CLASSICAL ATOMS & BONDING

General Chemistry I, Lecture Series 3

Pengxin Liu

Reading:
OGB8 §§1.4, 3.10

Outline

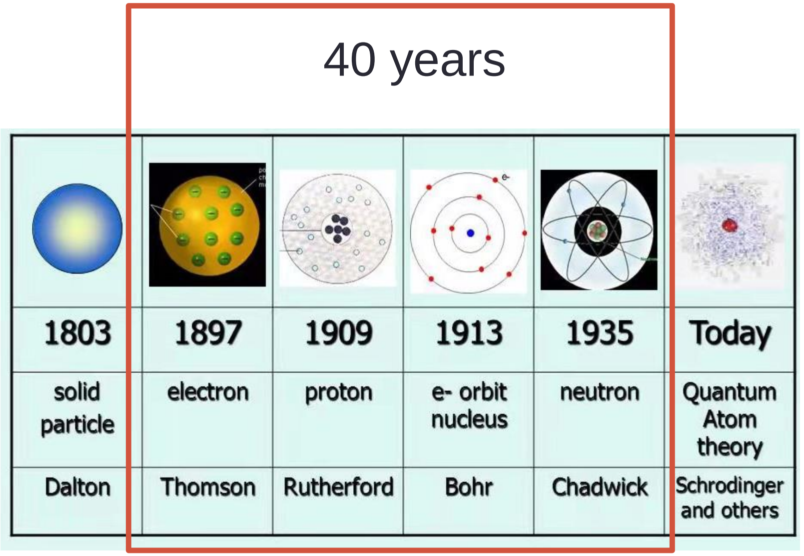
- Atomic structure
  - Electron and the nuclear
  - The Pudding Model
  - The Rutherford Model
  - Neutron
- Valence and Oxidation number
- Lewis Structure

Are atoms indivisible?

- Ancient Greek concept
- Dalton’s atom theory
- Avogadro’s law

- New experiments disagree
  - Electrolysis by Faraday
  - Glow discharge and cathode rays
  - Canal rays

- Finding of electron
- Finding of atomic structure



Electrolysis by Faraday

1833

The amount of water decomposed, and the formed H_2 and O_2 (HER and OER) are all proportional to the quantity of charge passed through the system.

