# Charge and Mass of an Electron

1911 measured charge of an electron
Oil drop experiment

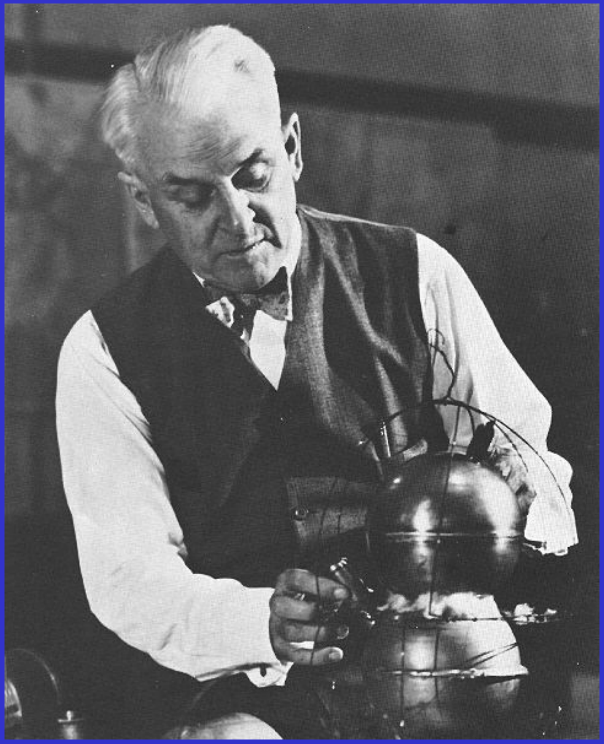
$q = -1.602\ 176\ 487(40)\ 10^{-19}$ C

Electric charge is quantized

Any charge is an integer multiple of the elementary charge $q$ (elektronu)

