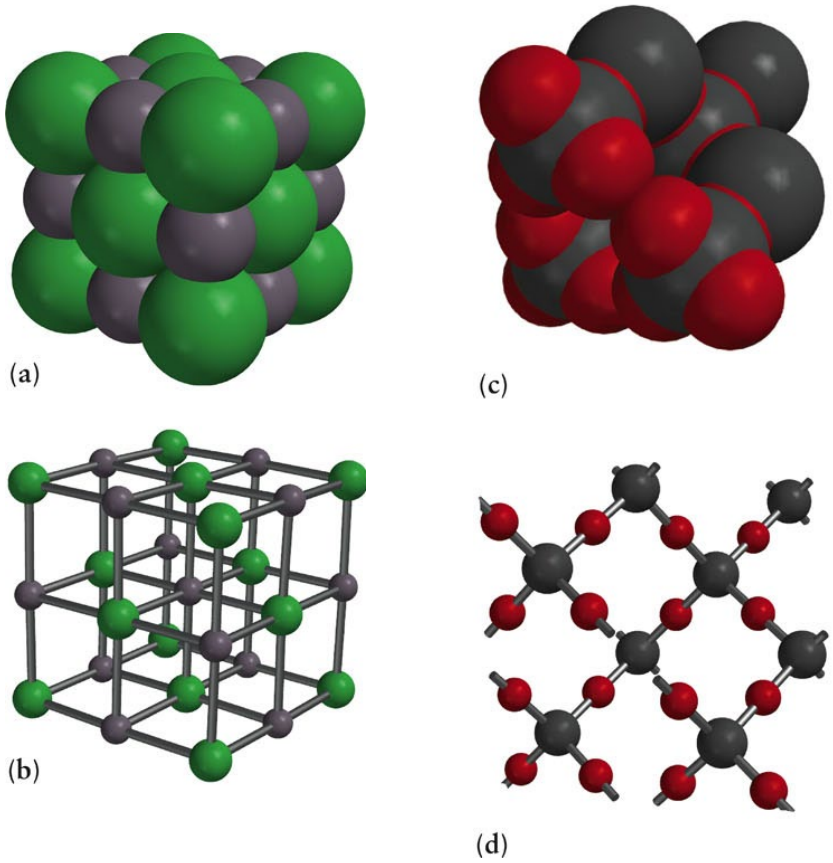


Extended Solid-State Ionic Compounds

- Each ion is surrounded by a group of ions of opposite charge.

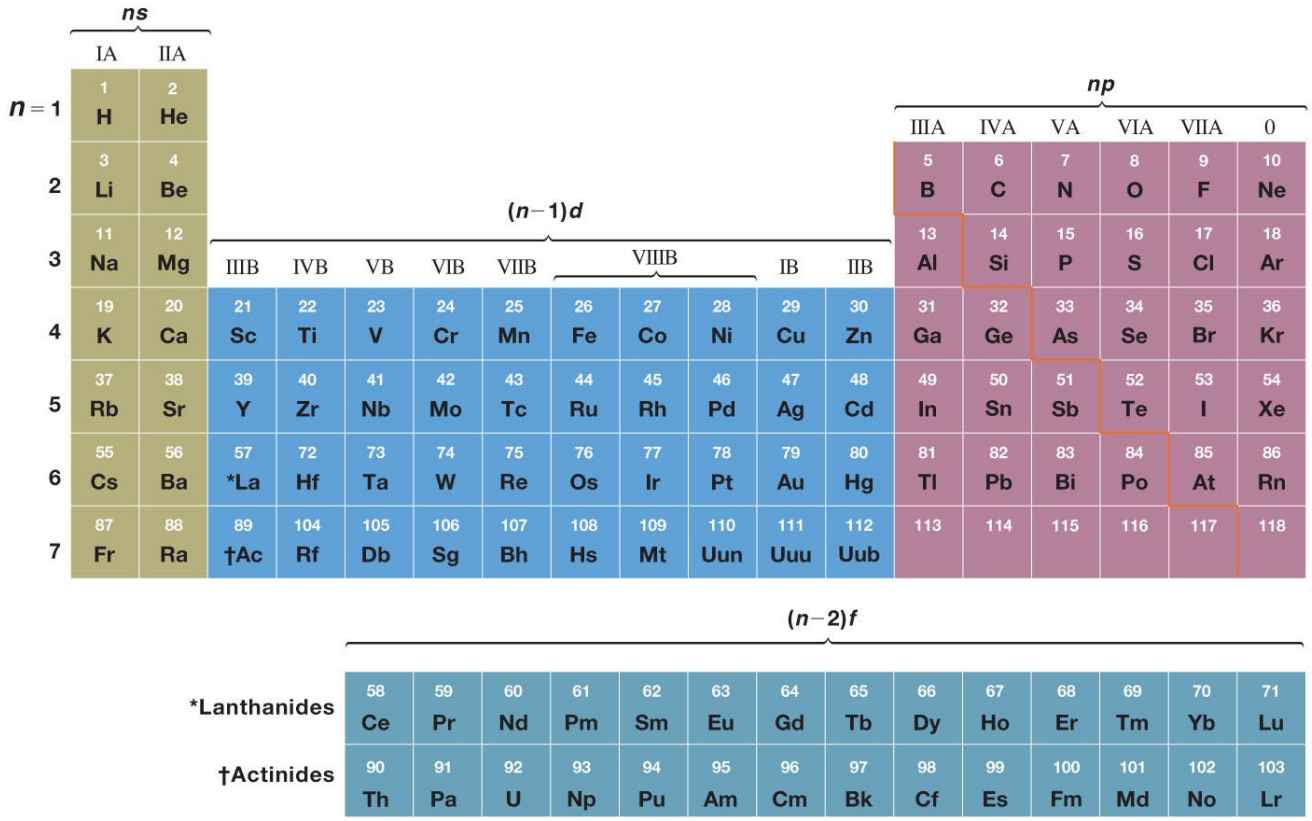
  - "NaCl"

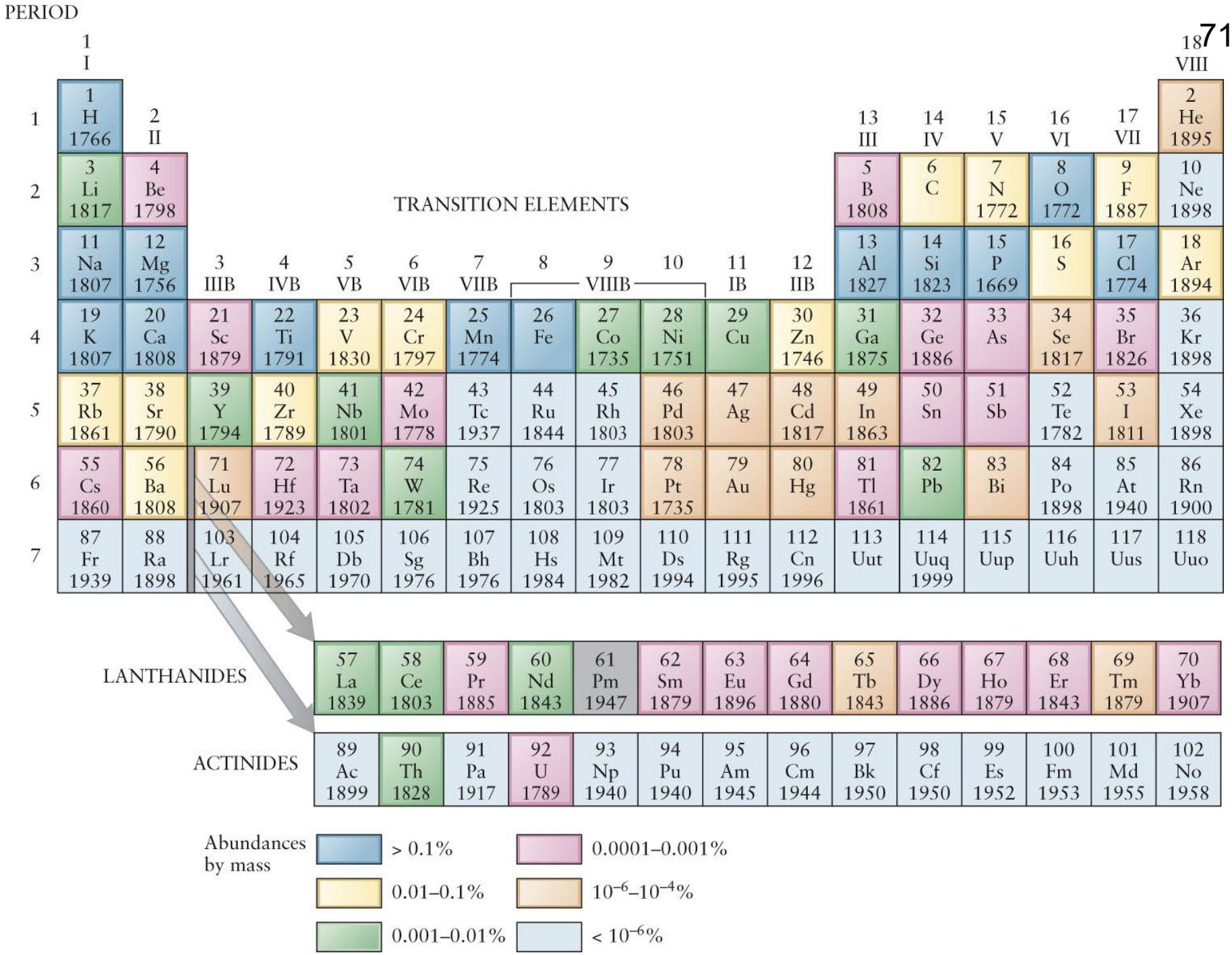
  - "SiO_2"



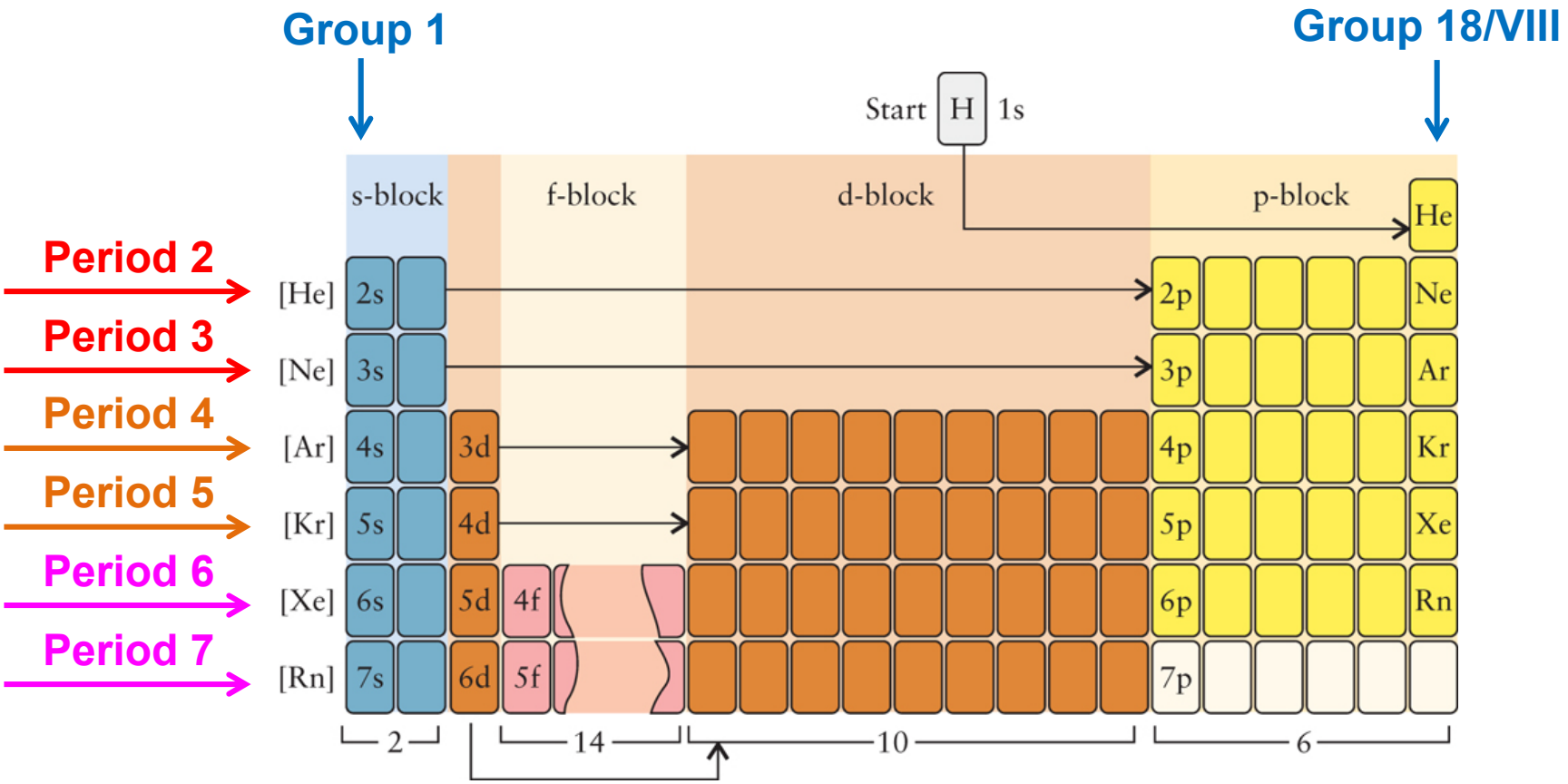
3.2 THE PERIODIC TABLE

- **Periodic law**: The chemical properties of the elements are periodic functions of the atomic number Z.