Electricity *vs.* reaction
Charge-to-mass ratio 荷质比

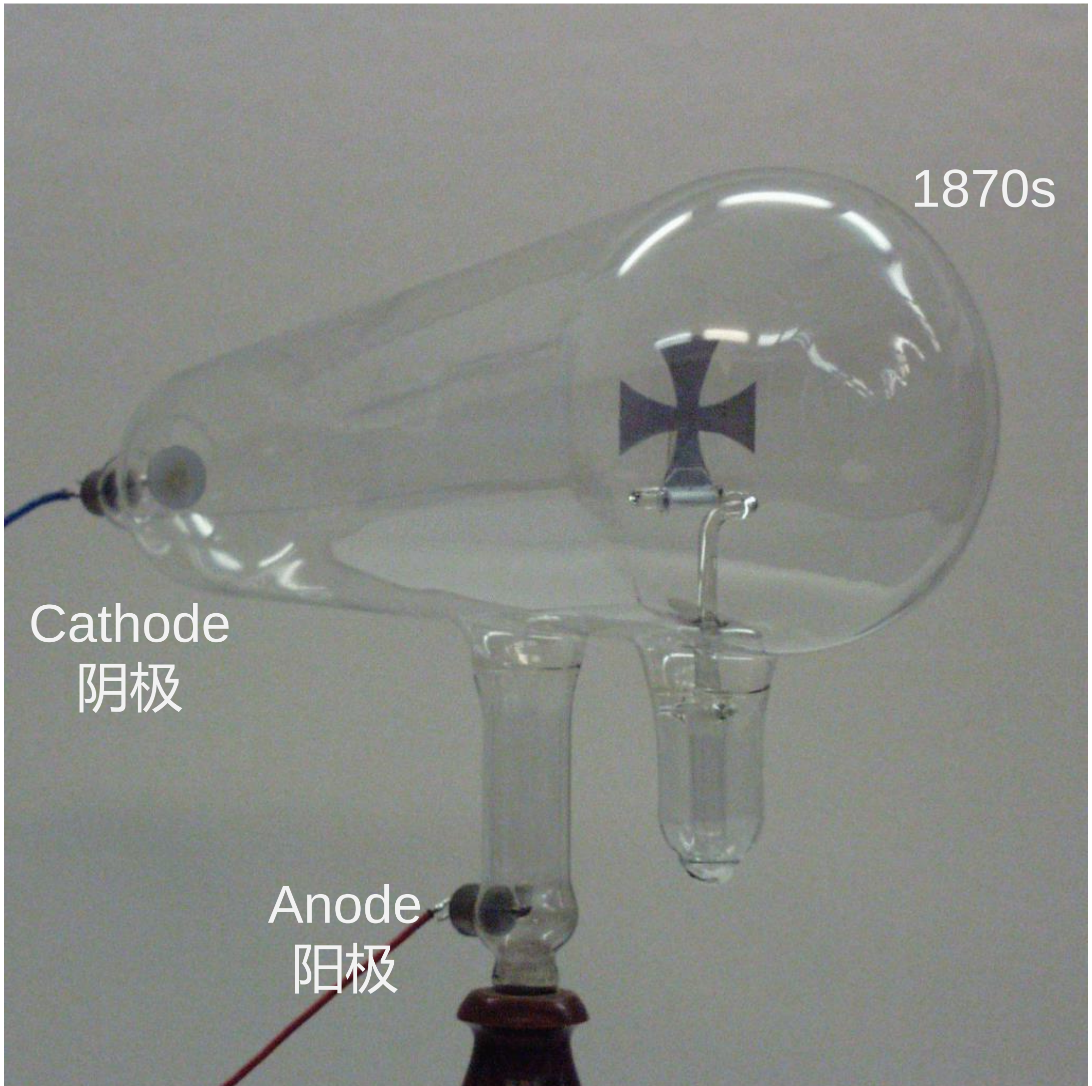
Electrochemistry 电化学

Anode 阳极
Anions 阴离子
Oxidation 氧化

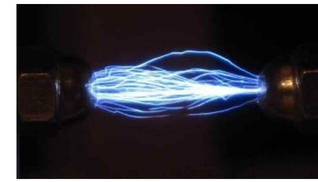
Cathode 阴极
Cations 阳离子
Reduction 还原

Electrode 电极
Ions 离子
Reaction 反应

Glow discharge and cathode rays



High voltage

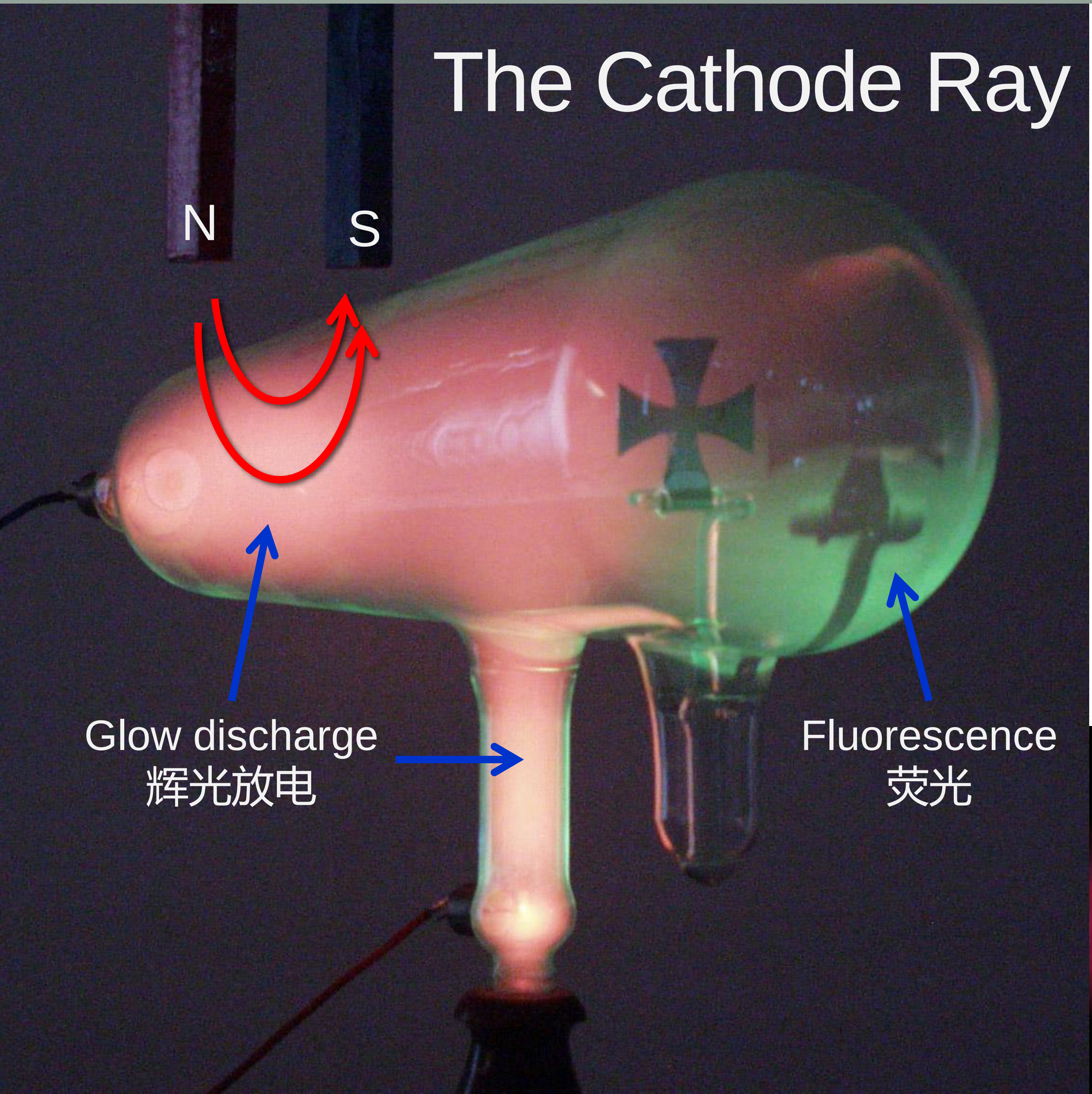


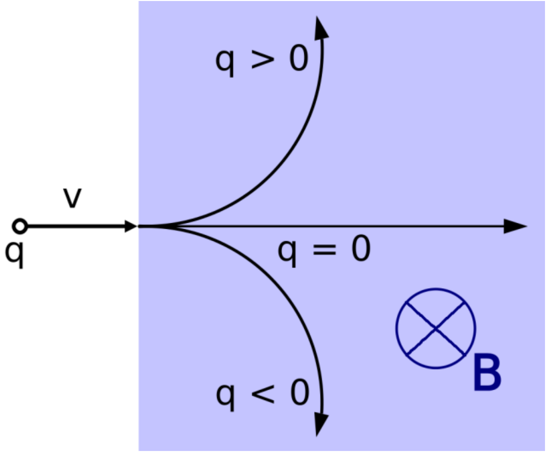
Glass-to-metal seal

Vacuum

Phosphor

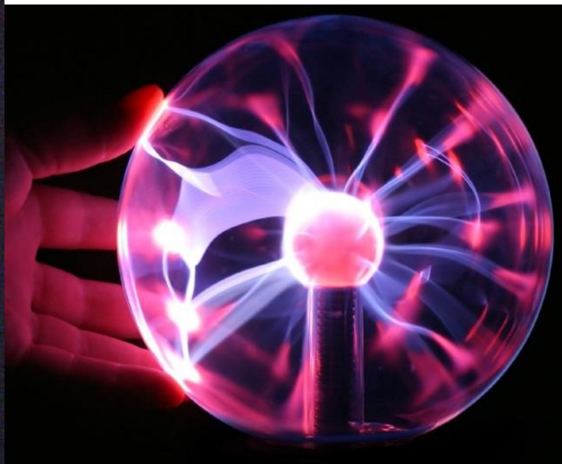
The Cathode Ray



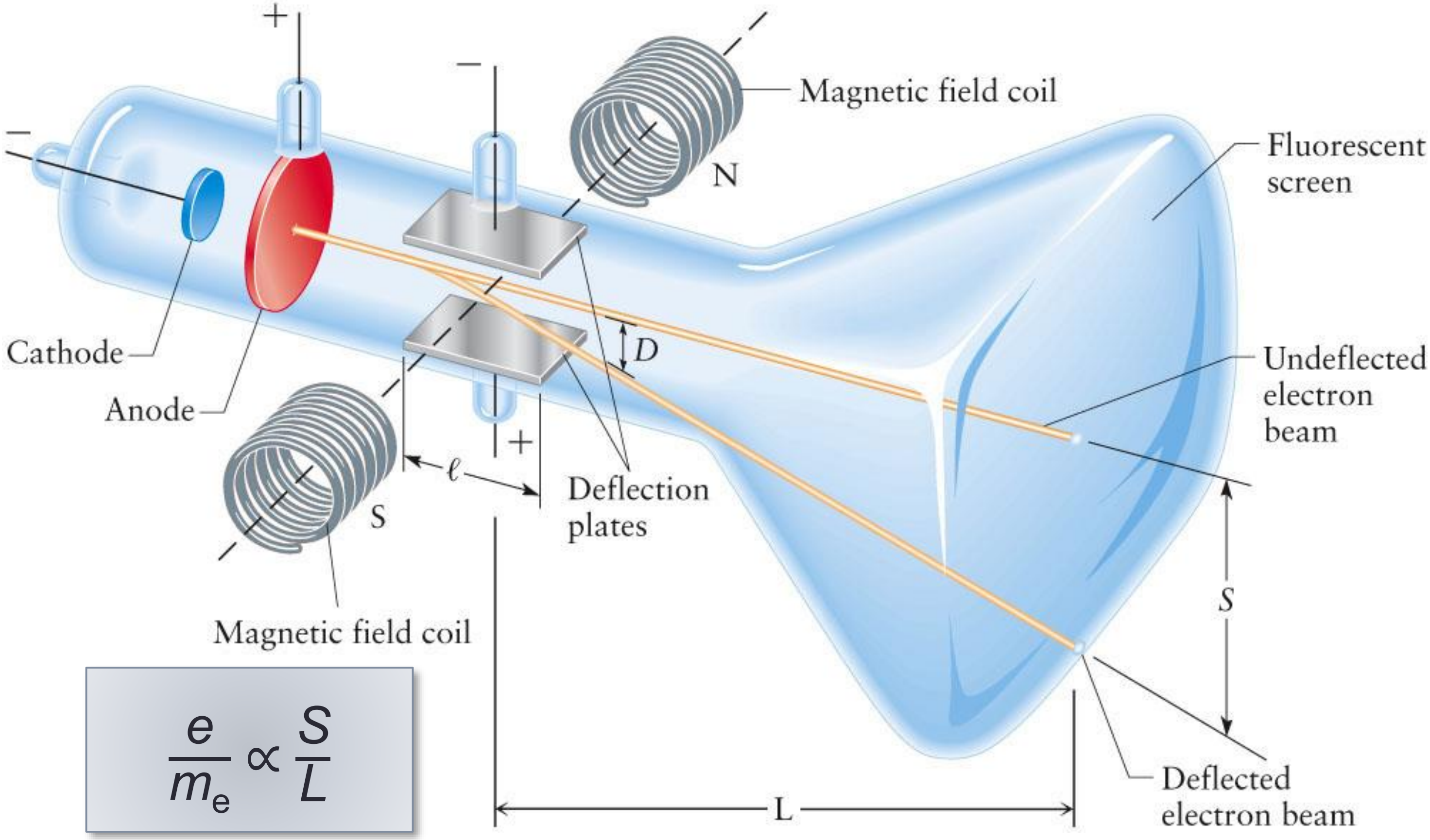


Lorentz force

Particles in the cathode ray are negatively charged.