From $q$ and $q/m_e$ calculated e mass

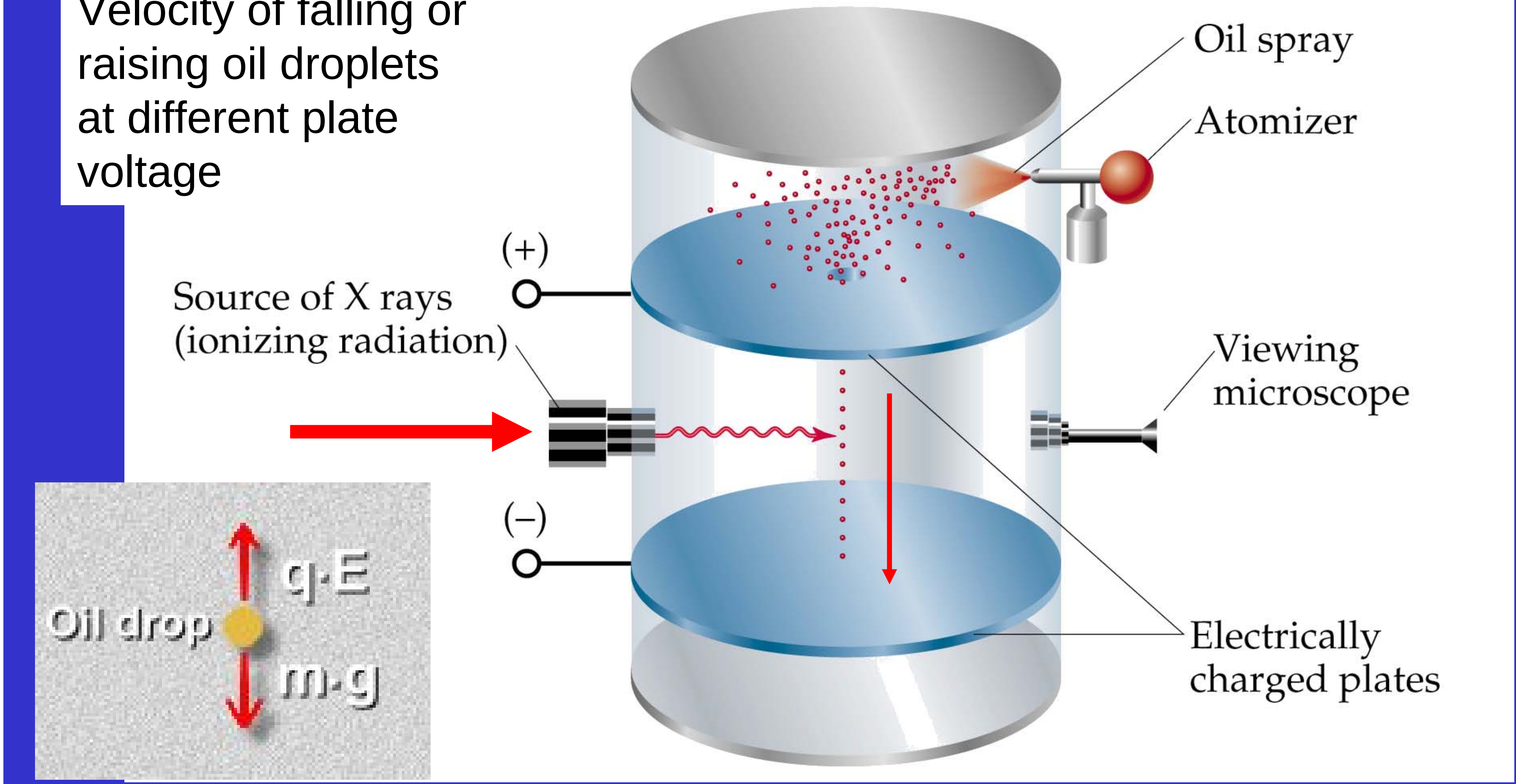
$m_e = 9.109\ 39\ 10^{-31}$ kg



Robert Millikan
(1868 - 1953)
NP in physics 1923

# Oil Drop Experiment

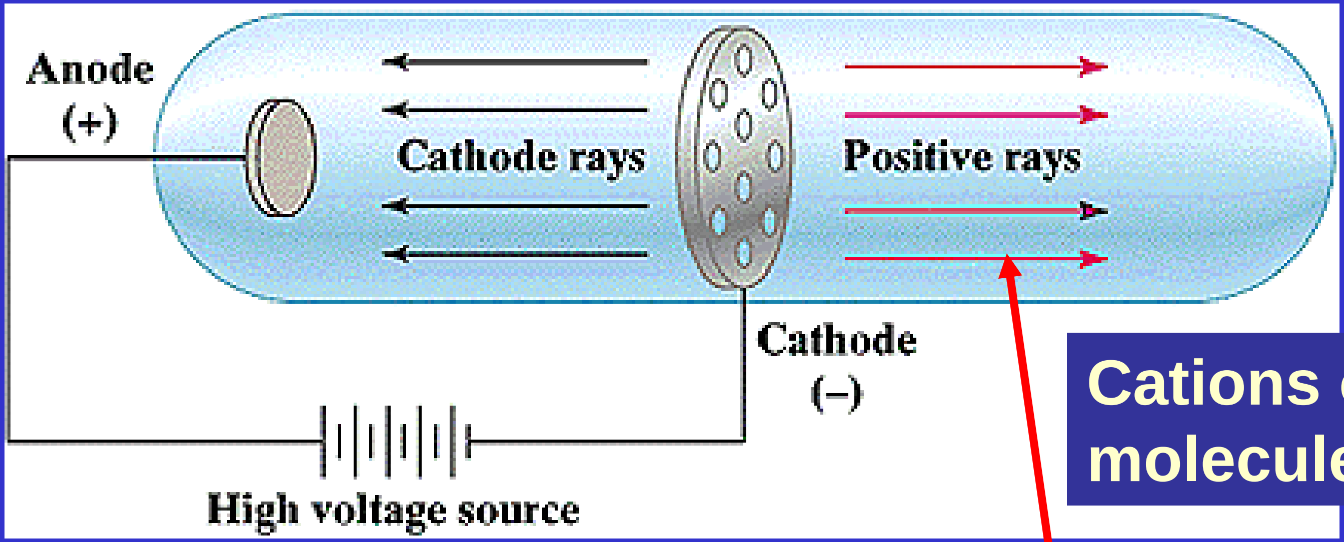
Velocity of falling or raising oil droplets at different plate voltage



Mass and radius of oil droplets?

# Anode (Canal) Rays

1886



**Cations of gas molecules**

Proton

$q/m_p = 9.579\ 10^7$ C $g^{-1}$

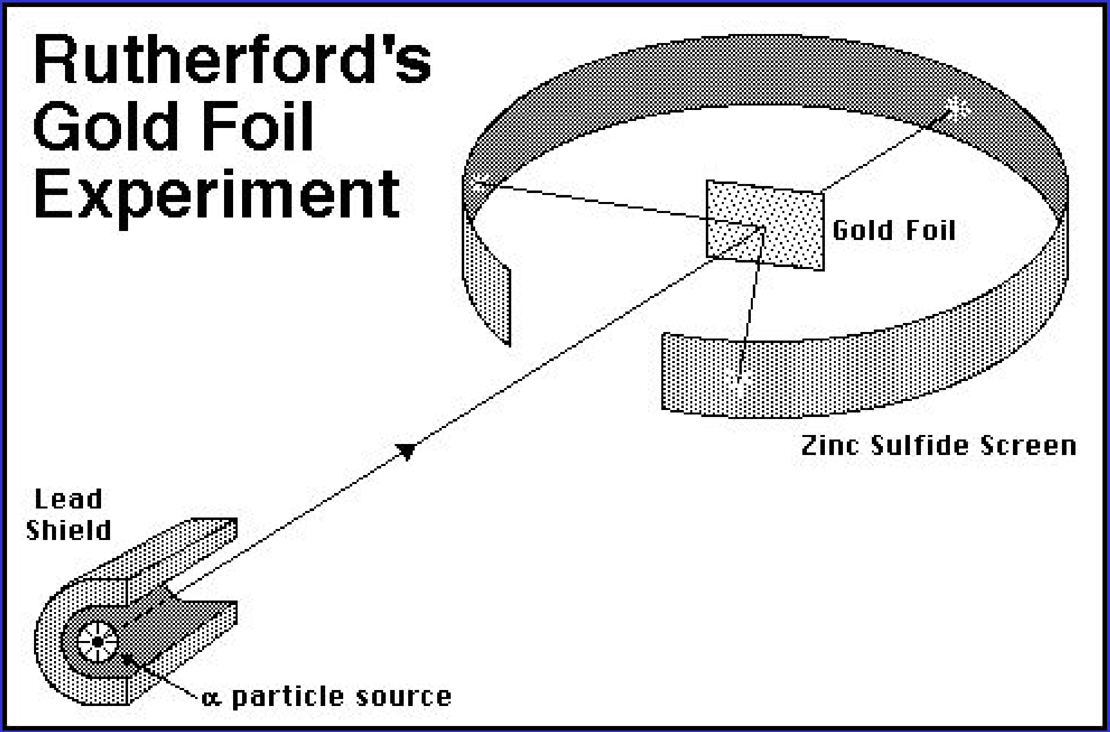
$m_p = 1.672648\ \ 10^{-27}$ kg

Anode rays are different for different gases used in the bulb, repelled by positive potential, **Integer multiples of** –*q*, smallest for $H_2$

$q_p$ = – elementary charge = $1.602\ 177\ 10^{-19}$ C

# Rutherford Gold Foil Experiment

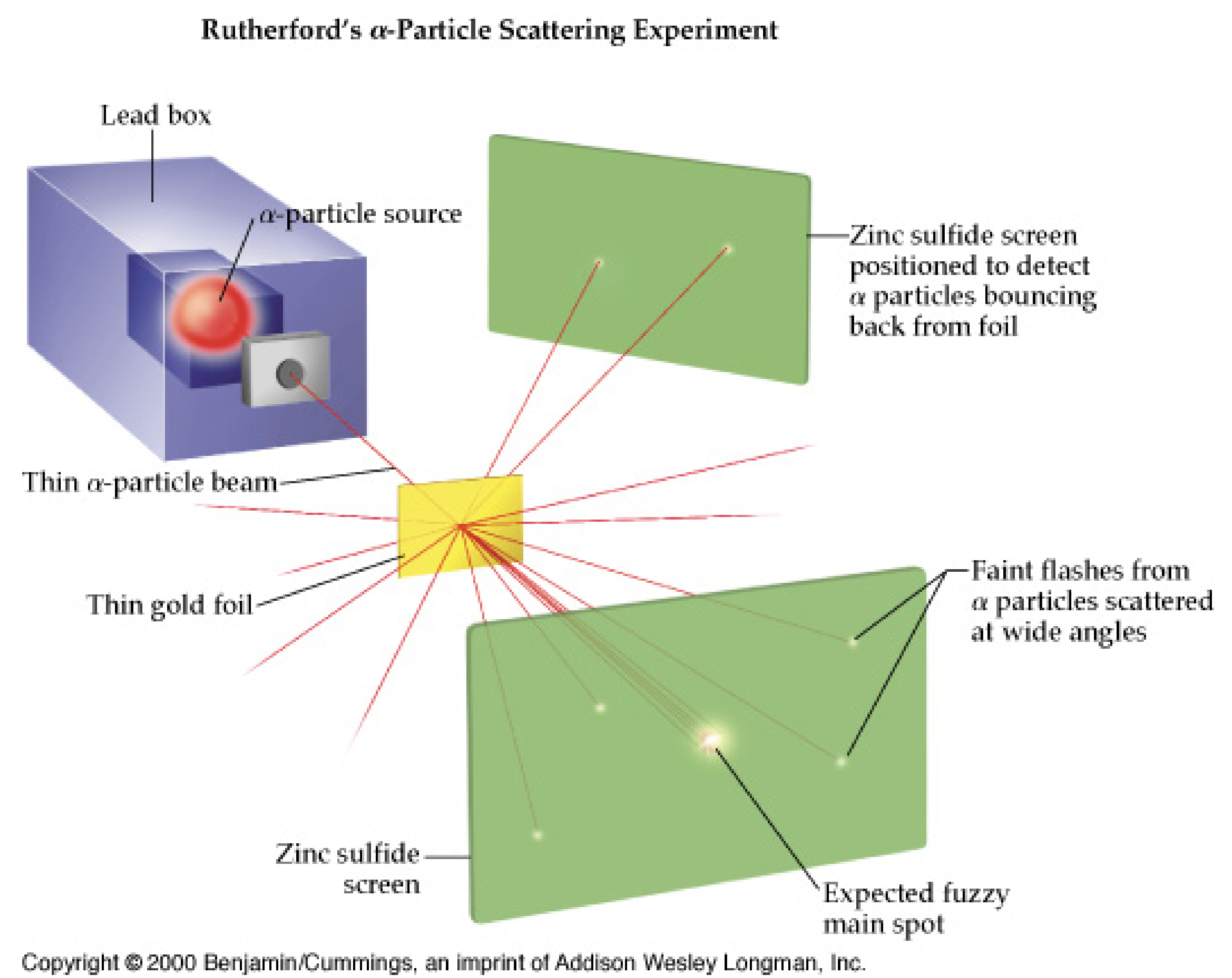
1911 Scattering of $\alpha$ particles on Au