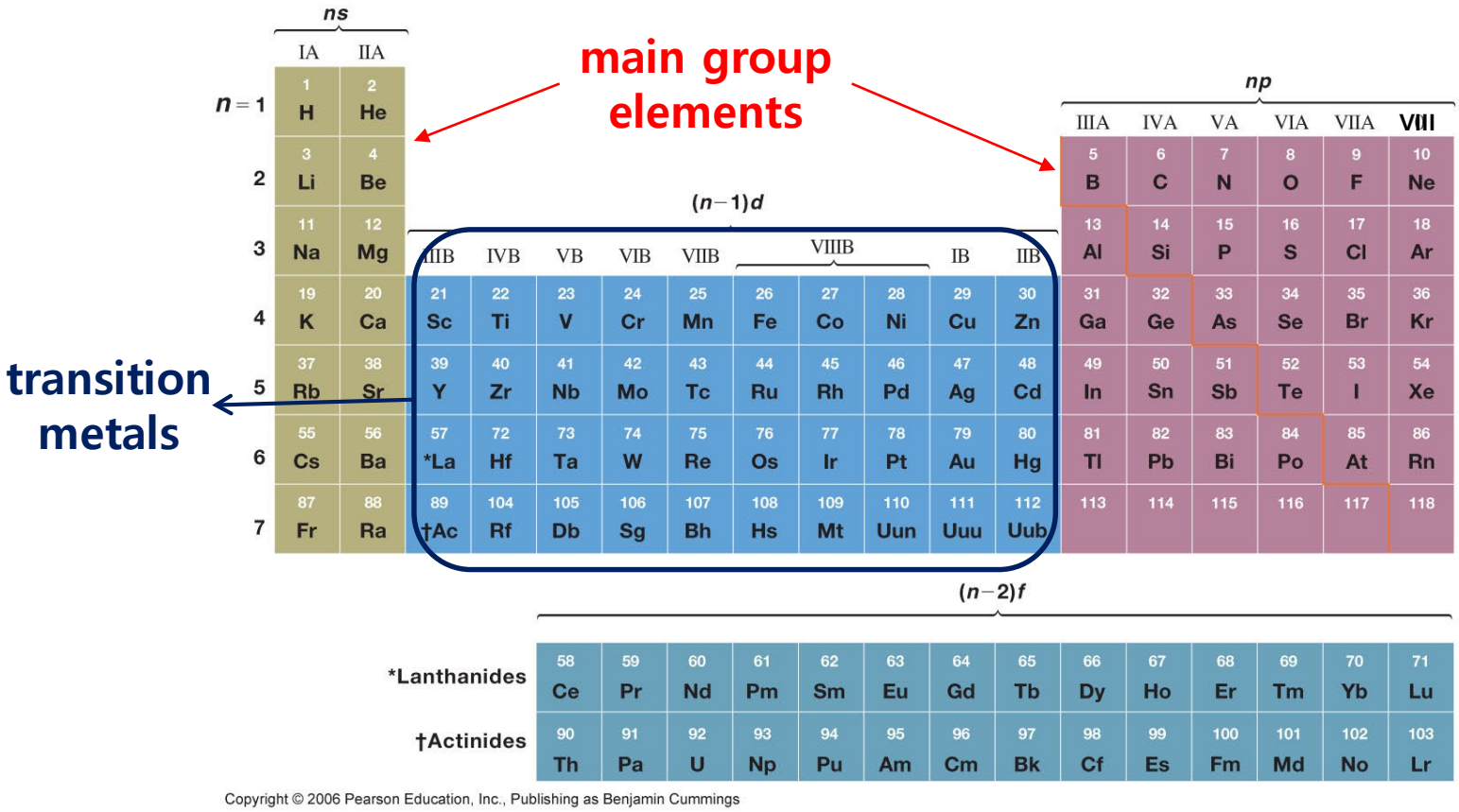



PERIOD
1 I
18 VIII
2 II
13 III
14 IV
15 V
16 VI
17 VII
TRANSITION ELEMENTS
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8
9 VIIIB
10
11 IB
12 IIB
1 H 1766
2 He 1895
3 Li 1817
4 Be 1798
5 B 1808
6 C
7 N 1772
8 O 1772
9 F 1887
10 Ne 1898
11 Na 1807
12 Mg 1756
13 Al 1827
14 Si 1823
15 P 1669
16 S
17 Cl 1774
18 Ar 1894
19 K 1807
20 Ca 1808
21 Sc 1879
22 Ti 1791
23 V 1830
24 Cr 1797
25 Mn 1774
26 Fe
27 Co 1735
28 Ni 1751
29 Cu
30 Zn 1746
31 Ga 1875
32 Ge 1886
33 As
34 Se 1817
35 Br 1826
36 Kr 1898
37 Rb 1861
38 Sr 1790
39 Y 1794
40 Zr 1789
41 Nb 1801
42 Mo 1778
43 Tc 1937
44 Ru 1844
45 Rh 1803
46 Pd 1803
47 Ag
48 Cd 1817
49 In 1863
50 Sn
51 Sb
52 Te 1782
53 I 1811
54 Xe 1898
55 Cs 1860
56 Ba 1808
71 Lu 1907
72 Hf 1923
73 Ta 1802
74 W 1781
75 Re 1925
76 Os 1803
77 Ir 1803
78 Pt 1735
79 Au
80 Hg
81 Tl 1861
82 Pb
83 Bi
84 Po 1898
85 At 1940
86 Rn 1900
87 Fr 1939
88 Ra 1898
103 Lr 1961
104 Rf 1965
105 Db 1970
106 Sg 1976
107 Bh 1976
108 Hs 1984
109 Mt 1982
110 Ds 1994
111 Rg 1995
112 Cn 1996
113 Uut
114 Uuq 1999
115 Uup
116 Uuh
117 Uus
118 Uuo
LANTHANIDES
57 La 1839
58 Ce 1803
59 Pr 1885
60 Nd 1843
61 Pm 1947
62 Sm 1879
63 Eu 1896
64 Gd 1880
65 Tb 1843
66 Dy 1886
67 Ho 1879
68 Er 1843
69 Tm 1879
70 Yb 1907
ACTINIDES
89 Ac 1899
90 Th 1828
91 Pa 1917
92 U 1789
93 Np 1940
94 Pu 1940
95 Am 1945
96 Cm 1944
97 Bk 1950
98 Cf 1950
99 Es 1952
100 Fm 1953
101 Md 1955
102 No 1958
Abundances by mass
> 0.1%
0.01–0.1%
0.001–0.01%
0.0001–0.001%
10^{-6}–10^{-4}%
< 10^{-6}%

- Periodic table places elements in **groups** (vertically) and **periods** (horizontally).



- Eight groups of **main-group elements (I to VIII)**
- Ten groups of **transition-metal elements (1B to VIIIB)**
- **Lanthanide elements** (atomic number 57-71)
  Actinide elements (atomic number 89-103)

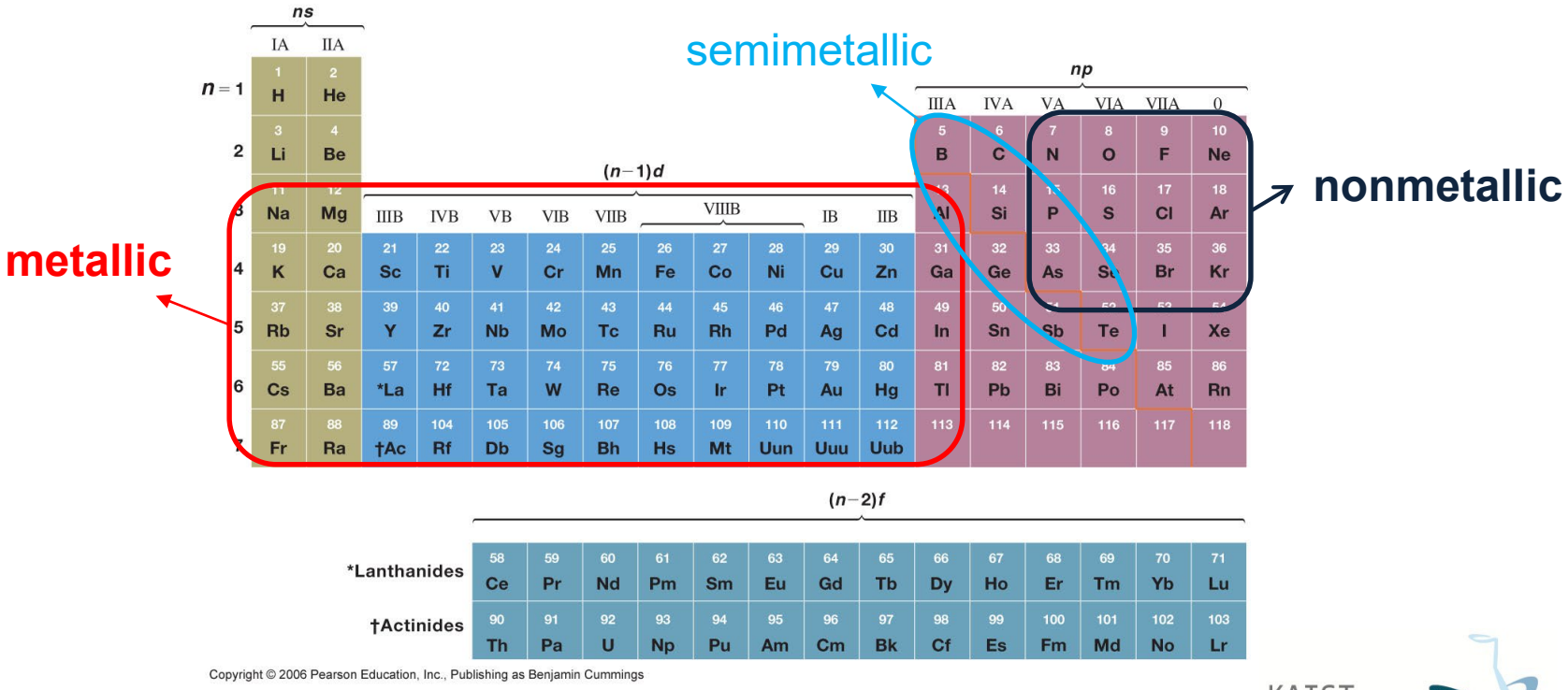


Physical and Chemical Properties

- **Metals** : metallic luster, good electricity and heat conductivity, malleability

Nonmetals : poor conductivity, brittleness

Metalloids (or semimetals) : resemble metals in some aspects and nonmetals in others



Group I
alkali metals

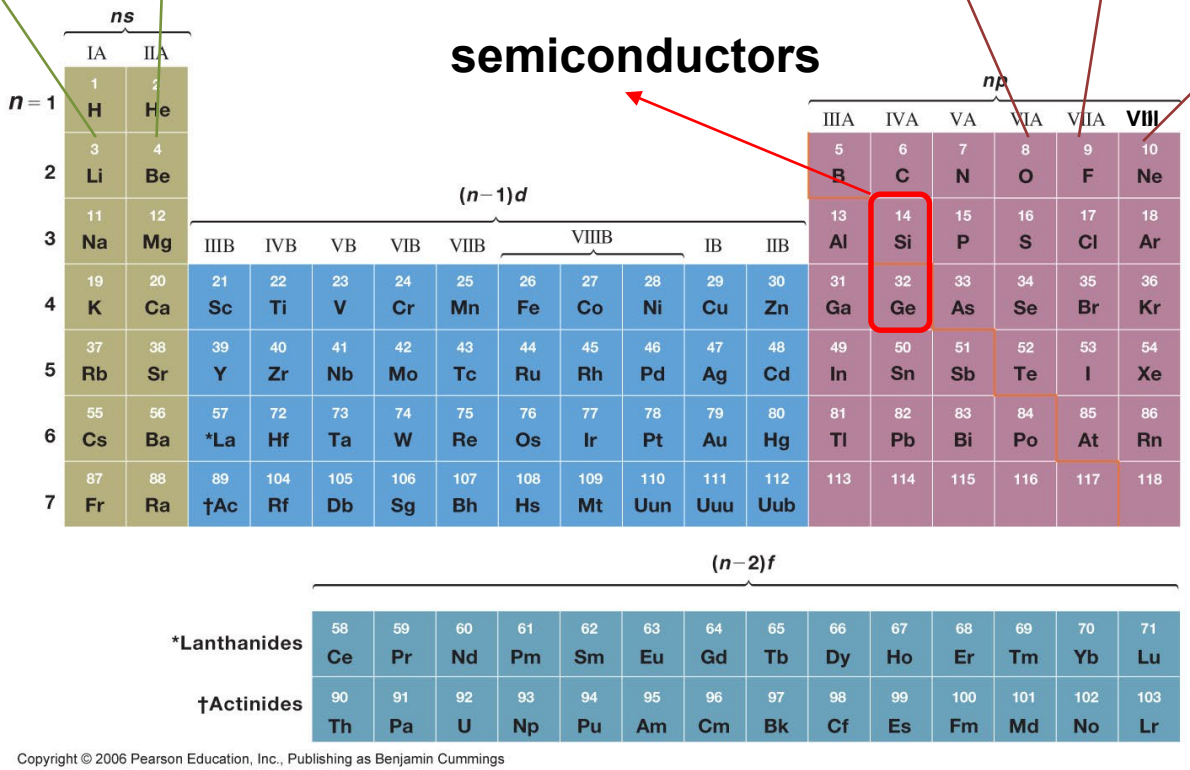
Group II
alkaline-earth metals

Group VI
chalcogens

Group VII
halogens

Group VIII
noble gases

semiconductors



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3.3 FORCES AND POTENTIAL ENERGY IN ATOMS

- By Coulomb's law,

$$F(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2} \qquad \text{potential} \qquad V(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

two charges, q_1 and q_2, distance r

permittivity of the vacuum, $\varepsilon_0 = 8.854 \times 10^{-12}\ C^2 J^{-1} m^{-1}$

- For Rutherford's planetary model with central nucleus of +Ze (*e* is magnitude of charge) surrounded by Z electrons, the potential energy associated with each electron,