The Cathode Ray Tube (CRT)



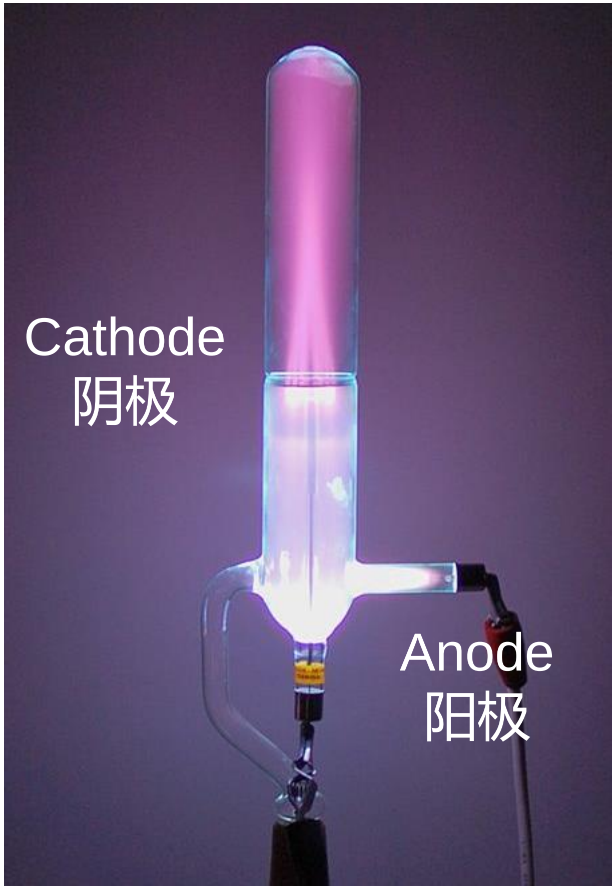
$$\frac{e}{m_e} \propto \frac{S}{L}$$

J. J. Thomson (Cambridge, 1856–1940)

$\frac{e}{m_e}$ is independent of the cathode material or the gas.

Charge of electron was later measured by Millikan etc.

Canal Rays from the Anode



Wilhelm Wien

- Canal rays are positively charged.
- Canal rays show different charge-to-mass ratios.
- The largest *e*/*m* for anode rays is that of proton

  Q/m for electron = -1.8×10^{11} C·kg^{-1}
  Q/m for proton = $+1.0\times10^{8}$ C·kg^{-1}

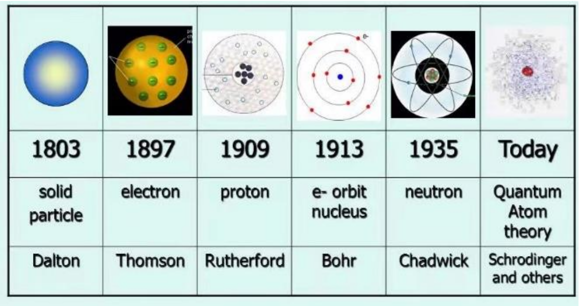
- More experiments showed $Q_p = -e$, so

$$\boxed{\frac{m_p}{m_e} = 1.8\times10^{3}}$$

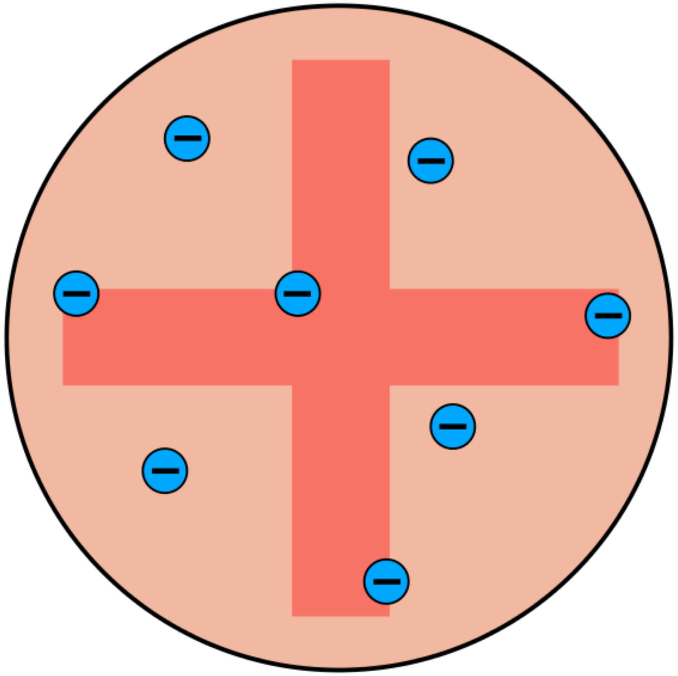
The Plum Pudding Model

J. J. Thomson

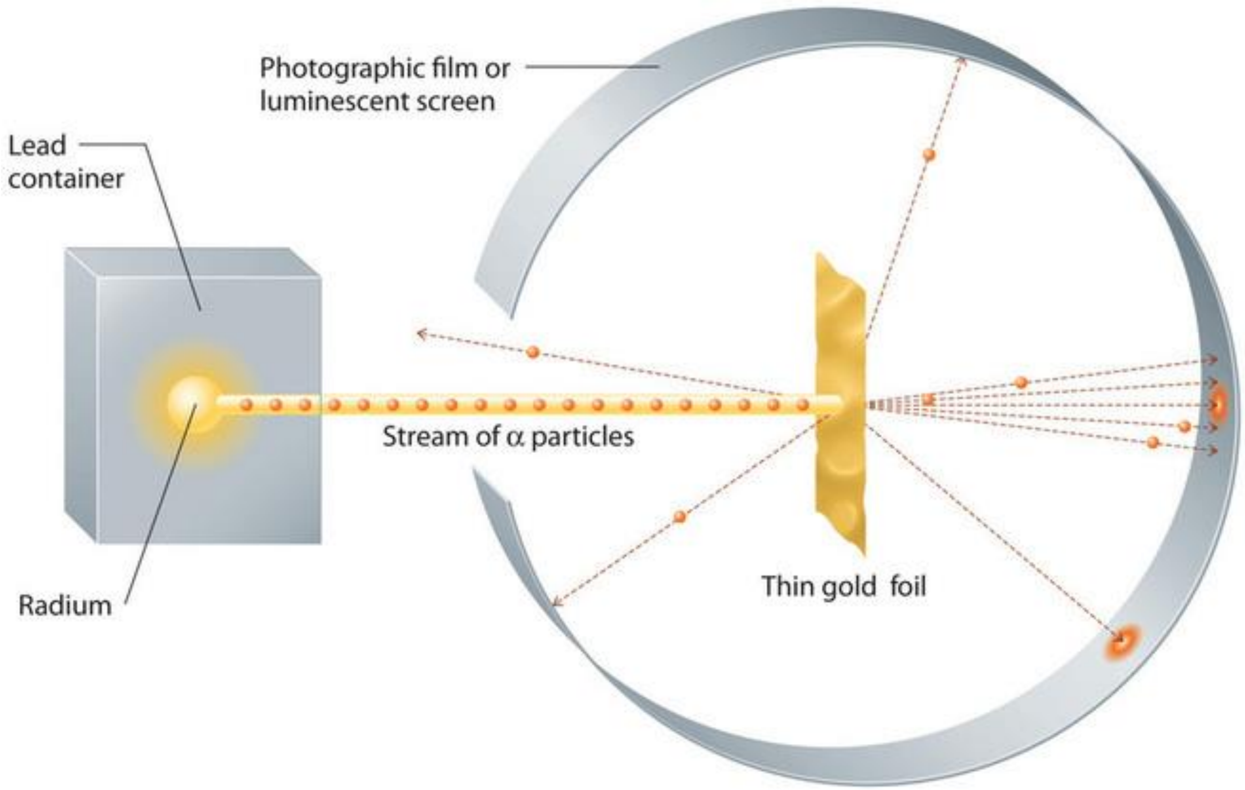
- 1897 Discovered electron
- 1904 Proposed the pudding model
- 1906 Nobel Prize in Physics