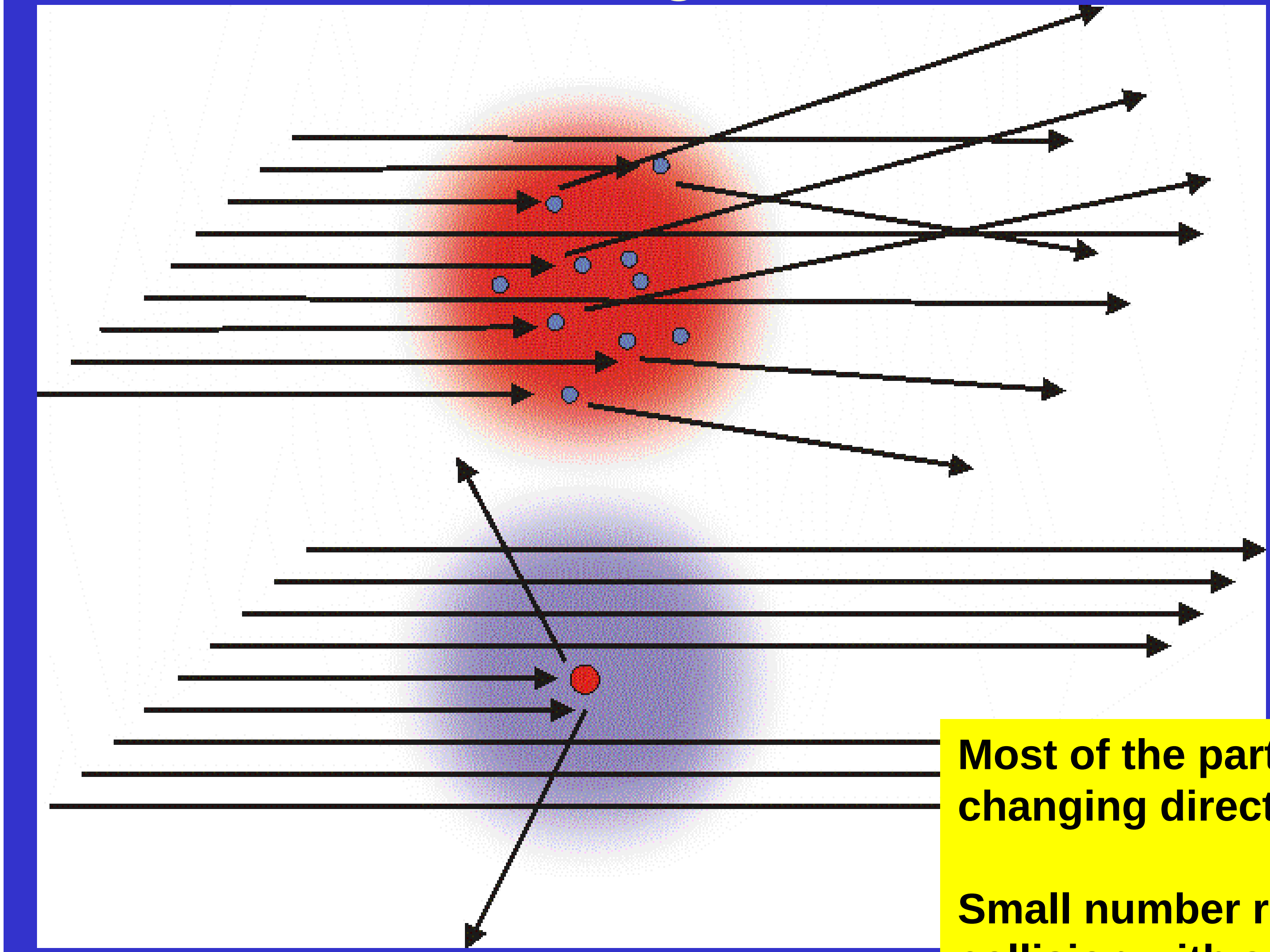
$^{214}$Po – source of $\alpha$ particles