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

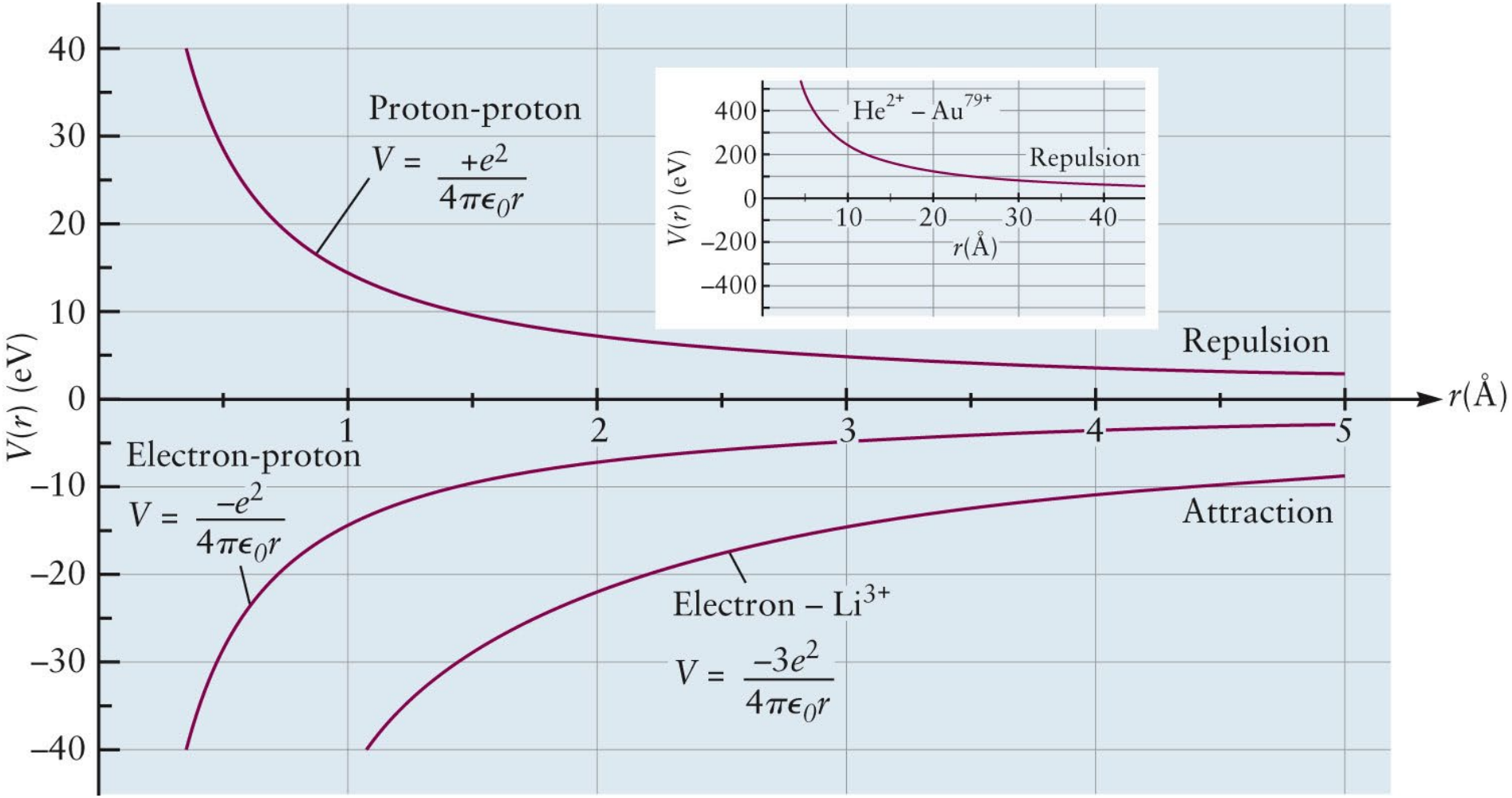
electron volt unit **eV**: kinetic energy gained by an electron accelerated through a potential difference of 1 volt. 1 eV = $1.60217646 \times 10^{-19}$ J.

i.e.) for a hydrogen atom, r = 1 Å

$$V(1\ Å) = -\frac{Ze^2}{4\pi\varepsilon_0 r} = -2.307 \times 10^{-18}\ J = -14.40\ eV$$

AN: ~6.02 X 10^{23}

ex) food calorie: ~1000 cal = 4.1843 kJ


Proton-proton
$V = \frac{+e^2}{4\pi\epsilon_0 r}$
Repulsion
Electron-proton
$V = \frac{-e^2}{4\pi\epsilon_0 r}$
Attraction
Electron – Li^{3+}
$V = \frac{-3e^2}{4\pi\epsilon_0 r}$
$V(r)$ (eV)
r(Å)
He^{2+} – Au^{79+}
Repulsion

- The force at any point on a potential energy curve $F = -\frac{dV}{dr}$

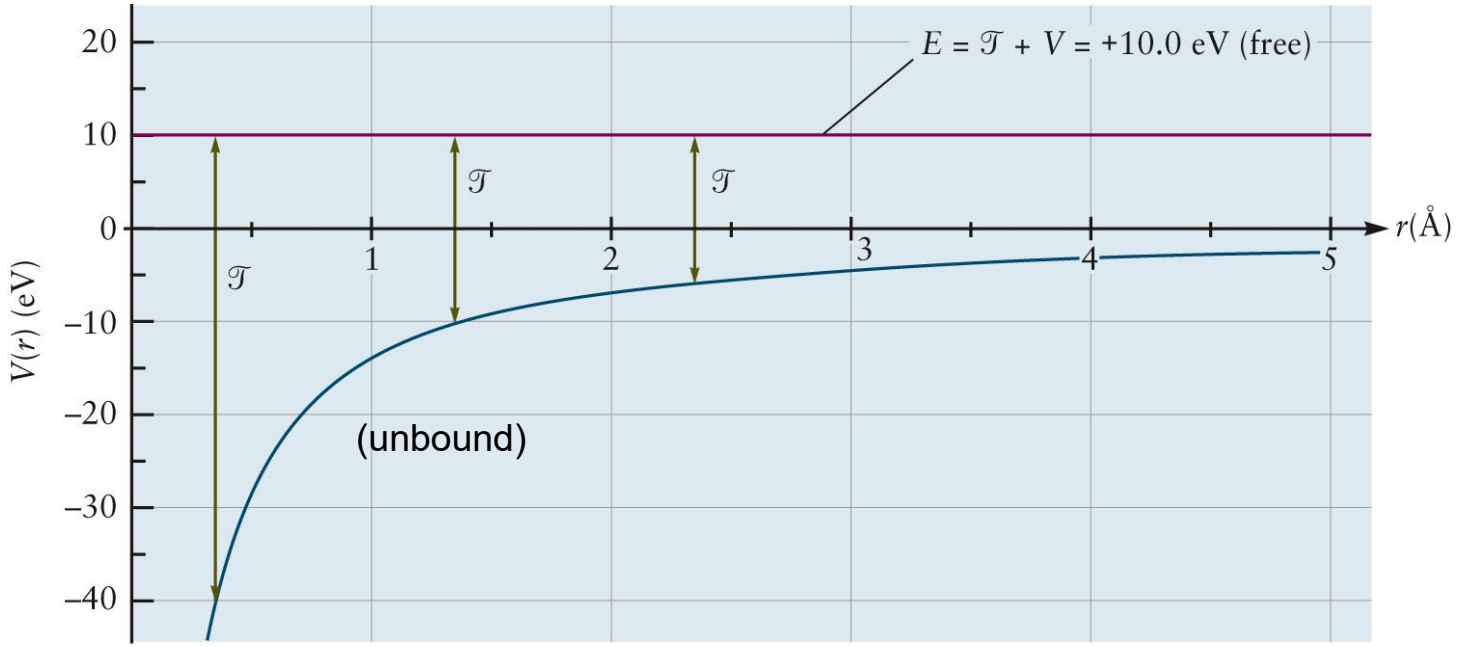
  The force between a proton and an electron,

$$F_{coul} = -\frac{d}{dr}\left(-\frac{Ze^2}{4\pi\varepsilon_0 r}\right) = \frac{d}{dr}\left(\frac{Ze^2}{4\pi\varepsilon_0 r}\right) = -\frac{Ze^2}{4\pi\varepsilon_0 r^2}$$

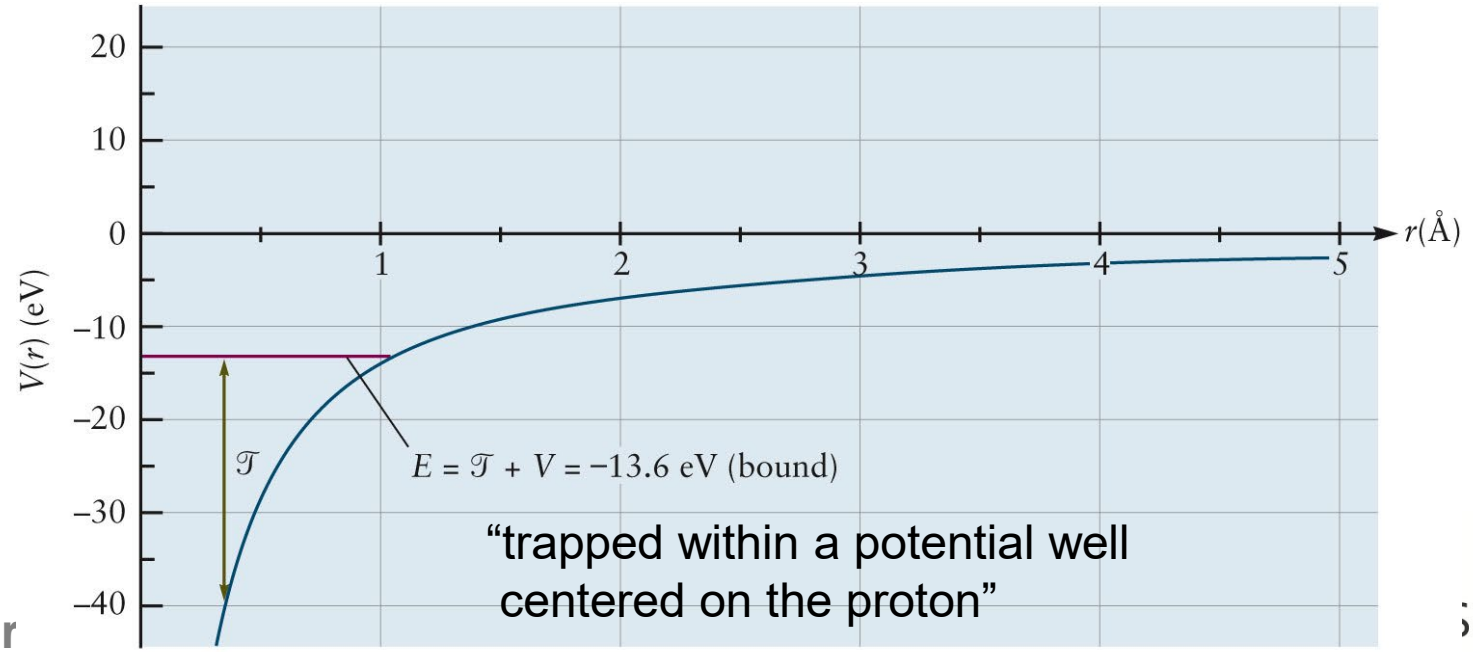
  is attractive at all positions and decreases in magnitude with increasing r.

- The total energy (kinetic and potential) of the electron in the hydrogen atom,

$$E = \frac{1}{2} m_e v^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$



(a)



(b)

"trapped within a potential well centered on the proton"

Gener

STRY

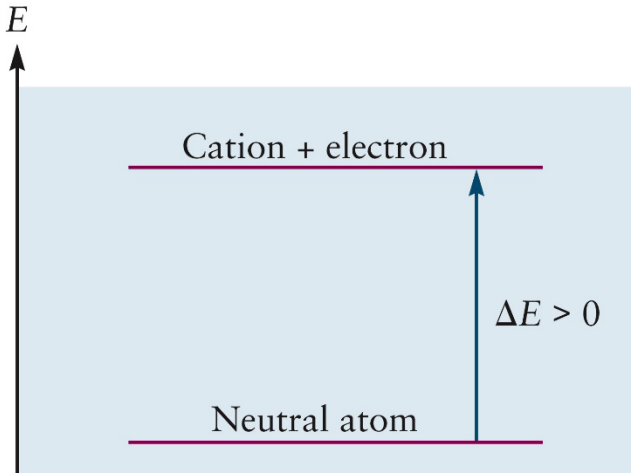
3.4 IONIZATION ENERGIES, THE SHELL MODEL OF THE ATOM, AND SHIELDING

- **Ionization energy, IE_1**

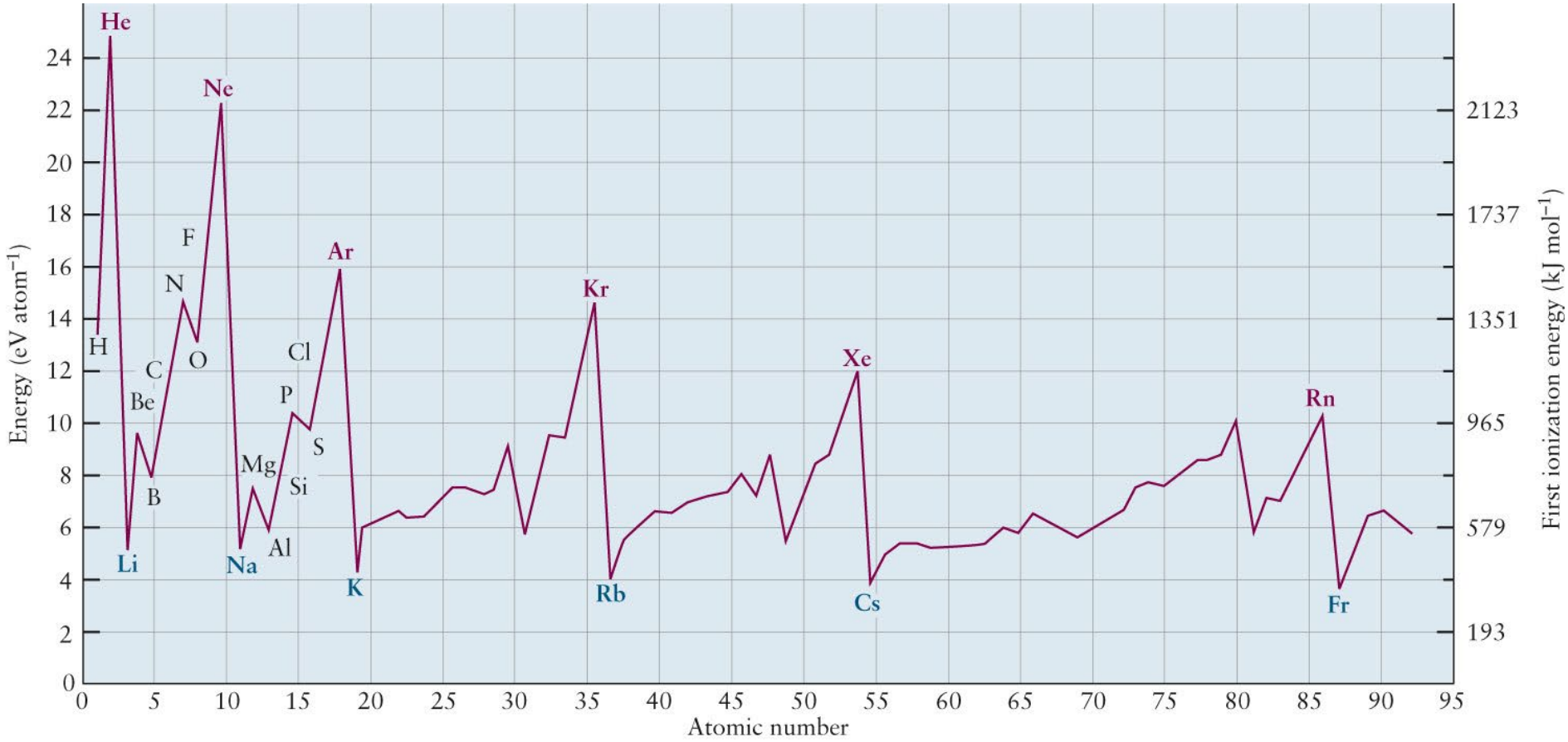
  the minimum energy necessary to remove an electron from a neutral atom in the gas phase and form positively charged ion in the gas phase

$$X(g) \longrightarrow X^+(g) + e \qquad \Delta E = IE_1$$

ΔE for ionization reactions is always positive.