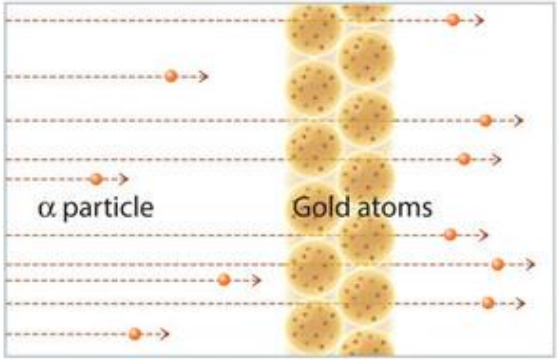
1803	1897	1909	1913	1935	Today
solid particle	electron	proton	e- orbit nucleus	neutron	Quantum Atom theory
Dalton	Thomson	Rutherford	Bohr	Chadwick	Schrodinger and others



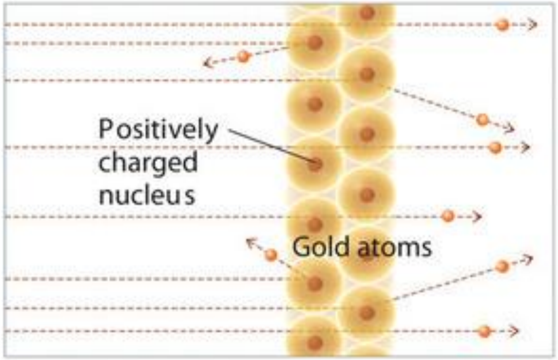
Rutherford's Gold Foil Experiment (1911)



(a) Rutherford's experiment

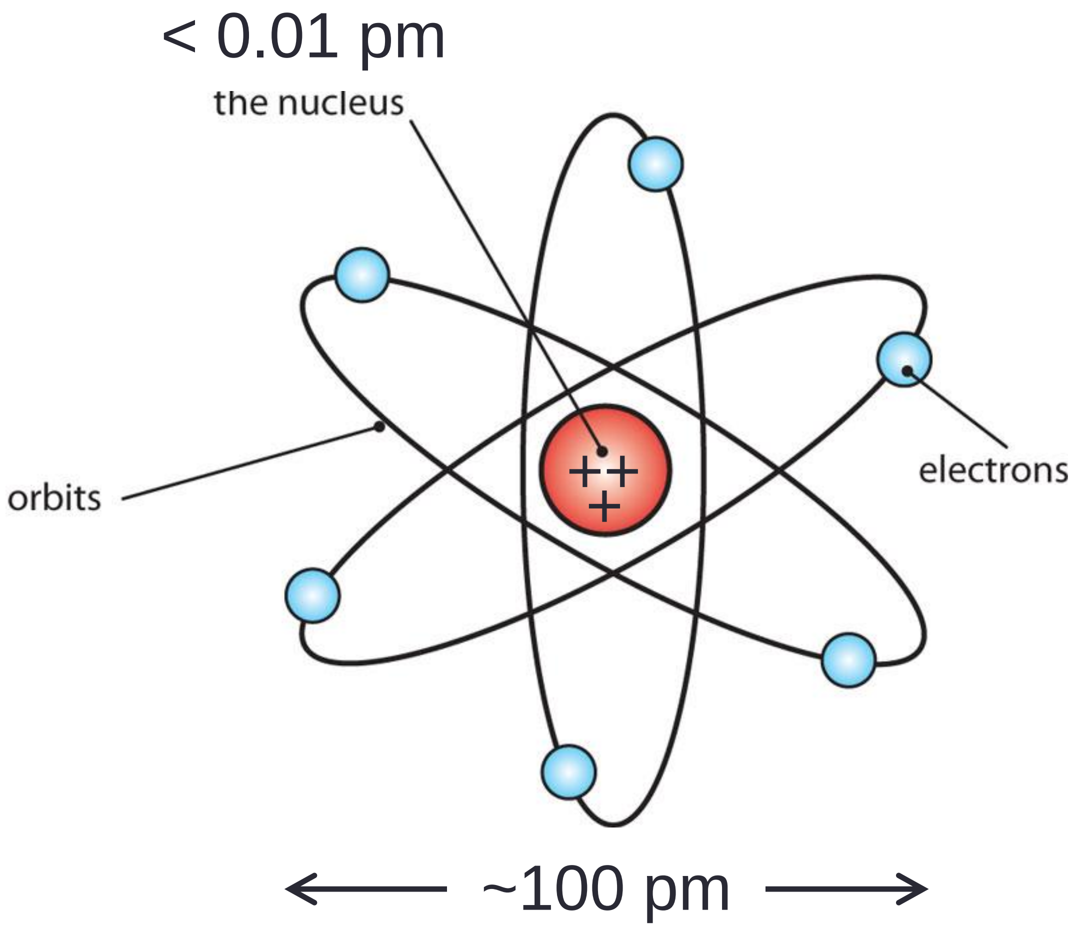


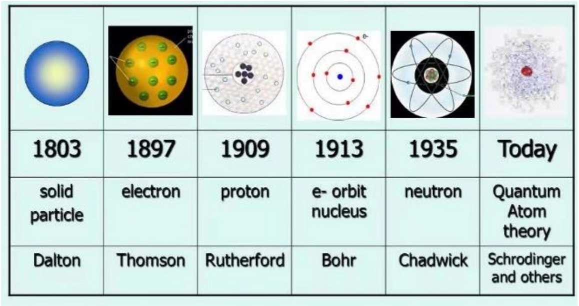
(b) What Rutherford expected if Thomson's model were correct



(c) What Rutherford actually observed

The Rutherford Model

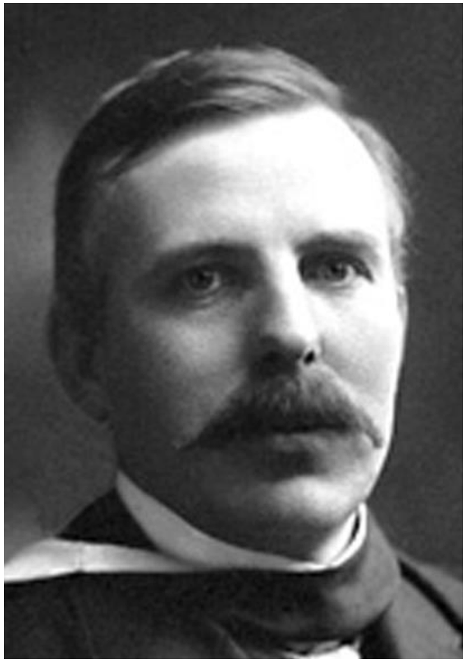




1803	1897	1909	1913	1935	Today
solid particle	electron	proton	e- orbit nucleus	neutron	Quantum Atom theory
Dalton	Thomson	Rutherford	Bohr	Chadwick	Schrodinger and others

IAEA
International Atomic Energy Agency

Rutherford



Ernest Rutherford (Cambridge, 1871–1937)