Ernest Rutherford
(1871-1937)
NP in Chemistry 1908

# Experiment - Scattering of α Particles on Au



# Scattering of $\alpha$ Particles on Au



Model 1
Thomson

Model 2
Rutherford

**Most of the particles passes without changing direction = empty space**

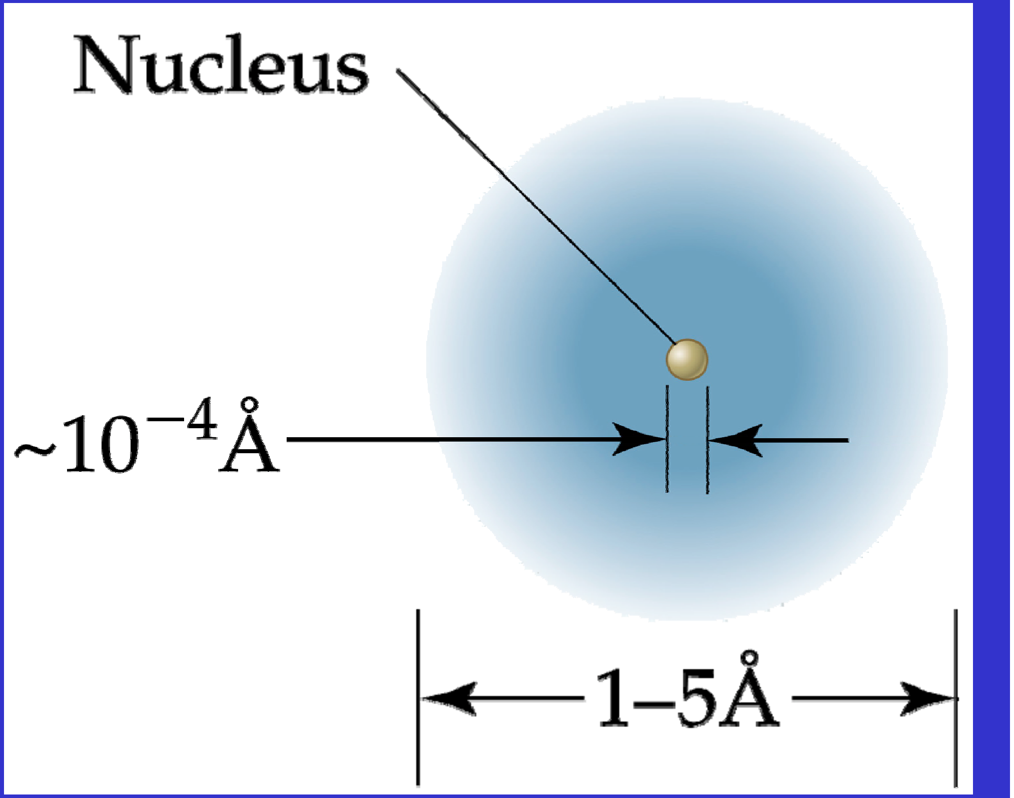
**Small number reflected back collision with a massive nucleus**

# Nuclear Atomic Model

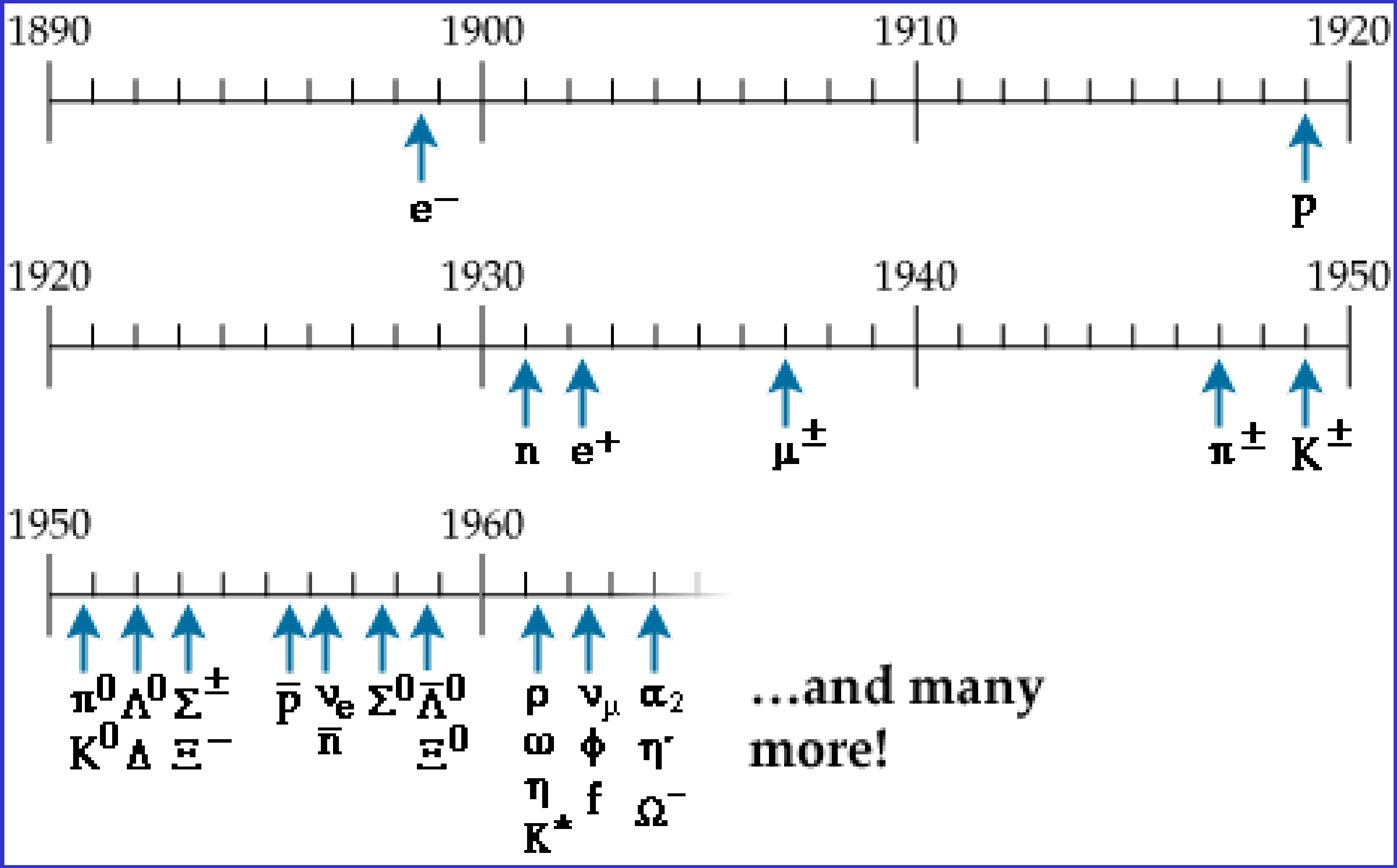
Most of the atom volume is formed by a cloud of negative charge with a small mass

Atomic nucleus consists of positive charge with high density (1.6 $10^{14}$ g $cm^{-3}$)