- The values increase moving across a period (from left to right), becoming large for each noble gas atom, and then fall abruptly for the alkali atom at the beginning of the next period.



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- **The second ionization energy, IE_2**

  the minimum energy required to remove a second electron

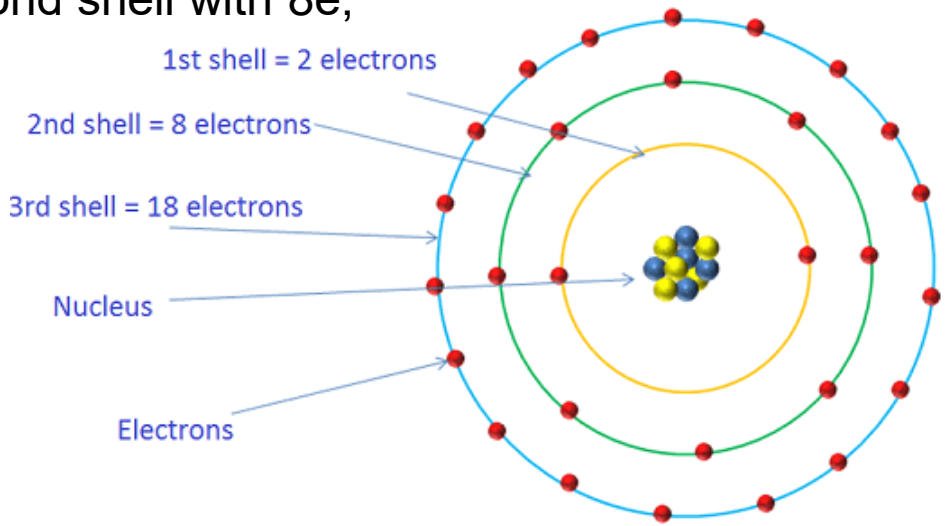
  $X^+(g) \longrightarrow X^{2+}(g) + e \qquad \Delta E = IE_2$

- The third, fourth, and higher ionization energies…

- **Shell model for atomic structure**

  The electrons are grouped into shells based upon the energy required to remove them from the atom.
  The shells correspond to the periods of the periodic table.

  i.e.) The first shell with 2e; the second shell with 8e, and the third shell with 8e



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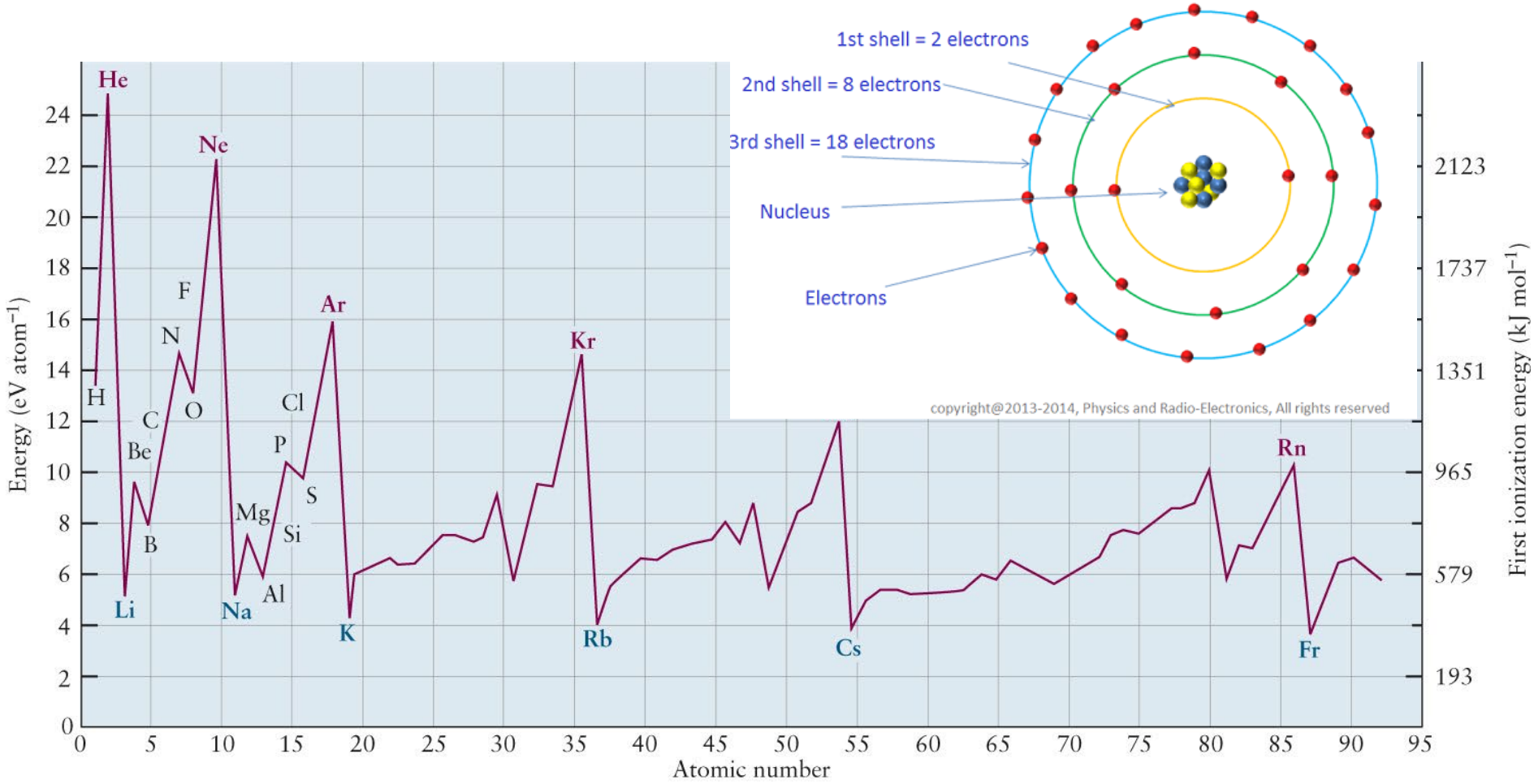

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TABLE 3.1

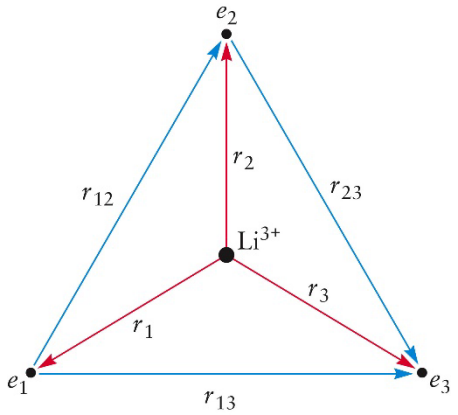
Successive Ionization Energies of the Elements Hydrogen through Argon (in eV Atom^{-1})

Z	Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7	IE_8	IE_9	IE_{10}
1	H	13.60									
2	He	24.59	54.42								
3	Li	5.39	75.64	122.45							
4	Be	9.32	18.21	153.89	217.71						
5	B	8.30	25.15	37.93	259.37	340.22					
6	C	11.26	24.38	47.89	64.49	392.08	489.99				
7	N	14.53	29.60	47.45	77.47	97.89	552.06	667.03			
8	0	13.62	35.12	54.93	77.41	113.90	138.12	739.32	871.39		
9	F	17.42	34.97	62.71	87.14	114.24	157.16	185.18	953.89	1103.08	
10	Ne	21.56	40.96	63.45	97.11	126.21	157.93	207.27	239.09	1195.79	1362.16
11	Na	5.14	47.29	71.64	98.91	138.39	172.15	208.47	264.18	299.87	1465.10
12	Mg	7.65	15.04	80.14	109.24	141.26	186.50	224.94	265.90	327.94	367.53
13	Al	5.99	18.83	28.45	119.99	153.71	190.47	241.43	284.59	330.21	398.57
14	Si	8.15	16.35	33.49	45.14	166.77	205.05	246.52	303.17	351.10	401.43
15	P	10.49	19.73	30.18	51.37	65.02	220.43	263.22	309.41	371.73	424.50
16	S	10.36	23.33	34.83	47.30	72.68	88.05	280.93	328.23	379.10	447.10
17	Cl	12.97	23.81	39.61	53.46	67.8	97.03	114.19	348.28	400.03	455.62
18	Ar	15.76	27.63	40.74	59.81	75.02	91.01	124.32	143.46	422.43	478.68
19	K	4.34	31.63	45.72	60.91	82.66	100.0	117.56	154.86	175.82	503.44
20	Ca	6.11	11.87	50.91	67.10	84.41	108.78	127.7	147.24	188.54	211.27
21	Sc	6.54	12.80	24.76	73.47	91.66	111.1	138.0	158.7	180.02	225.32

The Shell Model of the Atom

For Li with Z = 3,

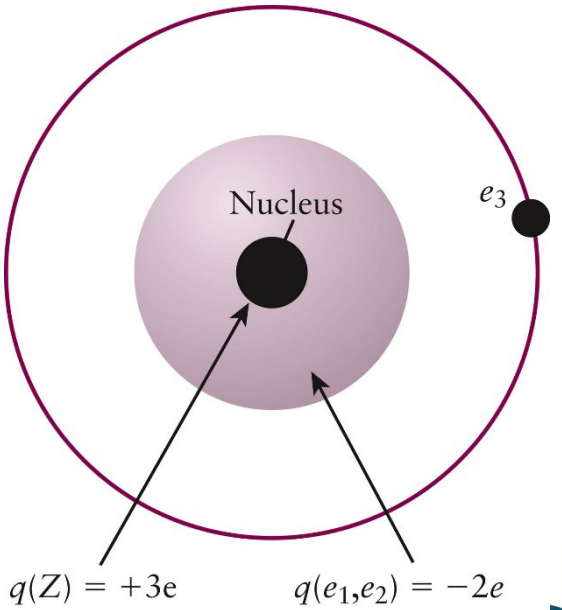
$$V = \frac{Ze^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{r_3}\right) + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}\right)$$



- **Effective potential energy**

  Taking into account both the attractive electron-nuclear forces and the average of the repulsive force among the electrons.

$$V_{eff}(r) = -\frac{Z_{eff}e^2}{4\pi\varepsilon_0 r}$$



The Shell Model of the Atom and Periodic Behavior in Chemical Bonding

- Electrons in the inner shells (core electrons) do not participate significantly in the chemical reactions.

- The outmost, partially filled shell (valence shell) contains the electrons involved in chemical bonding, the valence electrons.

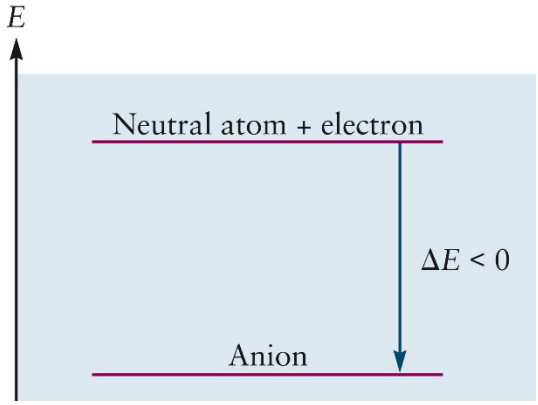
Z	Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7	IE_8	IE_9	IE_{10}
11	Na	5.14	47.29	71.64	98.91	138.39	172.15	208.47	264.18	299.87	1465.10
12	Mg	7.65	15.04	80.14	109.24	141.26	186.50	224.94	265.90	327.94	367.53
13	Al	5.99	18.83	28.45	119.99	153.71	190.47	241.43	284.59	330.21	398.57
14	Si	8.15	16.35	33.49	45.14	166.77	205.05	246.52	303.17	351.10	401.43
15	P	10.49	19.73	30.18	51.37	65.02	220.43	263.22	309.41	371.73	424.50
16	S	10.36	23.33	34.83	47.30	72.68	88.05	280.93	328.23	379.10	447.10
17	Cl	12.97	23.81	39.61	53.46	67.8	97.03	114.19	348.28	400.03	455.62
18	Ar	15.76	27.63	40.74	59.81	75.02	91.01	124.32	143.46	422.43	478.68

3.5 ELECTRON AFFINITY

- An anion is formed by the electron attachment reaction,

$X(g) + e \longrightarrow X^-(g)$ $\quad\quad$ ΔE = electron attachment energy

- **exothermic**, Energy is released



➢ **Electron affinity, EA_X**

the energy required to detach the electron from the anion X^- and give the neutral atom

$X^-(g) \longrightarrow X(g) + e$ $\quad\quad$ $\Delta E = EA_X$

TABLE 3.2

Electron Affinity of Selected Atoms (in kJ mol^{-1})

H							**He**
73							*
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
60	*	27	122	*	141	328	*
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
53	*	42	134	72	200	349	*
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
48	2	41	119	79	195	325	*
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
47	5	29	107	101	190	295	*
Cs	**Ba**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
46	14	19	35	91	183	270	*

*No stable anion A^- exists for this element in the gas phase.