J. J. Thomson's first graduate student at the Cavendish Laboratory.

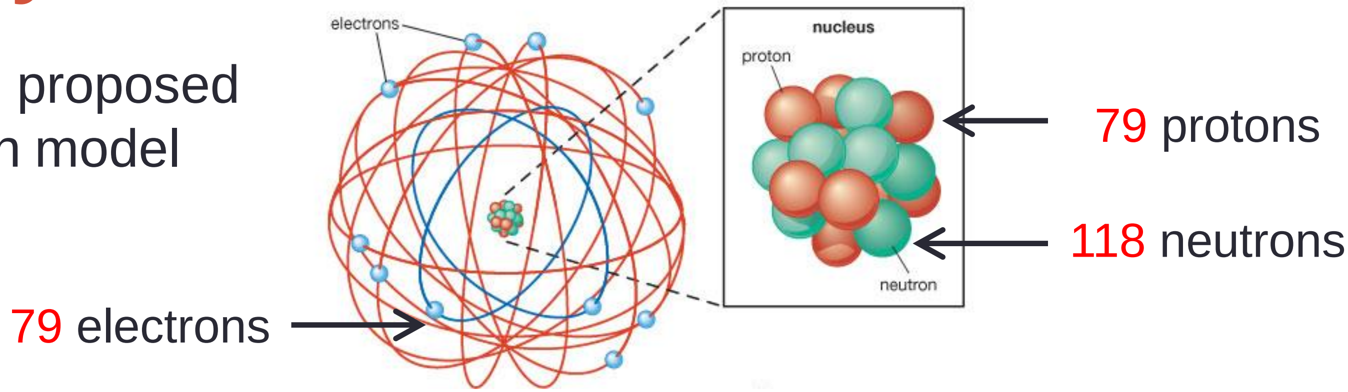
Nobel Prize in Chemistry in 1908 for discovery of radiation. He discovered alpha and beta rays, and proposed the laws of radioactive decay.

Unfortunately, Rutherford would have preferred to receive the Nobel Prize in Physics because he considered physics superior to chemistry.

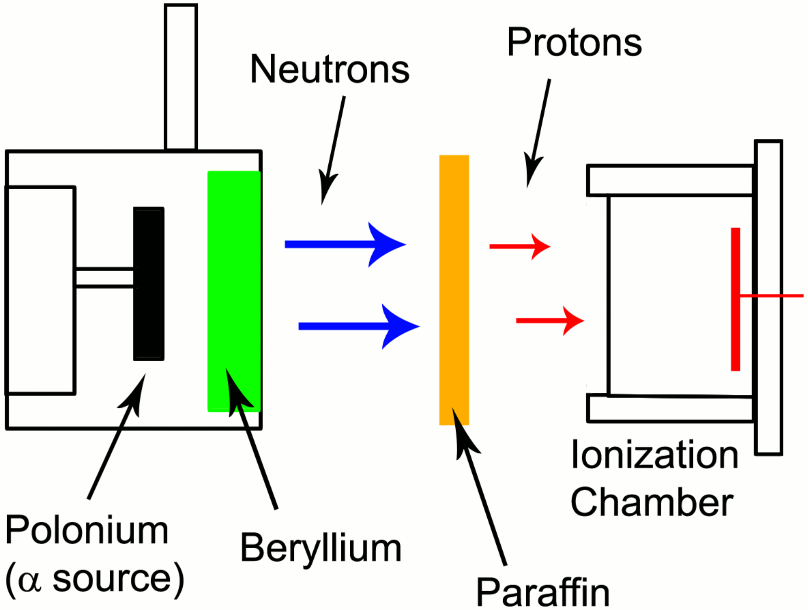
"All science is either physics or stamp collecting."

Discovery of Neutron

1920 Rutherford proposed a proton-electron model for the nucleus



1932 Chadwick discovered the neutron



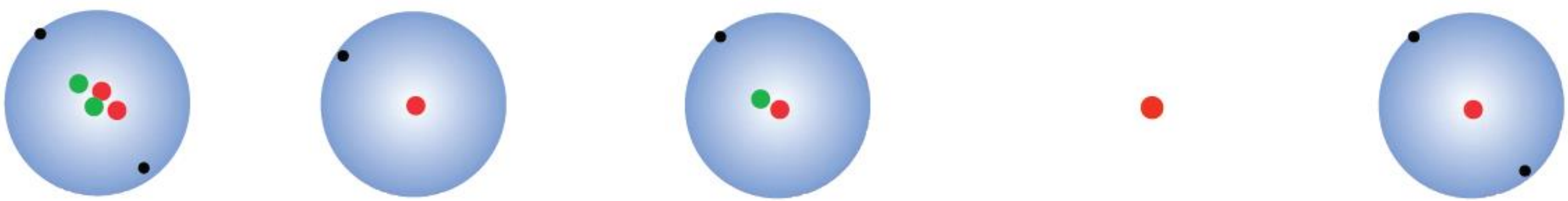
Summary

Mass number
A = p + n

Atomic number
(charge number)
Z = p

$$^{A}_{Z}\mathrm{X}$$

Anode	阳极
Anion	阴离子
Cathode	阴极
Cation	阳离子



Helium, $^{4}_{2}\mathrm{He}$ Protium, $^{1}_{1}\mathrm{H}$ Deuterium, $^{2}_{1}\mathrm{H}$ Hydrogen ion (proton), H^+ Hydride, H^-

Cation Anion

Hydrogen, $_{1}\mathrm{H}$ Ion

Generalized hydrogen element 元素

Outline

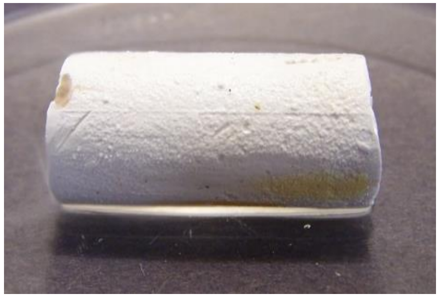
- Atomic structure
  - Electron and the nuclear
  - The Pudding Model
  - The Rutherford Model
  - Neutron
- Valence and Oxidation number
- Lewis Structure

How Are Atoms Bonded into Molecules?

Methane CH_4

Ethanol, C_2H_6O

Potassium permanganate, $KMnO_4$

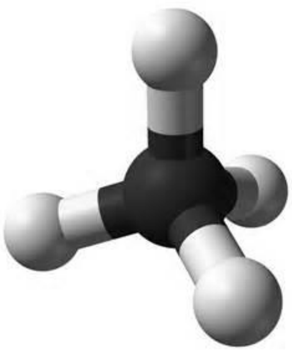


White phosphorus, P_4

Sodium chloride, NaCl

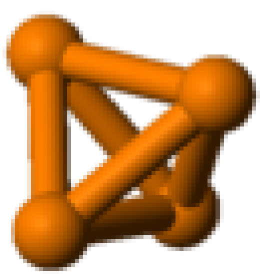
How Are Atoms Bonded into Molecules?