Mass of nucleus is 99.9% of atomic mass



# Discovery of Elementary Particles



# Elementary Particles

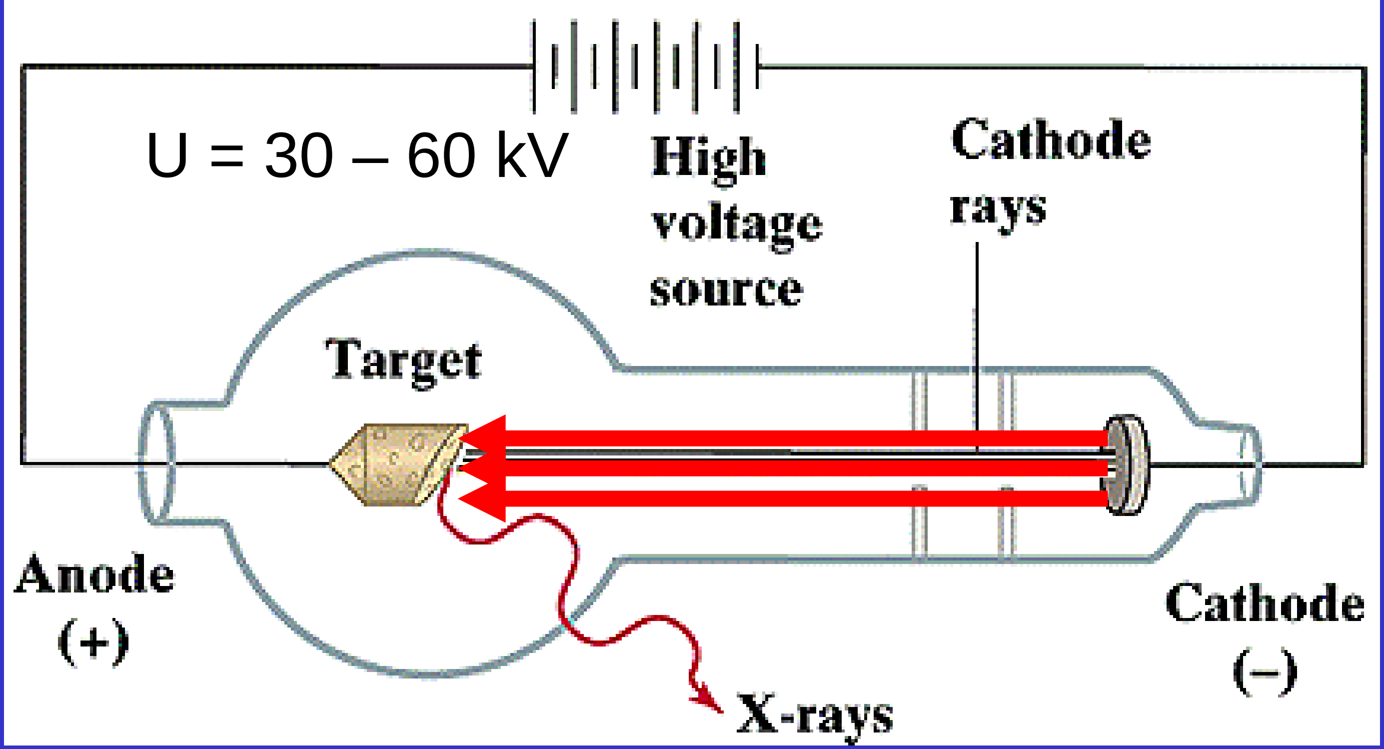
| Particle | Symbol | Electric charge | Spin | m, kg | m , amu |
|---|---|---|---|---|---|
| Electron | e | –1 | ½ | $9.11\ 10^{-31}$ | 0.0005486 |
| Proton | p | +1 | ½ | $1.673\ 10^{-27}$ | 1.007276 |
| Neutron | n | 0 | ½ | $1.675\ 10^{-27}$ | 1.008665 |