3.6 ELECTRONEGATIVITY: THE TENDENCY OF ATOMS TO ATTRACT ELECTRONS IN MOLECULES

➢ **Mulliken's electronegativity scale**

- electronegativity: measuring the tendency to attract electrons

EN (Mulliken) = $\frac{1}{2}$ C (IE_1 + EA) C (energy)$^{-1}$

- **Electron acceptors** (halogens)
  large IE_1 + large EA = highly electronegative

- **Electron donors** (alkali metals)
  small IE_1 + small EA = electropositve

➢ Pauling's electronegativity scale

- ionic character: partial charge separation in the bond

- **excess bond energy** Δ: ionic character due to partial charge transfer

$$\Delta = \Delta EAB - \sqrt{\Delta EAA \Delta EBB}$$

ΔEAA = A-A bond dissociation energy

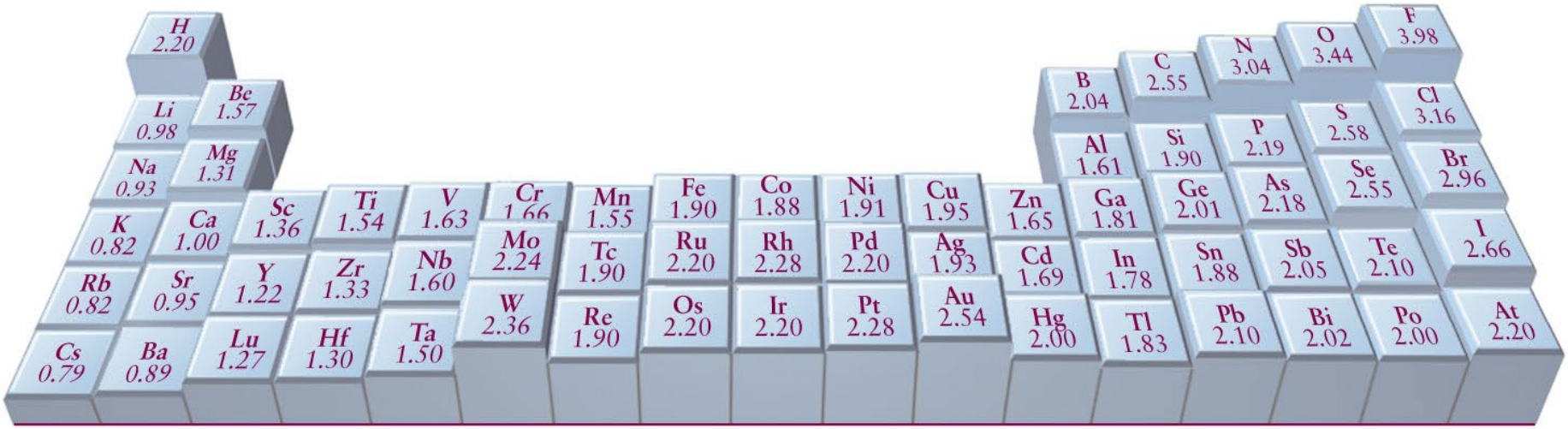
$\sqrt{\Delta EAA \Delta EBB}$ = covalent contribution of A-B

- **Electronegativity c**

$$c_A - c_B = 0.102\ \Delta^{1/2}$$

Δ in kJ mol^{-1}

➢ Modern electronegativity scale: relatively measured with respect to F



- The nature of the bond

EN difference	~ 0	covalent
	0.2 ~ 2	polar covalent
	> 2	ionic

3

CHAPTER

CHEMICAL BONDING: THE CLASSICAL DESCRIPTION

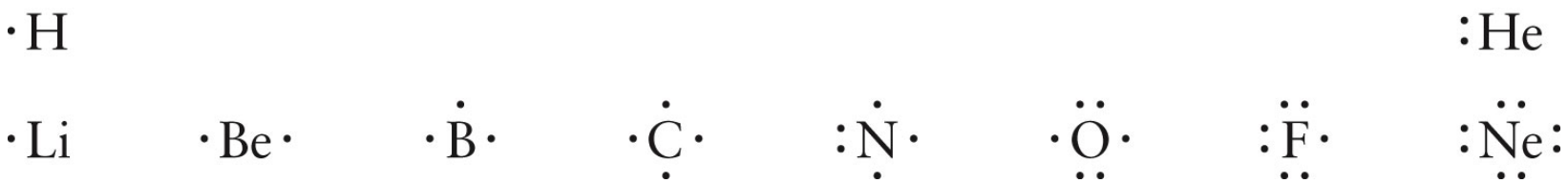
KAIST CHEMISTRY

3.8 IONIC BONDING

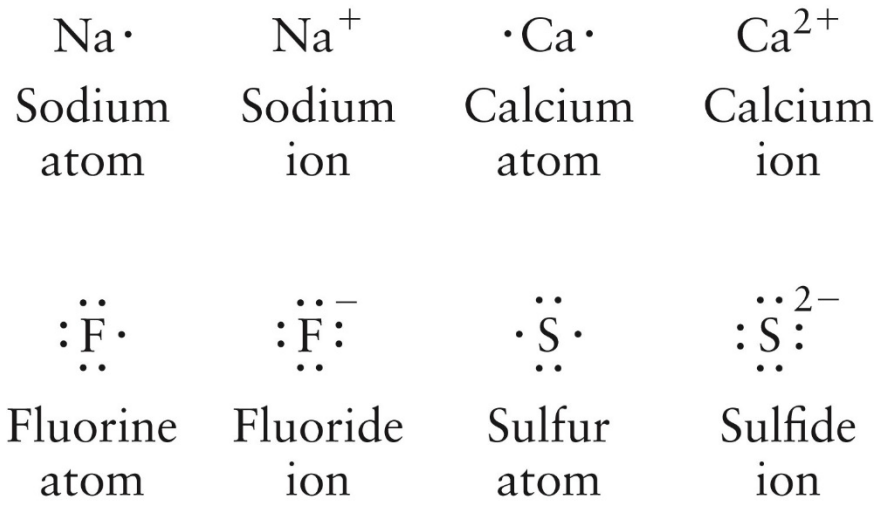
- **Lewis model**: representing the valence electrons as dots arranged around the chemical symbol for an atom.

  The first four dots are arranged individually around The four sides of the symbol for each element.

  If > 4 valence electrons, dots are then paired.



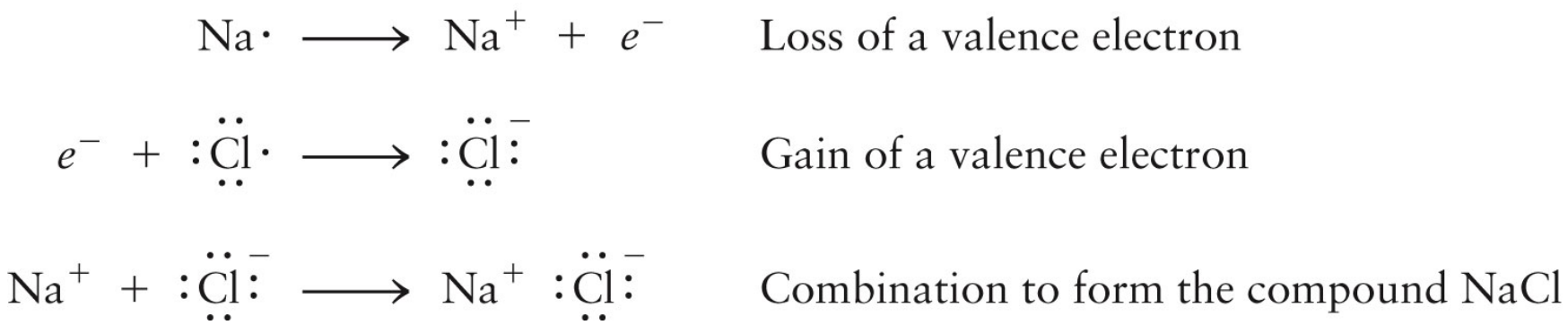
- Positive and negative ions

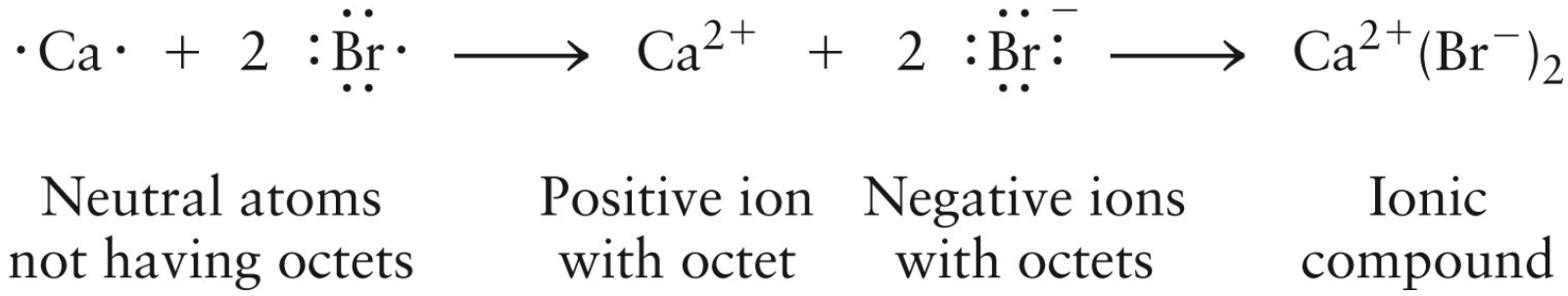


- Special stability results when an atom forms an ion whose outermost shell has the same number of electrons as of a noble-gas atom.

  i.e.) H, He: 2; the first few periods: 8 electrons, **octet**

- Lewis symbols with the formation first of a cation and anion then of an ionic compound.





- The energetics of formation of an ionic bond from two neutral gas-phase atoms (for potassium and fluorine),

$K \longrightarrow K^+ + e^-$ $\quad\quad \Delta E = IE_1 = +419\ kJ\ mol^{-1}$

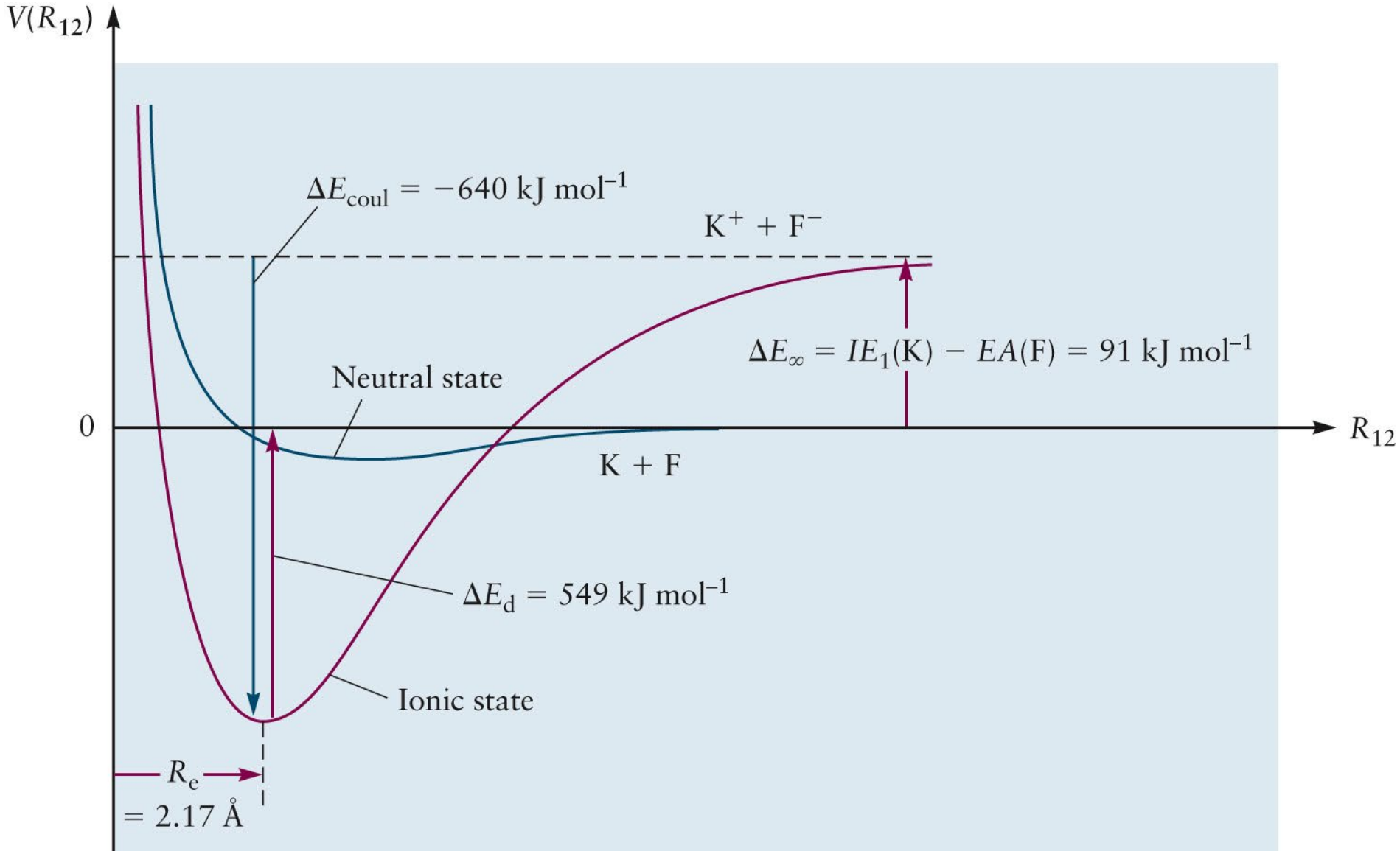
$F + e^- \longrightarrow F^-$ $\quad\quad \Delta E = -EA = -328\ kJ\ mol^{-1}$

$\Delta E_\infty = IE_1(K) - EA(F) = +91\ kJ\ mol^{-1}$

- Although the total potential energy increases, as the atoms approach with each other, their potential energy becomes negative due to Coulombic attraction forces.

$V(R_{12}) = \frac{q_1 q_2}{4\pi\varepsilon_0 R_{12}}$ (J per ion pair) $\quad\quad R_{12}$ = the separation of the ions

$= \frac{q_1 q_2}{4\pi\varepsilon_0 R_{12}} \frac{N_A}{10^3}$ (kJ mol^{-1})



- In the potential curve,

$$V(R_{12}) = Ae^{-\alpha R_{12}} - B\left(\frac{(e)(-e)}{R_{12}}\right) + \Delta E_{\infty}$$

repulsion

attraction
coulomb stabilization energy

- Dissociation energy

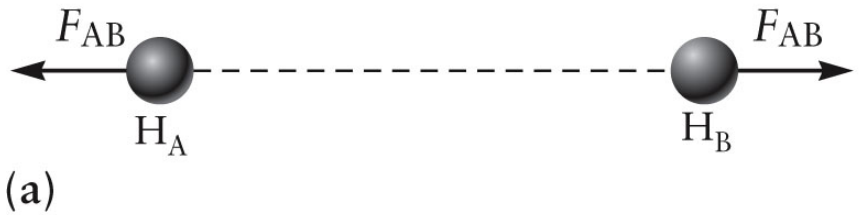
$$\Delta E_d \approx - \frac{q_1 q_2}{4\pi\varepsilon_0 R_e} \frac{N_A}{10^3} - \Delta E_{\infty}$$

where $\Delta E_{\infty} = IE_1(K) - EA(F)$

- In the real molecules, all bonds have some degree of covalency, and each ion shows polarization of the electron density.