empirical and molecular formulas

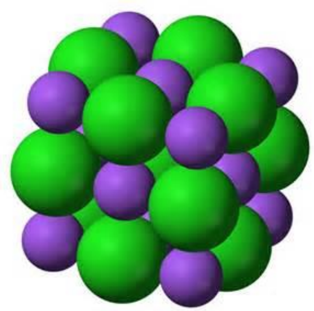


Methane CH_4

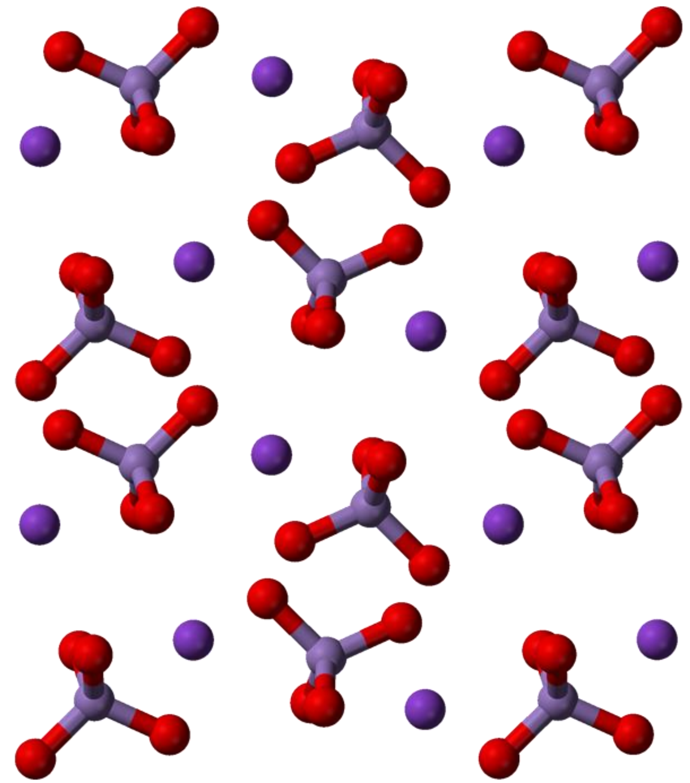
Ethanol, C_2H_6O



White phosphorus, P_4



Sodium chloride, NaCl



Potassium permanganate, $KMnO_4$

Oxidation Numbers: Rules

Rule 1 Oxidation numbers sum up to the total charge.

Rule 2 H, Li, Na, K … = +1; F, Cl, Br … = −1; O = −2.

Rule 3 Elements on the lower left corner prefer a (+) oxidation number;
Elements on the upper right corner prefer a (−) oxidation number.

Only one common oxidation number

+1	+2											+3	−4 +4	−3 +5	−2 +6	−1 +7	
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Oxidation Numbers: Examples

O_3	O(0)	LiH	Li(+1), H(−1)
N_2O	O(−2), N(+1)	ClO_4^-	O(−2), Cl(+7)
HSO_4^-	O(−2), H(+1), S(+6)	OF_2	F(−1), O(+2)
CuI	I(−1), Cu(+1)		

Only one common oxidation number

+1	+2											+3	−4 +4	−3 +5	−2 +6	−1 +7	
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

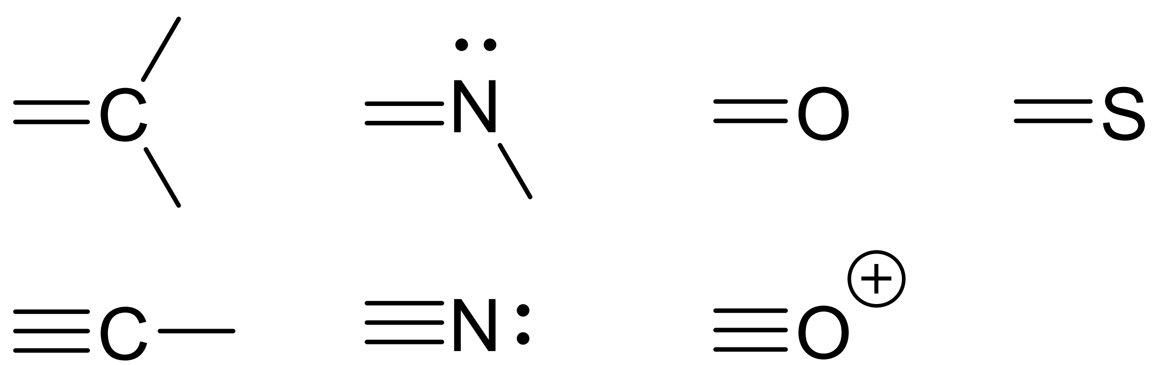
Valence (valence bond)

- borrowed from Late Latin *valentia* “power, capacity,” noun derivative of Latin *valent-*, *valens*, present participle of *valēre* “to have strength, be well”.

- the degree of combining power of an element as shown by the number of a monovalent element (such as hydrogen) with the element will combine.

Number of Valence Electrons

Electrons	0	1	2	3	4	5	6	7	8
Valence	0	1	2	3	4	3	2	1	0
Examples	H^+			C^+	N^+	O^+			
		H		B	C	N	O	F	Ne
					B^-	C^-	N^-	O^-	F^-



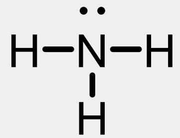
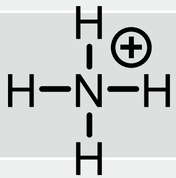
Valence *vs.* Oxidation Number