# X-Ray Radiation

1895 X-Rays pass through matter

Wilhelm K. Roentgen (1845-1923)
NP in Physics 1901

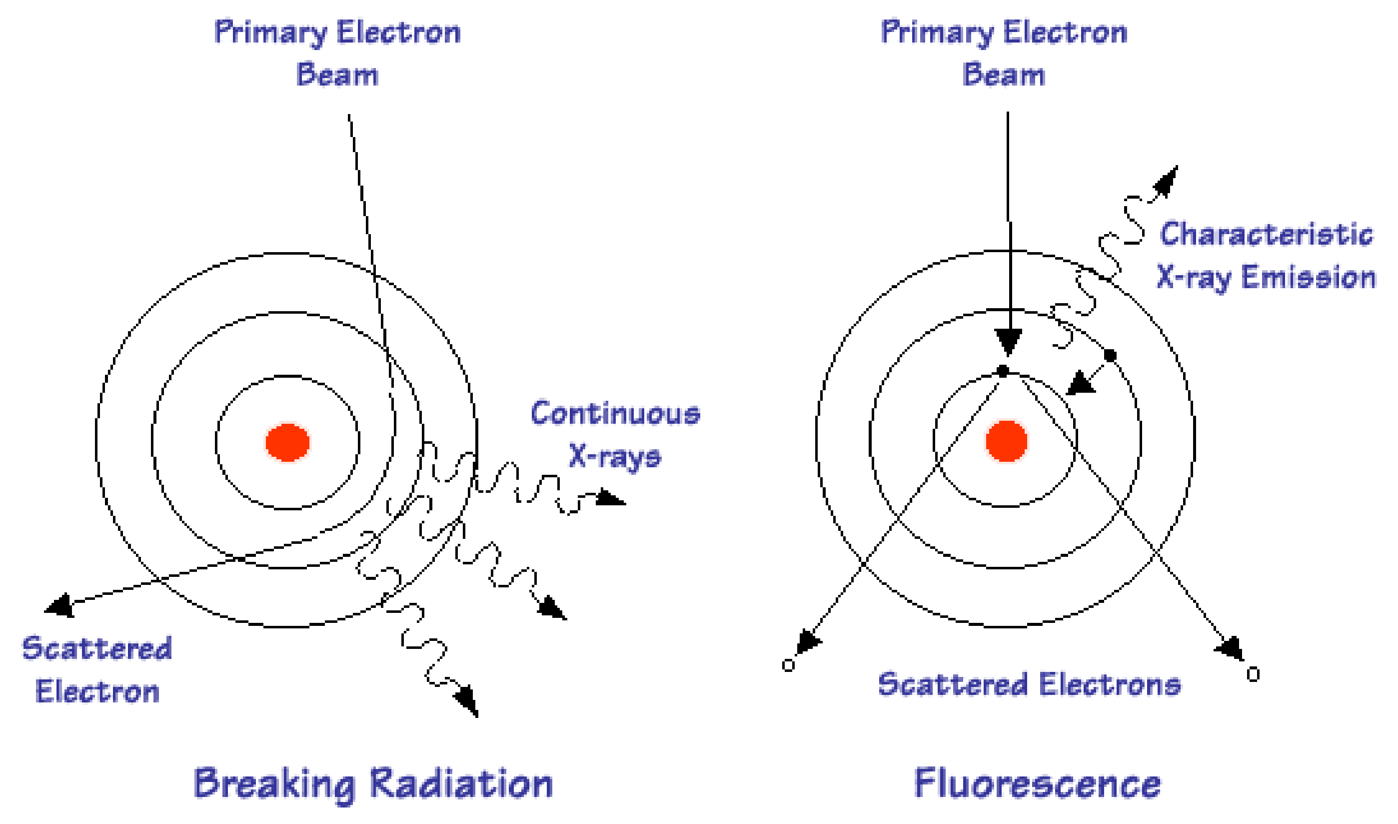
# X-Ray Radiation



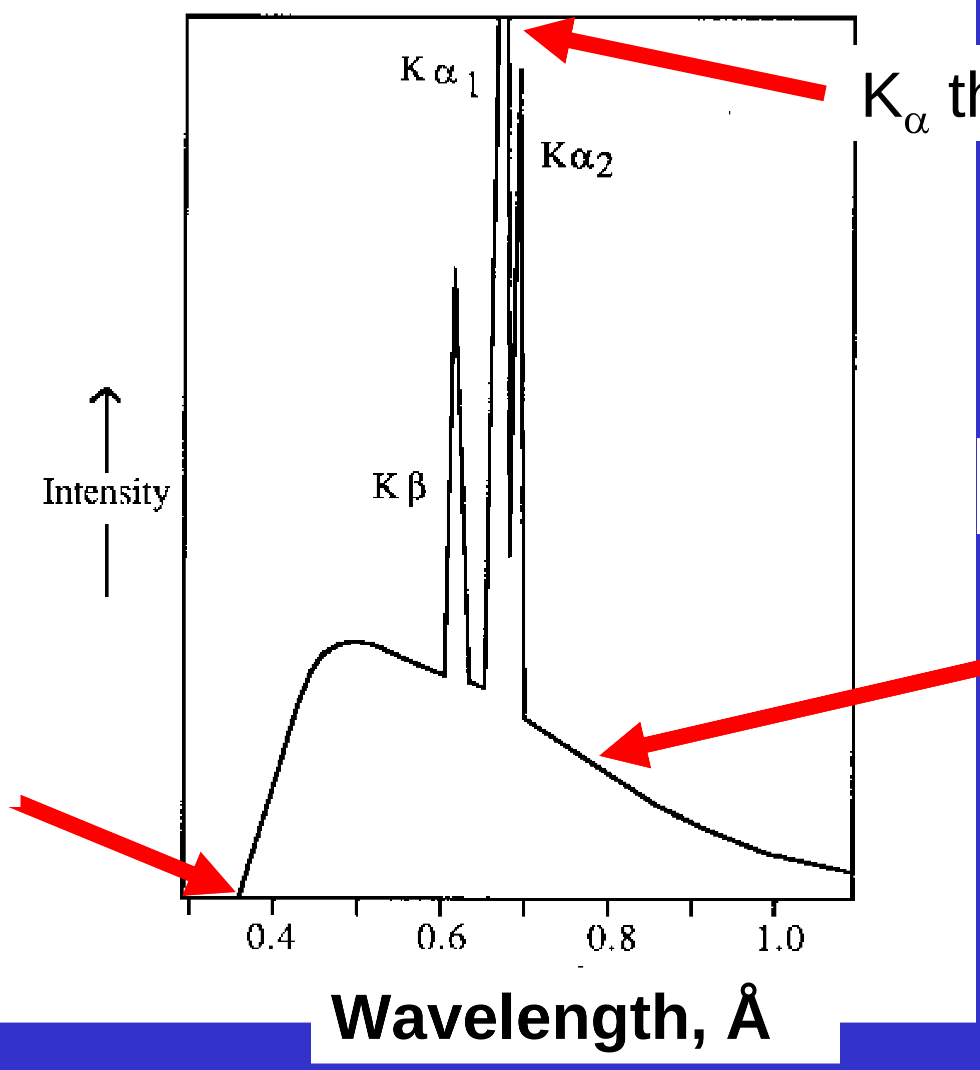
Wavelength λ = 0.1 – 100 Å **according to the anode**

Anode material: Cu $K_{\alpha}$ E = 8.05 keV λ = 1.541 Å

# Generation of X-Ray Radiation



# Spectrum of X-Rays



$K_\alpha$ the strongest line

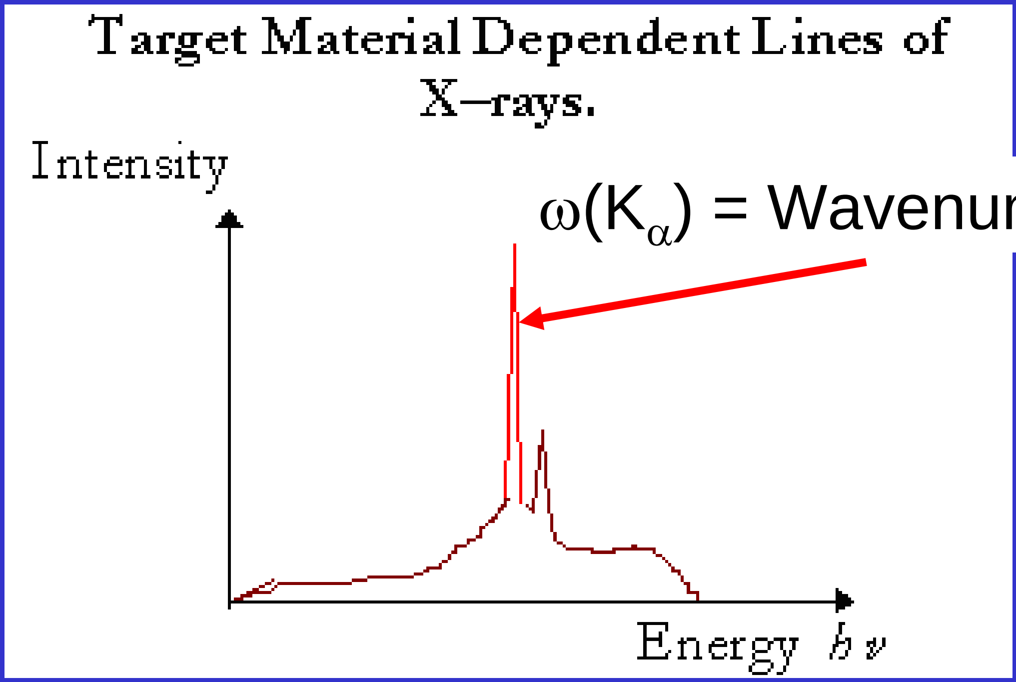
Characteristic lines for different elements