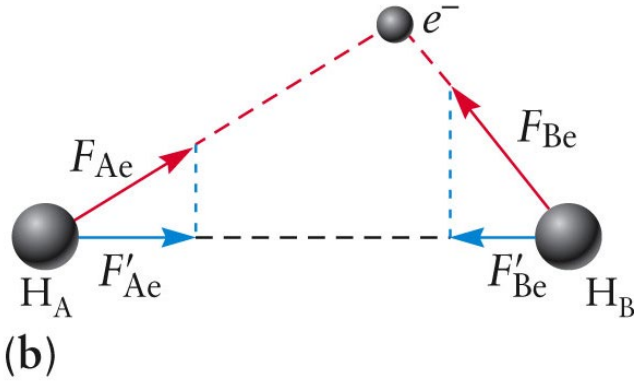
3.9 COVALENT AND POLAR COVALENT BONDING

- Origin of the covalent bond for H_2^+



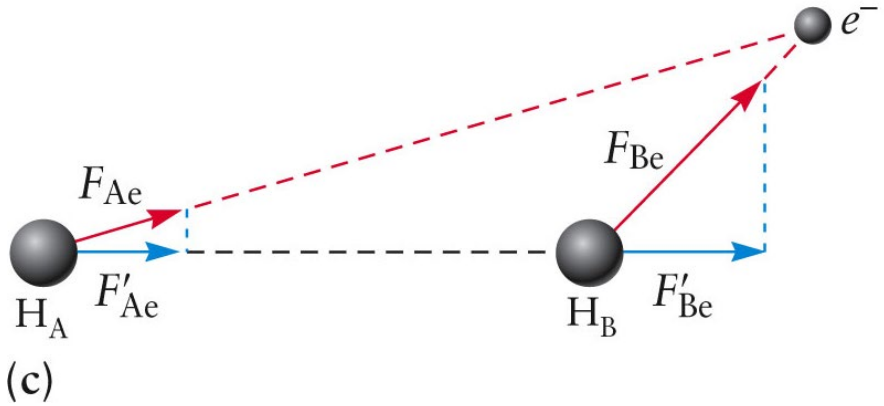
internuclear repulsion force

$$F_{AB} \propto \frac{(+ZAe)(+ZBe)}{R_{AB}^2}$$

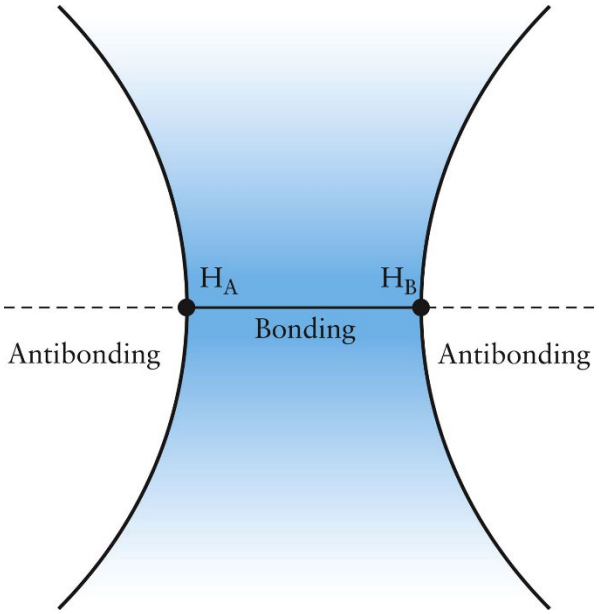


electron-nuclear attractive force

$$F_{Ae} \propto \frac{(-e)(+ZAe)}{r_{Ae}^2} \qquad F_{Be} \propto \frac{(-e)(+ZBe)}{r_{Be}^2}$$



an electron positioned in a region that will tend to pull the nuclei apart



Bonding region to pull the nuclei together

Antibonding region to pull the nuclei apart

For H_2^+, R_e = 1.06 Å,
ΔE_d = 255.5 kJ mol^{-1}

➢ **Bond Length**: the distance between the nuclei of the two atoms

TABLE 3.3

Properties of Diatomic Molecules

Molecule	Bond Length (Å)	Bond Energy (kJ mol^{-1})
H_2	0.751	433
N_2	1.100	942
O_2	1.211	495
F_2	1.417	155
Cl_2	1.991	240
Br_2	2.286	190
I_2	2.669	148
HF	0.926	565
HCl	1.284	429
HBr	1.424	363
HI	1.620	295
ClF	1.632	252
BrF	1.759	282
BrCl	2.139	216
ICl	2.324	208
NO	1.154	629
CO	1.131	1073

TABLE 3.4

Reproducibility of Bond Lengths

Bond	Molecule	Bond Length (Å)
O—H	H_2O	0.958
	H_2O_2	0.960
	HCOOH	0.95
	CH_3OH	0.956
C—C	Diamond	1.5445
	C_2H_6	1.536
	CH_3CHF_2	1.540
	CH_3CHO	1.50
C—H	CH_4	1.091
	C_2H_6	1.107
	C_2H_4	1.087
	C_6H_6	1.084
	CH_3Cl	1.11
	CH_2O	1.06

Bond lengths measured experimentally by rotational spectroscopy.

➢ **Bond Energy** (or bond dissociation energy), ΔE_d

The energy required to break one mole of the particular bond

i.e.) $H_2(g) \rightarrow 2H(g)$ $\Delta E = \Delta E_d = 433$ kJ mol^{-1}

- Bonds generally grow weaker with increasing atomic number.

i.e.) HF > HCl > HBr> HI

- Bond strength decreases dramatically in the diatomic molecules from N_2 (942 kJ mol^{-1}) to O_2 (495 kJ mol^{-1}) to F_2 (155 kJ mol^{-1}).

➢ Bond Order

the number of shared electron pairs between the two atoms.
predicted by models of covalent bond formation.

TABLE 3.5

Three Types of Carbon–Carbon Bonds

Bond	Molecule	Bond Length (Å)	Bond Energy (kJ mol^{-1})
C—C	C_2H_6 (or H_3CCH_3)	1.536	345
C=C	C_2H_4 (or H_2CCH_2)	1.337	612
C≡C	C_2H_2 (or HCCH)	1.204	809

TABLE 3.6

Average Bond Lengths (in Å)

C—C	1.54	N—N	1.45	C—H	1.10
C=C	1.34	N=N	1.25	N—H	1.01
C≡C	1.20	N≡N	1.10	O—H	0.96
C—O	1.43	N—O	1.43	C—N	1.47
C=O	1.20	N=O	1.18	C≡N	1.16

➢ Polar covalent bond

bonds in which there is a partial transfer of charge
not fully ionic nor fully covalent, but instead a mixture

EN difference	~ 0	covalent
	0.2 ~ 2	polar covalent
	> 2	ionic

➢ Dipole moment, μ

If two charges of equal magnitude and opposite sign, +q and –q,
are separated by a distance R,

$\mu = qR$ unit: 1 D (debye) = 3.336×10^{-30} C m

If δ is the fraction of a unit charge in a diatomic molecule ($q = \delta e$),

$\mu(D) = [R(Å)/0.2082\ Å]\ \delta$

i.e.) HF $\mu = 1.82$ D, $R = 0.917$ Å, $\delta = 0.41$

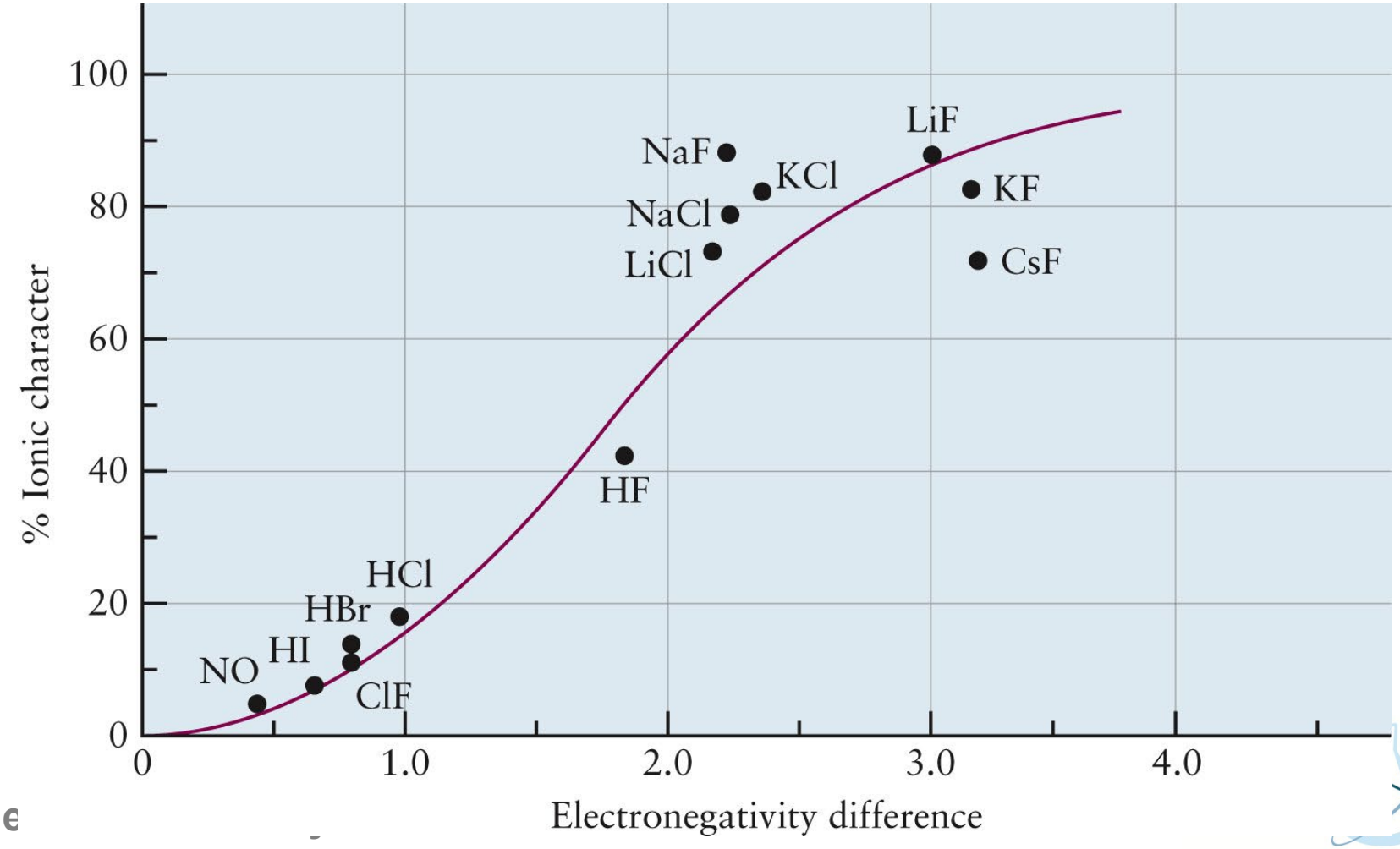
TABLE 3.7

Dipole Moments of Diatomic Molecules

Molecule	Bond Length (Å)	Dipole Moment (D)	% Ionic Character (100 δ)
H_2	0.751	0	0
CO	1.131	0.112	2
NO	1.154	0.159	3
HI	1.620	0.448	6
ClF	1.632	0.888	11
HBr	1.424	0.828	12
HCl	1.284	1.109	18
HF	0.926	1.827	41
CsF	2.347	7.884	70
LiCl	2.027	7.129	73
LiH	1.604	5.882	76
KBr	2.824	10.628	78
NaCl	2.365	9.001	79
KCl	2.671	10.269	82
KF	2.176	8.593	82
LiF	1.570	6.327	84
NaF	1.931	8.156	88

- **Percent ionic character**: degree of full charge (δ) x 100%

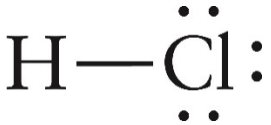
  - The degree of ionic character is reasonably correlated with the Pauling EN differences.



3.10 ELECTRON PAIR BONDS AND LEWIS DIAGRAMS FOR MOLECULS

- **Lewis diagram for the molecule**: the valence electrons from each atoms are redistributed and shared by the two atoms.

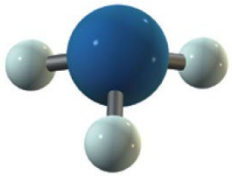
- A shared pair of electrons by a short line (-)



- **Octet rule**: Whenever possible, the electrons in a covalent compound are distributed in such a way that each main group element (except H) is surrounded by eight electrons (an octet).

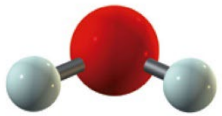
  For the octet, the atom attains the special stability of a noble-gas shell.

- **lone pairs**: the unshared electron pairs



(a)

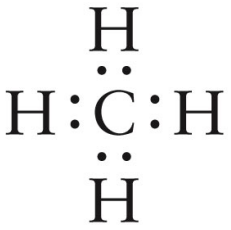
NH_3

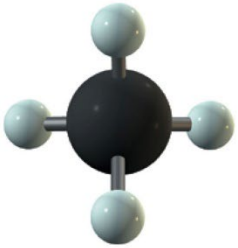


(b)

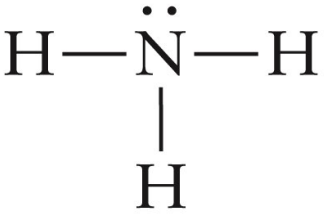
H_2O

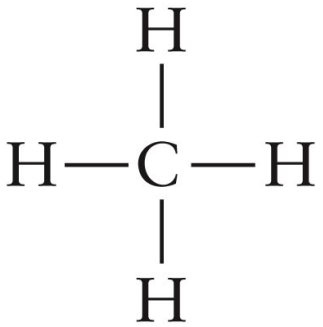
CH_4





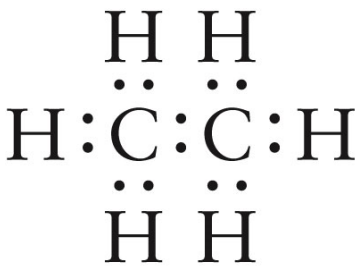
(c)

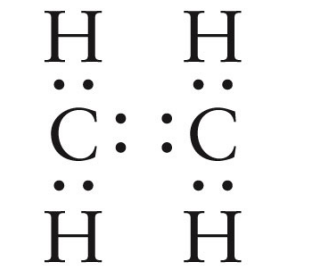


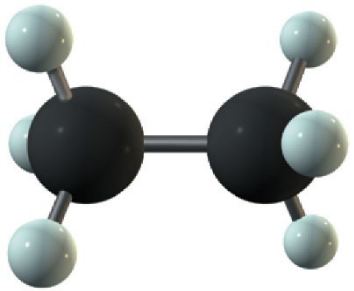


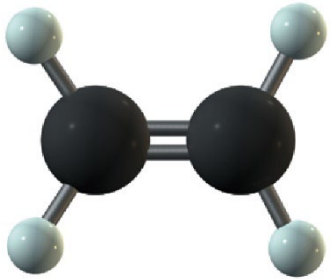
For O_2,  or

For N_2,  or 



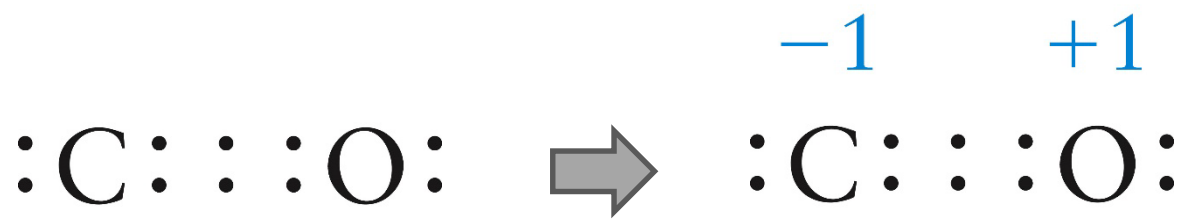


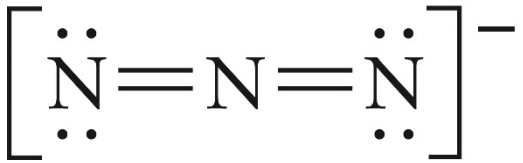


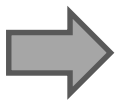


- **Formal charge**: the charge an atom in a molecule would have if the electrons in this Lewis diagram were divided equally among the atoms that share them.

$$\text{formal charge} = \text{number of valence electrons} - \text{number of electrons in lone pairs} - \frac{1}{2}\left(\text{number of electrons in bonding pairs}\right)$$







?