Valence 成键数

= Number of shared electrons

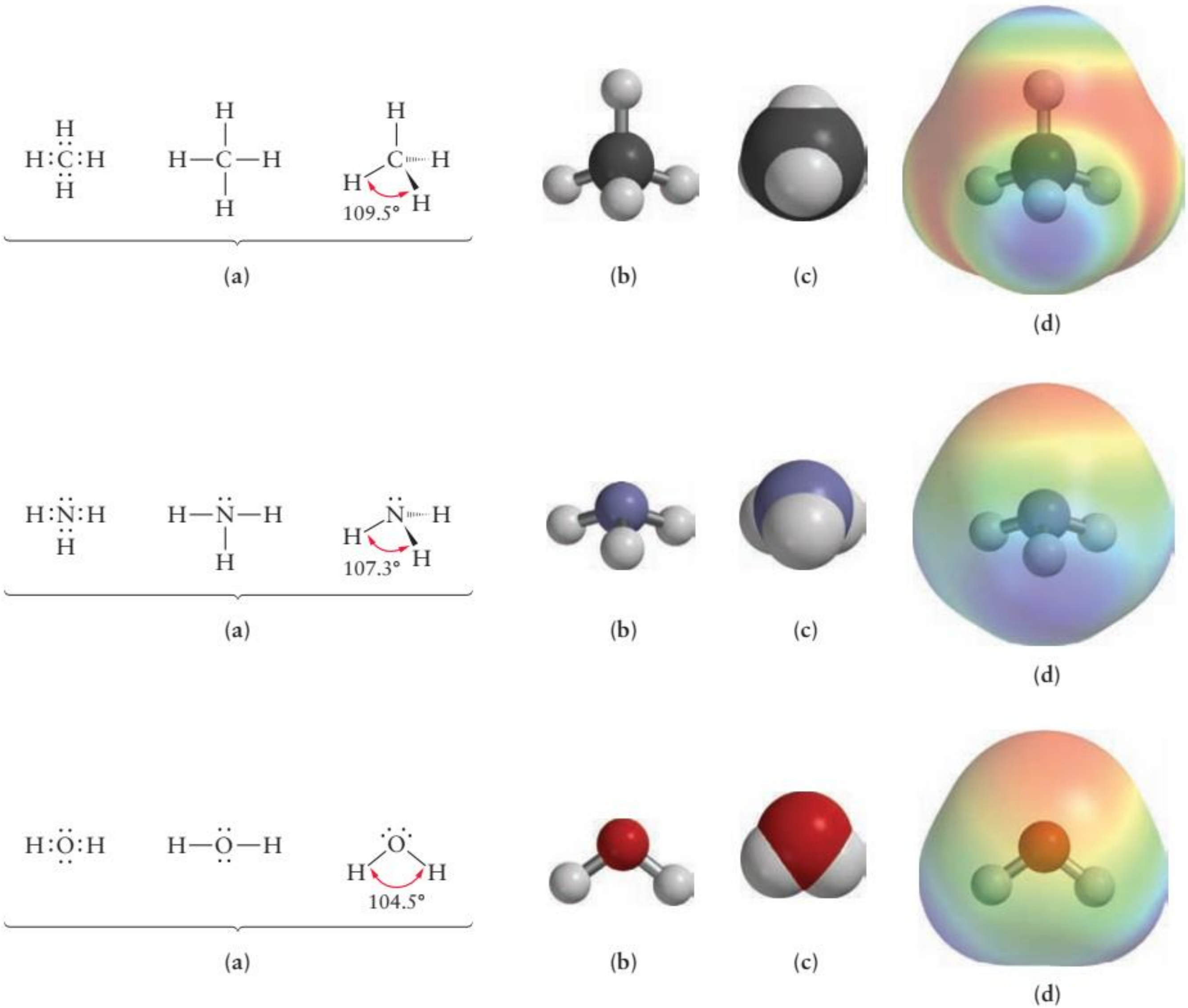
Oxidation number 氧化数

= Number of lost electrons

F^-, Cl^-	V = 0	ON = −1	V < |ON|
	V = 3	ON = −3	V = |ON|
	V = 4	ON = −3	V > |ON|
Cl–Hg–Hg–Cl	V = 2	ON = 1	V > |ON|

Outline

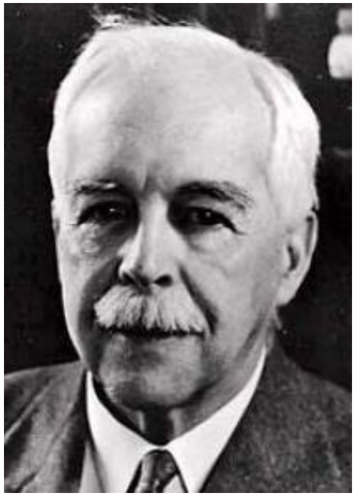
- Atomic structure
  - Electron and the nuclear
  - The Pudding Model
  - The Rutherford Model
  - Neutron
- Valence and Oxidation number
- Lewis Structure



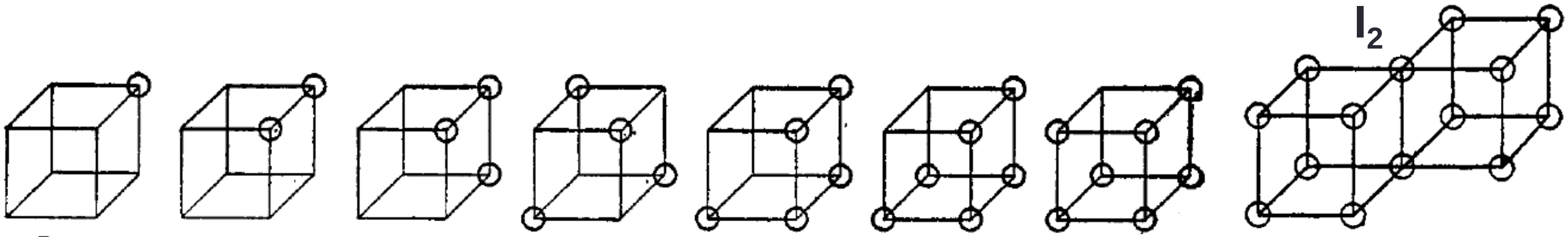
(a) Lewis dot diagrams, line structures, and line angle representations (b) ball and stick models (c) space-filling models (d) electrostatic potential energy diagrams (elpots).

Octet Rule

1. A shared pair = a covalent bond.
   A lone pair = no bonding.
2. Each atom achieves its own noble-gas shell of electrons.
3. Share as many electrons as possible.



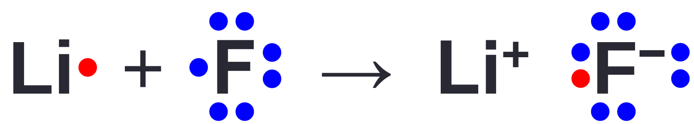
Gilbert N. Lewis
(Berkeley, 1875–1946)



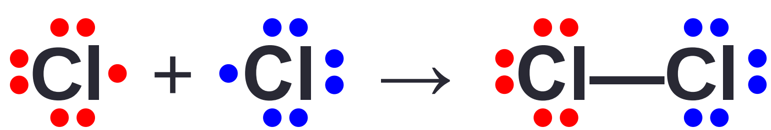
Lewis, G. N. "The Atom and the Molecule", *J. Am. Chem. Soc.* **1916**, *38*, 762–785.