1 Ångström = $10^{-10}$ m

Bremsstrahlung

Minimum
eV = hν

# Moseley's Law



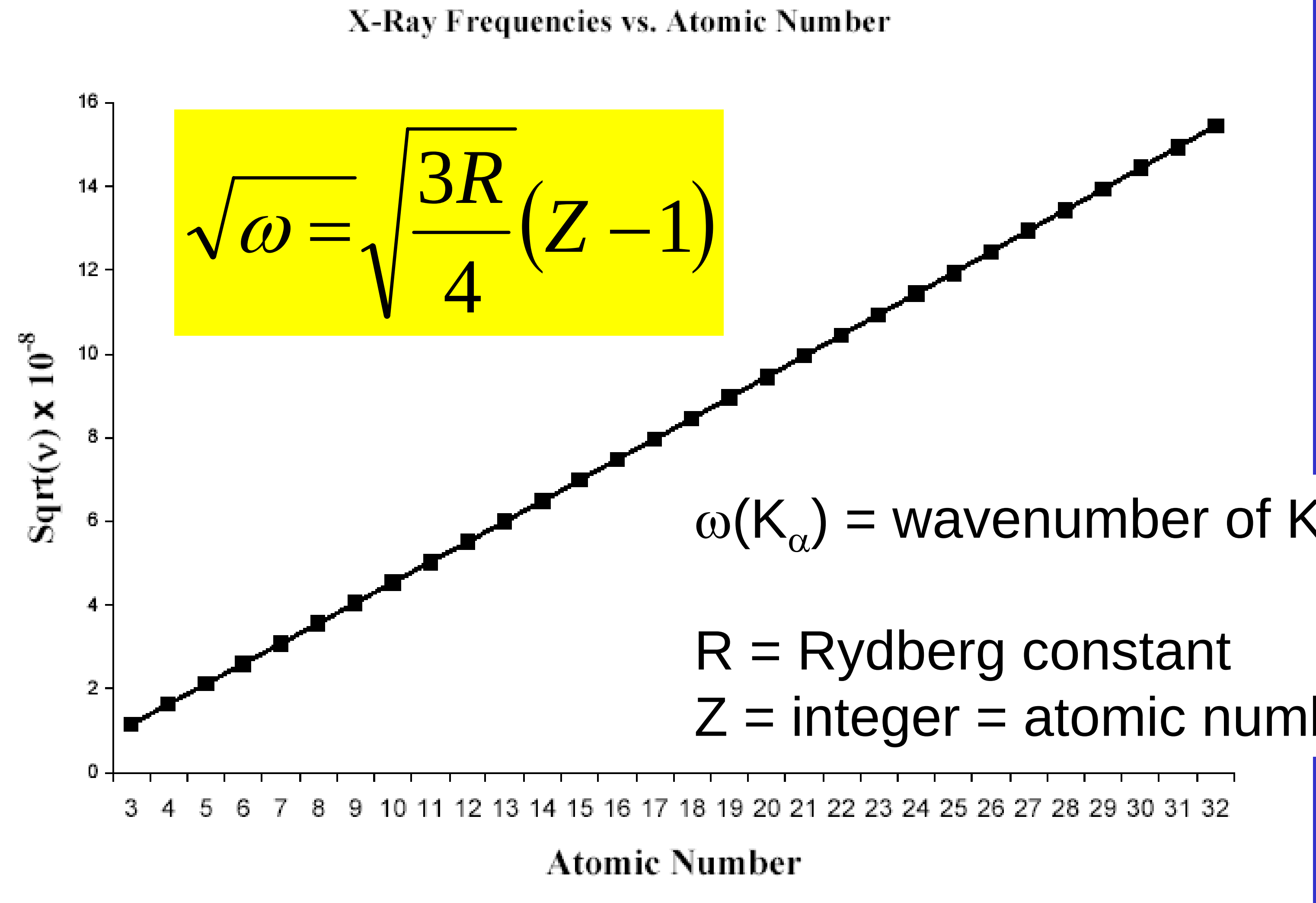
$\omega(K_\alpha)$ = Wavenumber of $K_\alpha$ line

Henry Moseley
(1887-1915)
Killed by a sniper

Wavenumber $\omega$ of $K_\alpha$ line is characteristic for different elements

$$\sqrt{\omega(K_\alpha)} = C\,(Z-1)$$

# Moseley’s Law



$$\sqrt{\omega} = \sqrt{\frac{3R}{4}}(Z-1)$$

$\omega(K_\alpha)$ = wavenumber of $K_\alpha$ line

R = Rydberg constant
Z = integer = atomic number

1913

# Moseley’s Law

Corrected order of elements in the periodical system

| | | |
|---|---|---|
| Z = 27 | Co | 58.933 |
| Z = 28 | Ni | 58.71 |

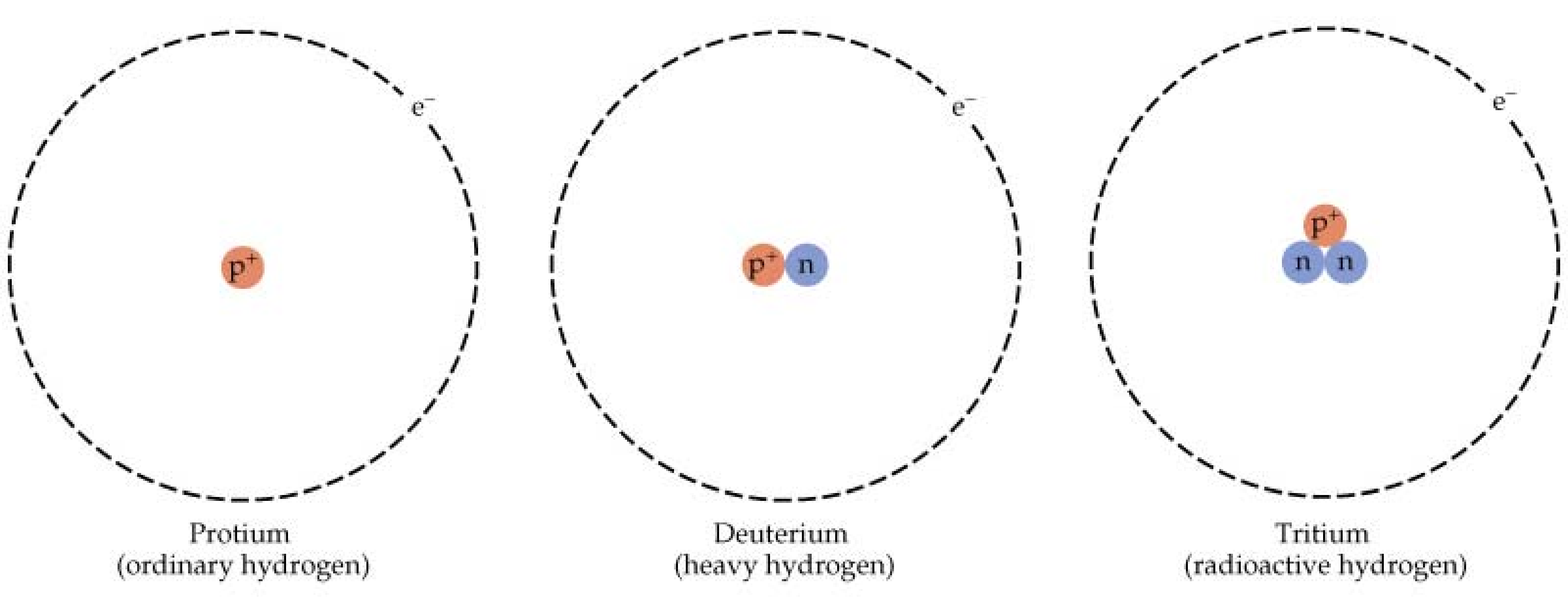
Forecasted new elements:
Z = 43 (Tc), 61 (Pm), 72 (Hf), 75 (Re)