Drawing Lewis Diagram

1. Count and add the **valence electrons** from all the atoms present.

2. Calculate the total number of electrons needed if each atom has its own noble-gas shell of electrons around it (following **octet**).

3. **Bonding electrons** = # in step 2 - # in step 1

4. Assign two bonding electrons to each **bond**.

5. Assign **double or triple bonds**.
   double bonds for C, N, O, S; triple bonds for C, N, O

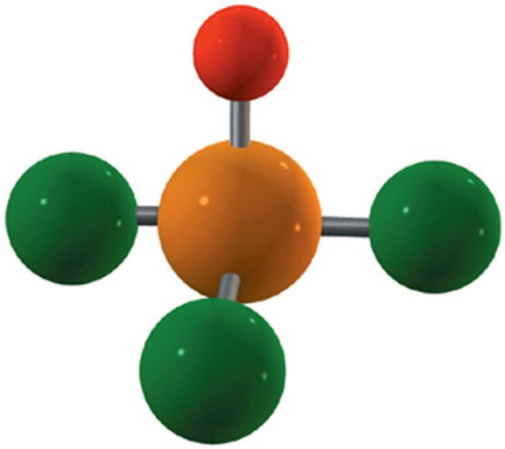
6. Assign the remaining electrons as **lone pairs** to the atoms.

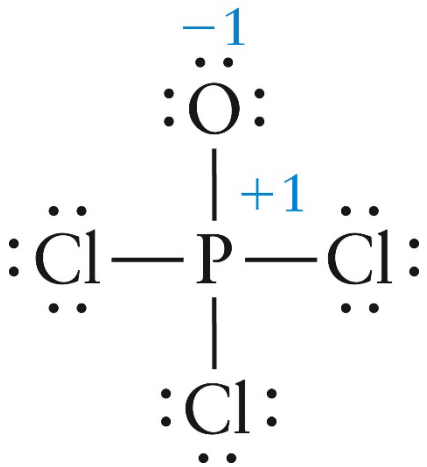
7. Determine the **formal charge**.

8. If more than one diagram possible, choose the one with the **smallest magnitudes** of formal charge, and with any negative formal charges placed on the most electronegative atoms.

Example 3.9

Write a Lewis electron dot diagram for phosphoryl chloride, $POCl_3$. Assign formal charges to all the atoms.

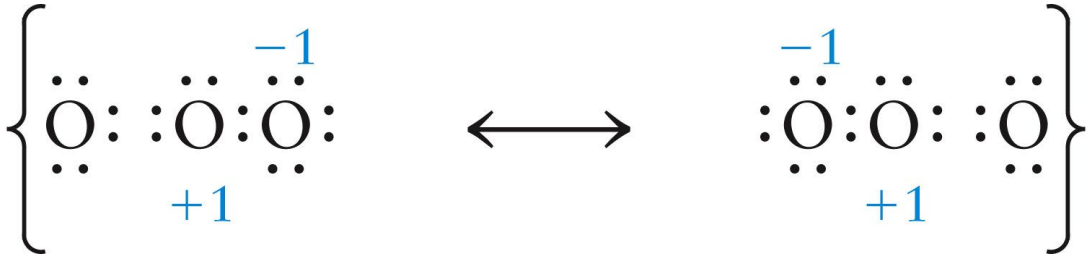




Resonance Forms

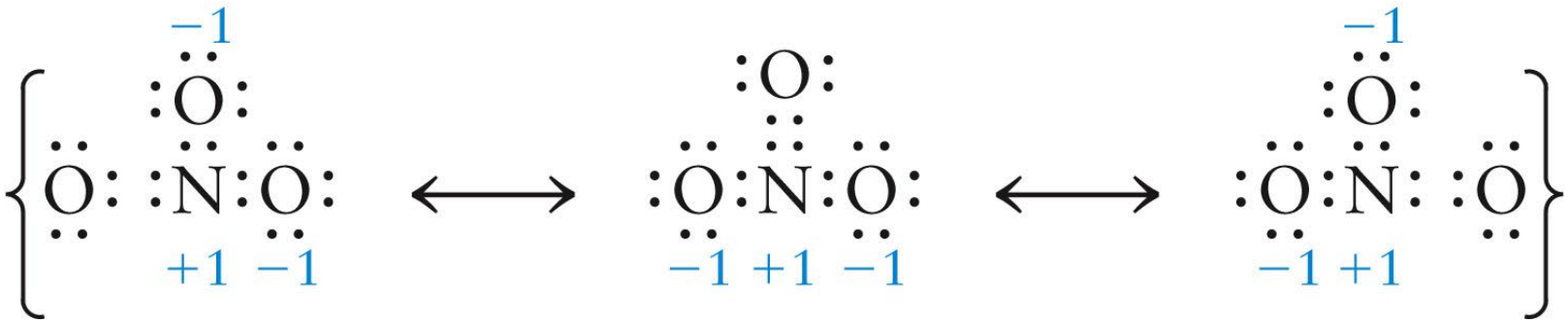
- For ozone (O_3), multiple equivalent Lewis diagrams can be written.
  The O-O bonds are identical, with the bond length in between.

➢ **Resonance**: a hybrid including features of each of the acceptable individual diagram.



Example 3.10

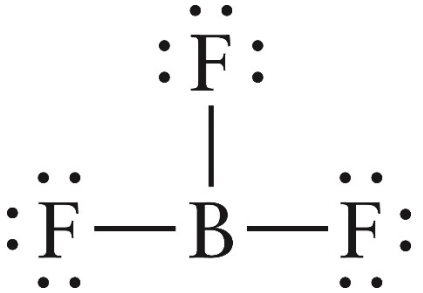
Draw three resonance forms for the nitrate ion NO_3^-, and estimate the bond lengths.



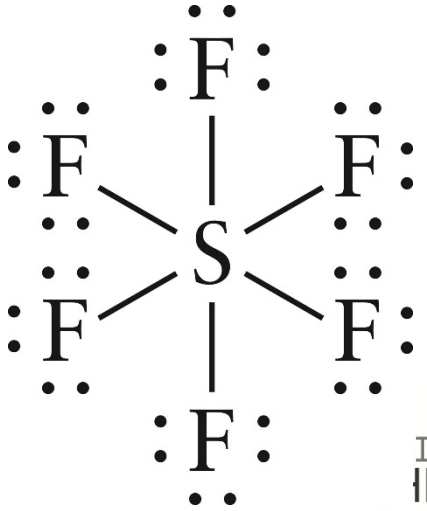
Breakdown of the Octet Rule

Case 1: Odd-Electron Molecules

Case 2: Octet-Deficient Molecules

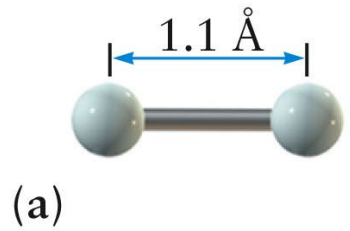


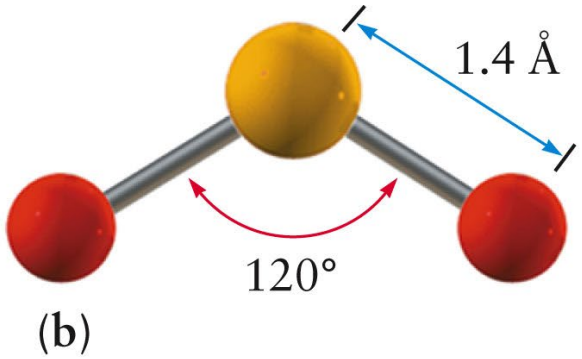
Case 3: Valence Shell Expansion



3.11 THE SHAPES OF MOLECULES: VALENCE SHELL ELECTRON-PAIR REPULSION THEORY

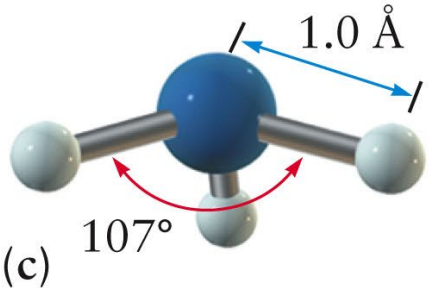
H_2

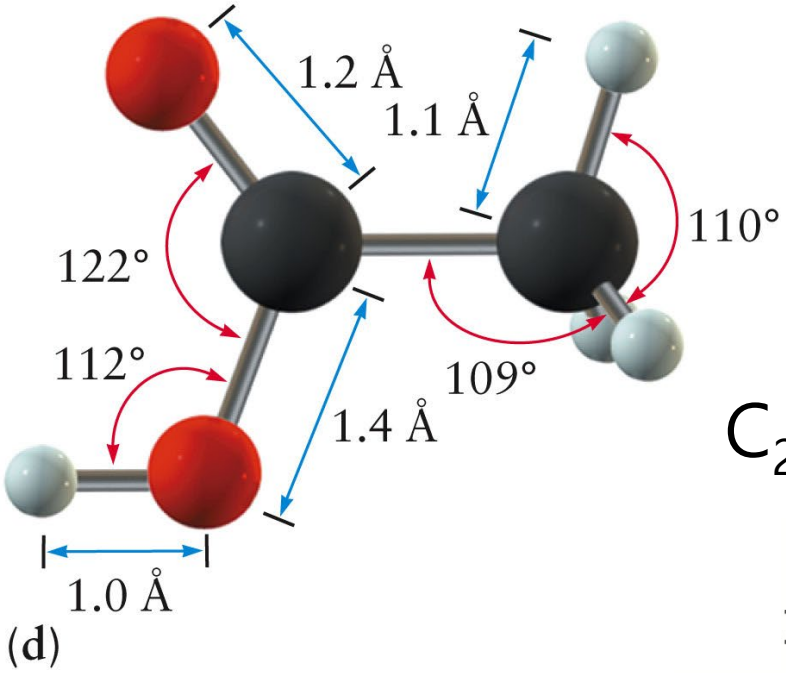




SO_2

NH_3





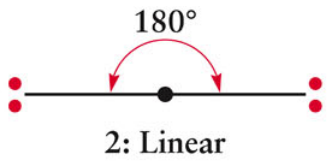
$C_2H_4O_2$

➢ The Valence Shell Electron-Pair Repulsion Theory (VSEPR)

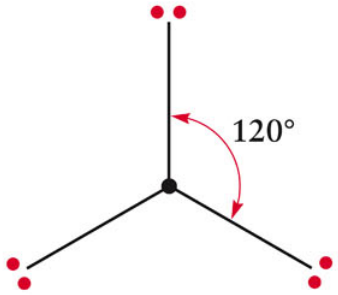
- Electron pairs in the valence shell of an atom repel each other. The arrangement depends on the number of electron pairs.

- **steric number, SN**, determined from the Lewis diagram.

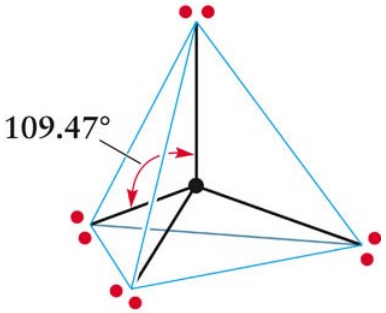
$$SN = \begin{pmatrix}\text{number of atoms}\\ \text{bonded to central atom}\end{pmatrix} + \begin{pmatrix}\text{number of lone pairs}\\ \text{on central atom}\end{pmatrix}$$



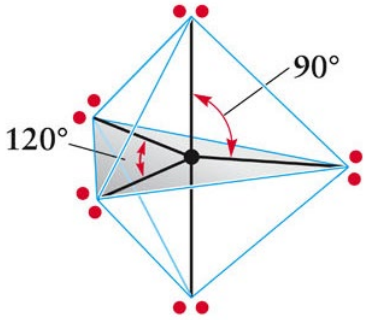
2: Linear



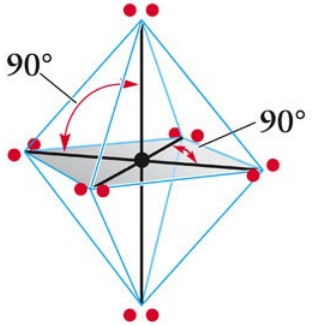
3: Trigonal planar



4: Tetrahedral



5: Trigonal bipyramidal



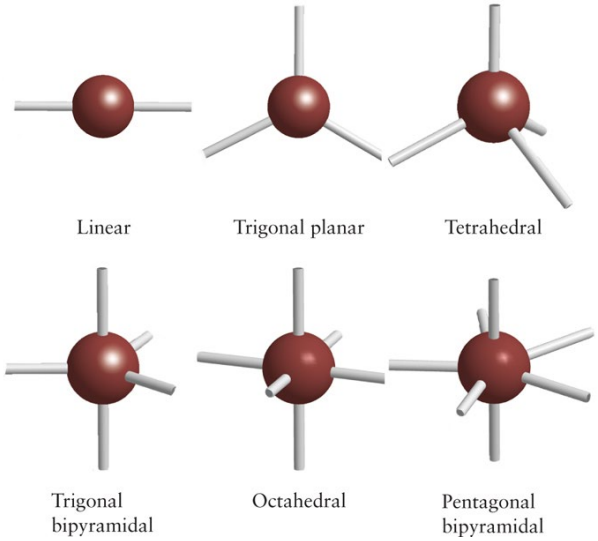
6: Octahedral

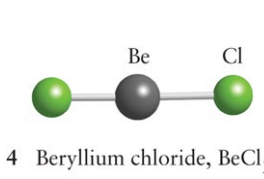
➢ Generic "VSEPR formula", AX_nE_m

- A = central atom; X_n = n atoms bonded to central atom
  E_m = m lone pairs on central atom

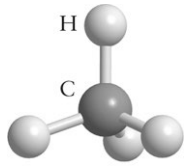
  i.e. BF_3 (AX_3), SO_3^{2-} (AX_3E), CH_4 (AX_4), PCl_5 (AX_5)

➢ **Rule 1** Regions of high electron concentration (bonds and lone pairs on the central atom) repel one another and, to minimize their repulsions, these regions move as far apart as possible while maintaining the same distance from the central atom.