Lewis Diagram: Examples

$1s^2\ 2s^2\ 2p^6$

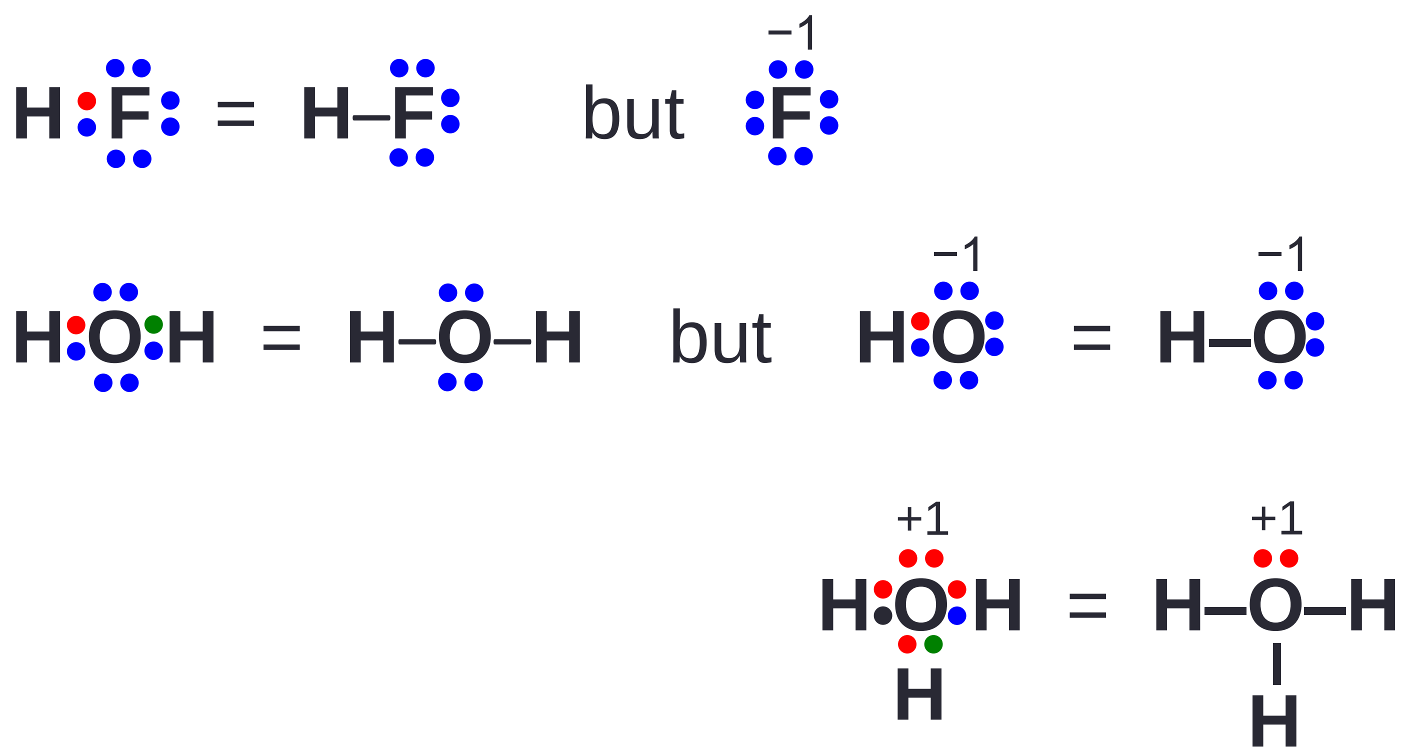


$2s^1$ $2s^2\ 2p^5$



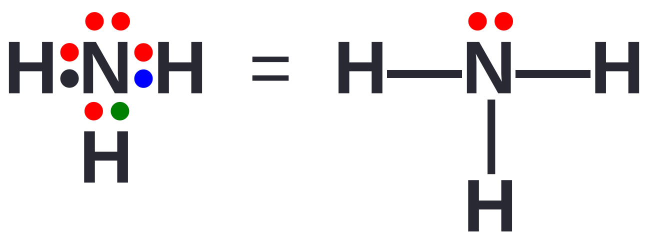
$3s^2\ 3p^5$

Lewis Diagram: Ions



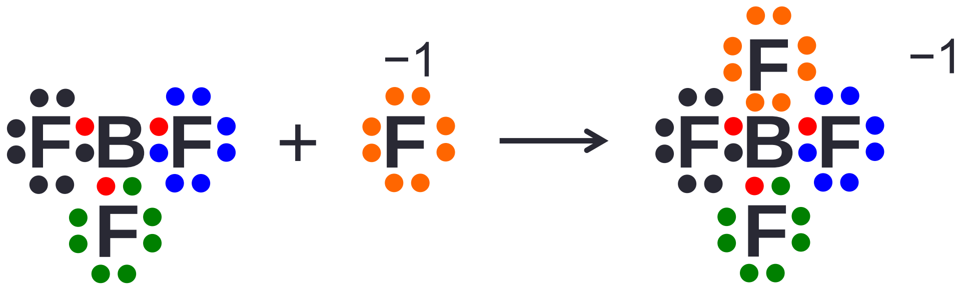
Lewis Diagram: Covalent bonds

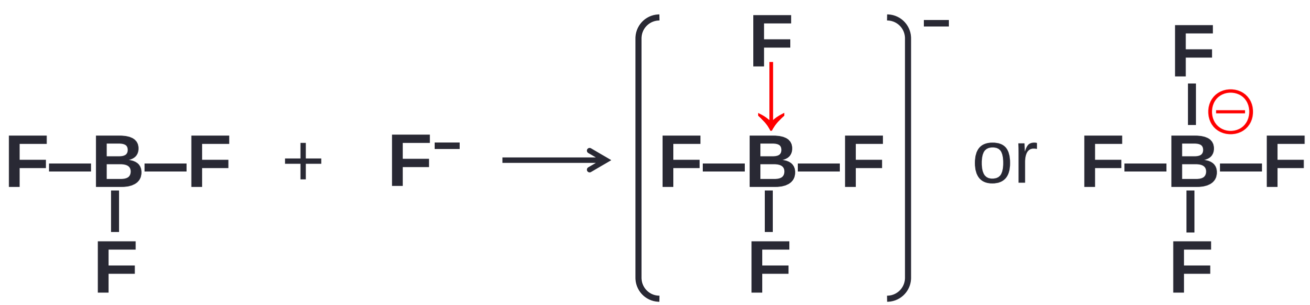
$2s^2\ 2p^3$



$2s^2\ 2p^2$

Lewis Acid and Base





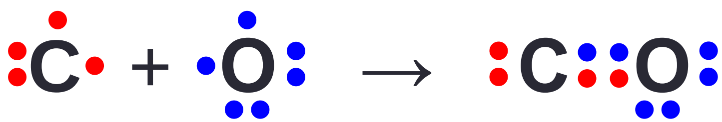
Lewis acid	Lewis base	Lewis adduct/complex 加合物/配合物

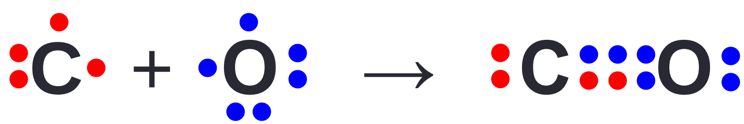
How to draw Lewis Diagrams

1. Count the total number of valence electrons available by first using the group numbers to add the valence electrons from all the atoms present. If the species is a negative ion, *add* additional electrons to achieve the total charge. If it is a positive ion, *subtract* enough electrons to result in the total charge.
2. Calculate the total number of electrons that would be needed if each atom had its *own* noble-gas shell of electrons around it (two for hydrogen, eight for carbon and heavier elements).
3. Subtract the number in step 1 from the number in step 2. This is the number of shared (or bonding) electrons present.
4. Assign two bonding electrons (one pair) to each bond in the molecule or ion.
5. If bonding electrons remain, assign them in pairs by making some double or triple bonds. In some cases, there may be more than one way to do this.

   In general, double bonds form only between atoms of the elements C, N, O, and S. Triple bonds are usually restricted to C, N, or O.
6. Assign the remaining electrons as lone pairs to the atoms, giving octets to all atoms except hydrogen.
7. Determine the formal charge on each atom and write it next to that atom. Check that the formal charges add up to the correct total charge on the molecule or polyatomic ion. (This step not only guides you to the better diagrams, it also provides a check for inadvertent errors such as the wrong number of dots).
8. If more than one diagram is possible, choose the one with the smallest magnitudes of formal charges (0, +1, −1) and with any negative formal charges placed on the most electronegative atoms.

Which one is correct?



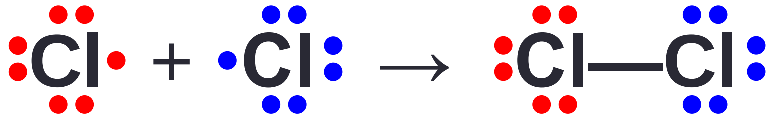


How about CO_2?

Formal Charge

- Assume that electrons in all chemical bonds are shared equally between atoms, regardless of relative electronegativity.
- When determining the best Lewis structure (or predominant resonance structure) for a molecule, the structure is chosen such that the formal charge on each of the atoms is as close to zero as possible.

$$\text{Atoms Formal Charge} = [\text{valence electrons}] \text{ - } [\text{lone pair electrons}] - \frac{\text{bonding electrons}}{2}$$

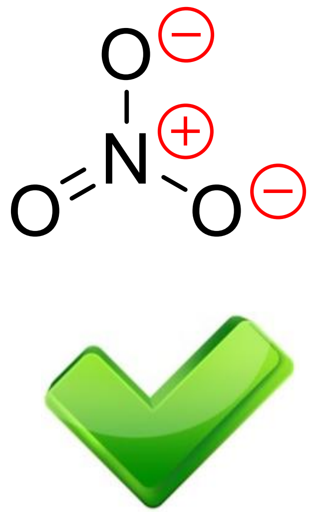


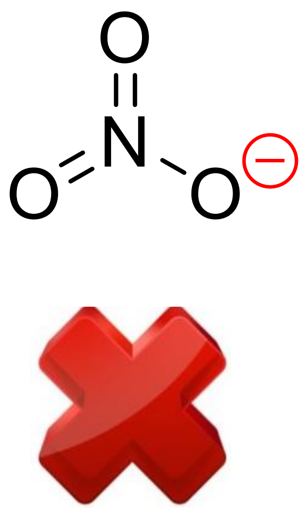
Formal Charge for heteronuclear molecule

Coordinate bond
配位键

Formal charge
形式电荷

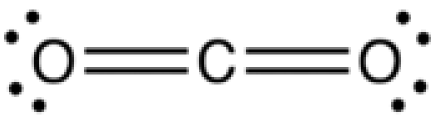
Formal Charge for heteronuclear molecule





Formal Charge has **NO** physical meaning

Formal charge is a tool for estimating the distribution of electric charge within a molecule. The concept of oxidation states constitutes a competing method to assess the distribution of electrons in molecules.



	O	C	O
Formal Charge	0	0	0
Oxidation State	2–	4+	2–

Next lecture series: Bohr Model

Reading: OGB8 §§4.1, 4.2, 4.3