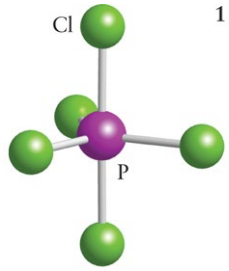




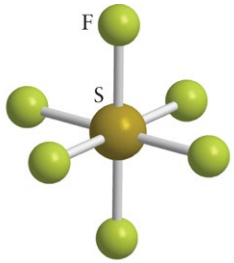
4 Beryllium chloride, $BeCl_2$



1 Methane, CH_4



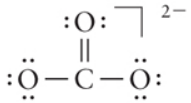
3 Phosphorus pentachloride, PCl_5



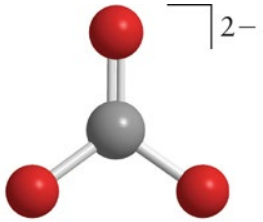
2 Sulfur hexafluoride, SF_6

- **Rule 2** There is no distinction between single and multiple bonds: a multiple bond is treated as a single regions of high electron concentration.

9 Carbon dioxide, CO_2

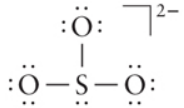


10 Carbonate ion, CO_3^{2-}

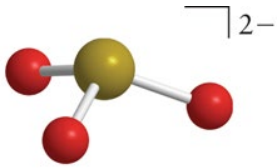


11 Carbonate ion, CO_3^{2-}

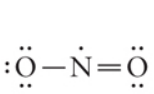
- **Rule 3** All regions of high electron density, lone pairs and bonds, are included in a description of the electronic arrangement, but only the positions of atoms are considered when identifying the shape of a molecule.



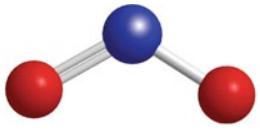
16 Sulfite ion, SO_3^{2-}



17 Sulfite ion, SO_3^{2-}



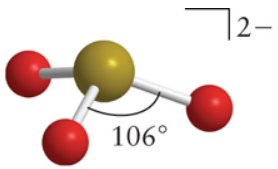
18 Nitrogen dioxide, NO_2



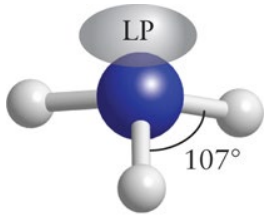
19 Nitrogen dioxide, NO_2

➢ **Rule 4** The strength of repulsions are in the order
lone pair-lone pair > lone pair-atom > atom-atom

- AX_3E type



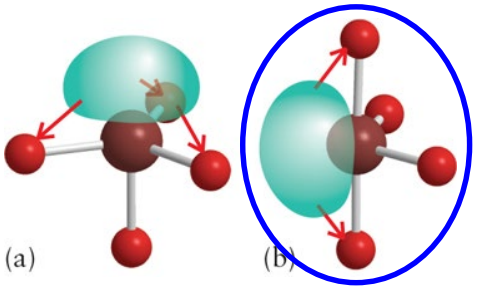
20 Sulfite ion, SO_3^{2-}



21 Ammonia, NH_3

trigonal pyramidal

- AX_4E type

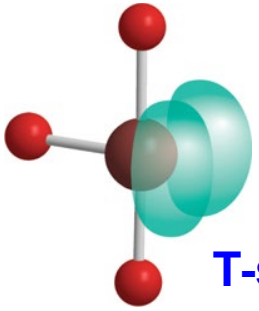


axial equatorial

more stable

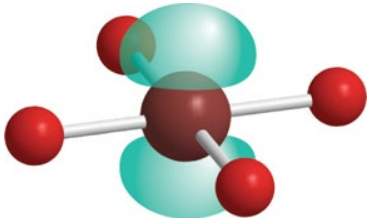
seesaw shaped

- AX_3E_2 type



T-shaped

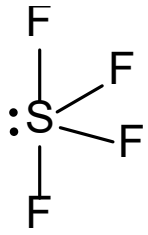
- AX_4E_2 type



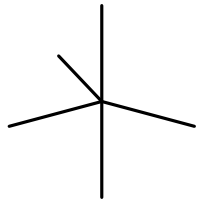
square planar

➢ **Predicting a molecular shape** of SF_4

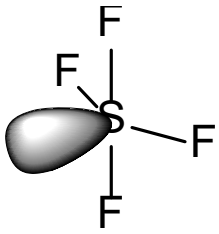
Step 1 Draw the Lewis structure.



Step 2 Assign the electron arrangement around the central atom.



Step 3 Identify the molecular shape. AX_4E.



Step 4 Allow for distortions.

bent seesaw shape

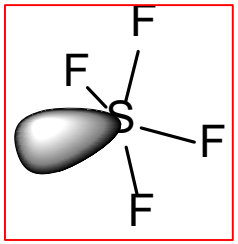
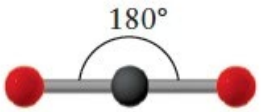
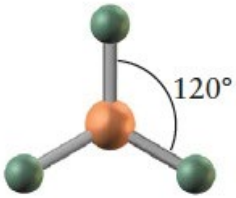
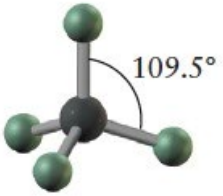
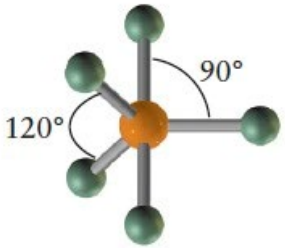
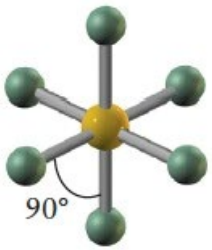
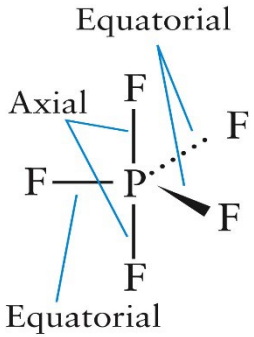


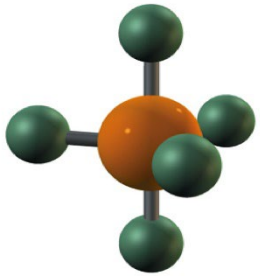
TABLE 3.8

Molecular Shapes Predicted by the Valence Shell Electron-Pair Repulsion Theory

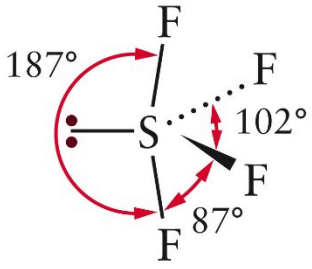
Molecule	Steric Number	Predicted Geometry	Example
AX_2	2	Linear 	CO_2
AX_3	3	Trigonal planar 	BF_3
AX_4	4	Tetrahedral 	CF_4
AX_5	5	Trigonal bipyramidal 	PF_5
AX_6	6	Octahedral 	SF_6



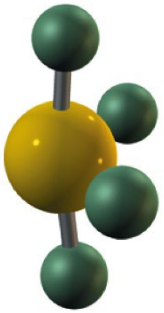
(a) PF_5



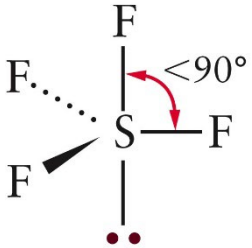
Trigonal bipyramid



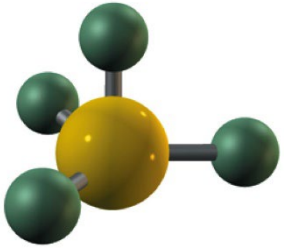
(b) SF_4



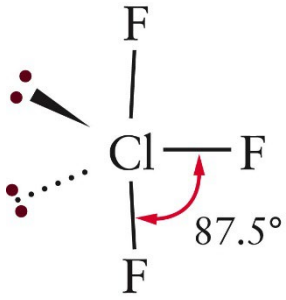
Seesaw
(low-energy, favored)



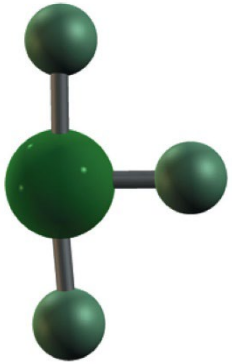
(c) SF_4



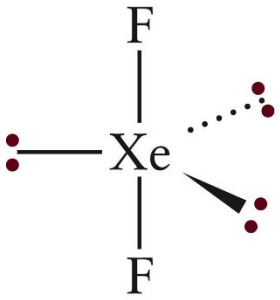
Distorted pyramid
(high-energy, not favored)



(d) ClF_3



Distorted T

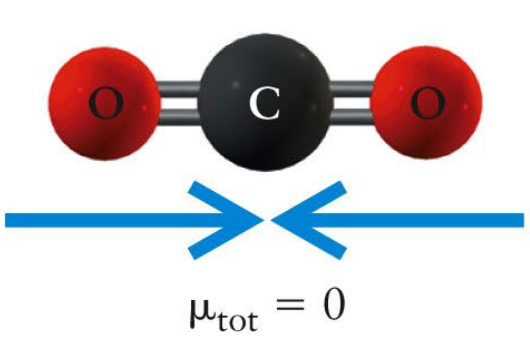


(e) XeF_2

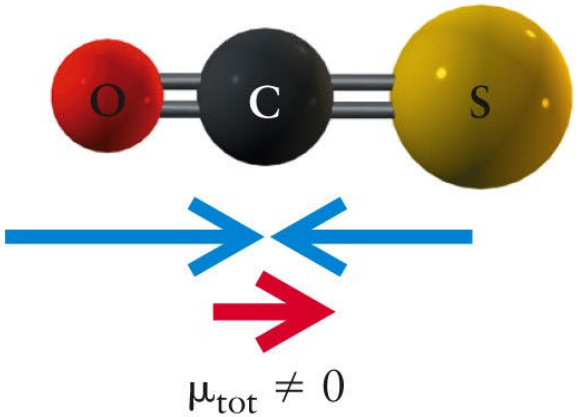
Linear

➢ Dipole moments of polyatomic molecules

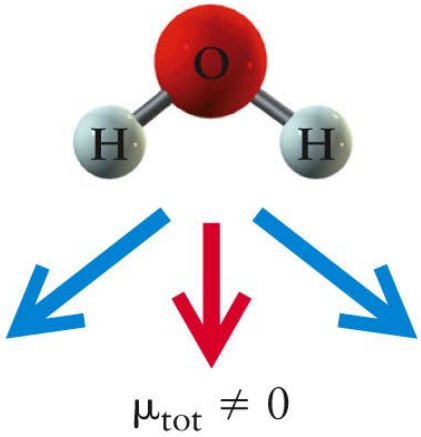
By a vector sum of each bond dipoles, non-zero dipole molecules are **polar**, and no net dipole molecules are **non-polar**.



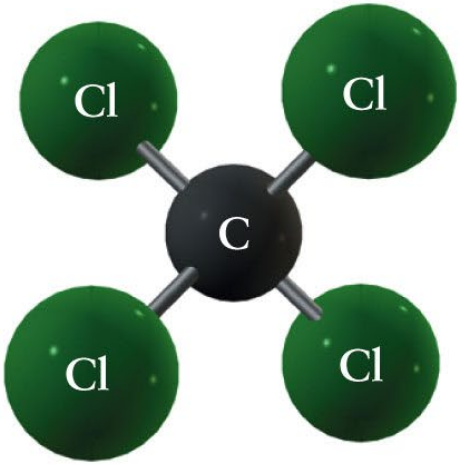
(a)



(b)



(c)



(d)

3.12 OXIDATION NUMBERS

1. The oxidation number in a neutral molecule must add up to zero.

2. Alkali-metal atoms = +1, alkaline-earth atoms = +2

3. Fluorine = always -1, halogens = generally -1

4. Hydrogen = +1, except in metal hydride (LiH) = -1

5. Oxygen = -2, except in compounds with O-O bonds.

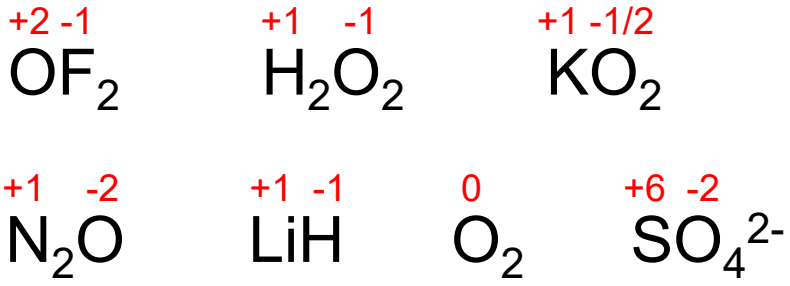


TABLE 3.9

Formulas and Names of Some Common Anions

F^-	Fluoride
Cl^-	Chloride
Br^-	Bromide
I^-	Iodide
H^-	Hydride
O^{2-}	Oxide
S^{2-}	Sulfide
O_2^{2-}	Peroxide
O_2^-	Superoxide
OH^-	Hydroxide
CN^-	Cyanide
CNO^-	Cyanate
SCN^-	Thiocyanate
MnO_4^-	Permanganate
CrO_4^{2-}	Chromate
$Cr_2O_7^{2-}$	Dichromate
CO_3^{2-}	Carbonate
HCO_3^-	Hydrogen carbonate
NO_2^-	Nitrite
NO_3^-	Nitrate
SiO_4^{4-}	Silicate
PO_4^{3-}	Phosphate
HPO_4^{2-}	Hydrogen phosphate
$H_2PO_4^-$	Dihydrogen phosphate
SO_3^{2-}	Sulfite
SO_4^{2-}	Sulfate
HSO_4^-	Hydrogen sulfate
ClO^-	Hypochlorite
ClO_2^-	Chlorite
ClO_3^-	Chlorate
ClO_4^-	Perchlorate

- Formal charges are used to identify preferred Lewis diagrams.
  Oxidation numbers are used to identify oxidation-reduction reactions.