Corrected periodic law (Mendeleev 1869):

Element properties are function of its atomic number
(not atomic mass)

**Z = Atomic (proton) number**
**Z = number of protons in a nucleus**

# Isotopes



Protium
(ordinary hydrogen)

Deuterium
(heavy hydrogen)

Tritium
(radioactive hydrogen)

$^1H$ $^2H = D$ $^3H = T$

Differs in physical properties

Boiling points (K) : $H_2$ 20.4, $D_2$ 23.5, $T_2$ 25.0

# Natural Abundance, %

| | |
|---|---|
| $^{1}H$ | 99.985 |
| $^{2}H$ | 0.015 |
| $^{12}C$ | 98.89 |
| $^{13}C$ | 1.11 |
| $^{14}N$ | 99.63 |
| $^{15}N$ | 0.37 |

| | |
|---|---|
| $^{16}O$ | 99.759 |
| $^{17}O$ | 0.037 |
| $^{18}O$ | 0.204 |
| $^{32}S$ | 95.00 |
| $^{33}S$ | 0.76 |
| $^{34}S$ | 4.22 |
| $^{36}S$ | 0.014 |

# Variations of Natural Abundance, %

| | | |
|---|---|---|
| $^{10}B$ | 18.927 - 20.337 | 19.9 (7) |
| $^{11}B$ | 81.073 - 79.663 | 80.1 (7) |
| $^{16}O$ | 99.7384 - 99.7756 | 99.757 (16) |
| $^{17}O$ | 0.0399 - 0.0367 | 0.038 (1) |
| $^{18}O$ | 0.2217 - 0.1877 | 0.205 (14) |

Changes in relative content of isotopes

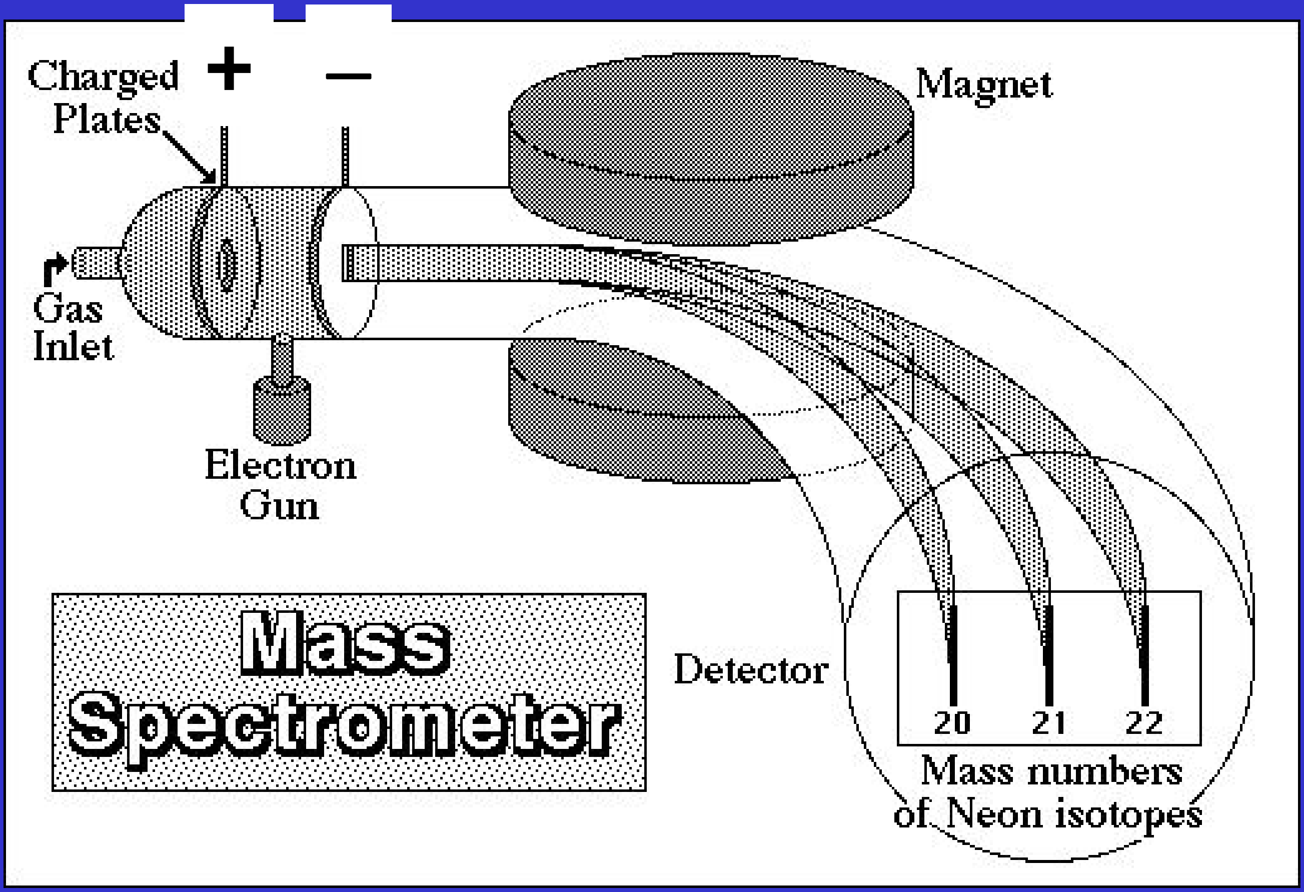
geochemistry – origin and age of rocks

# Mass Spectrometry

**Ne → $Ne^+ + e^-$**

J. J. Thomson discovered 2 isotopes of Ne

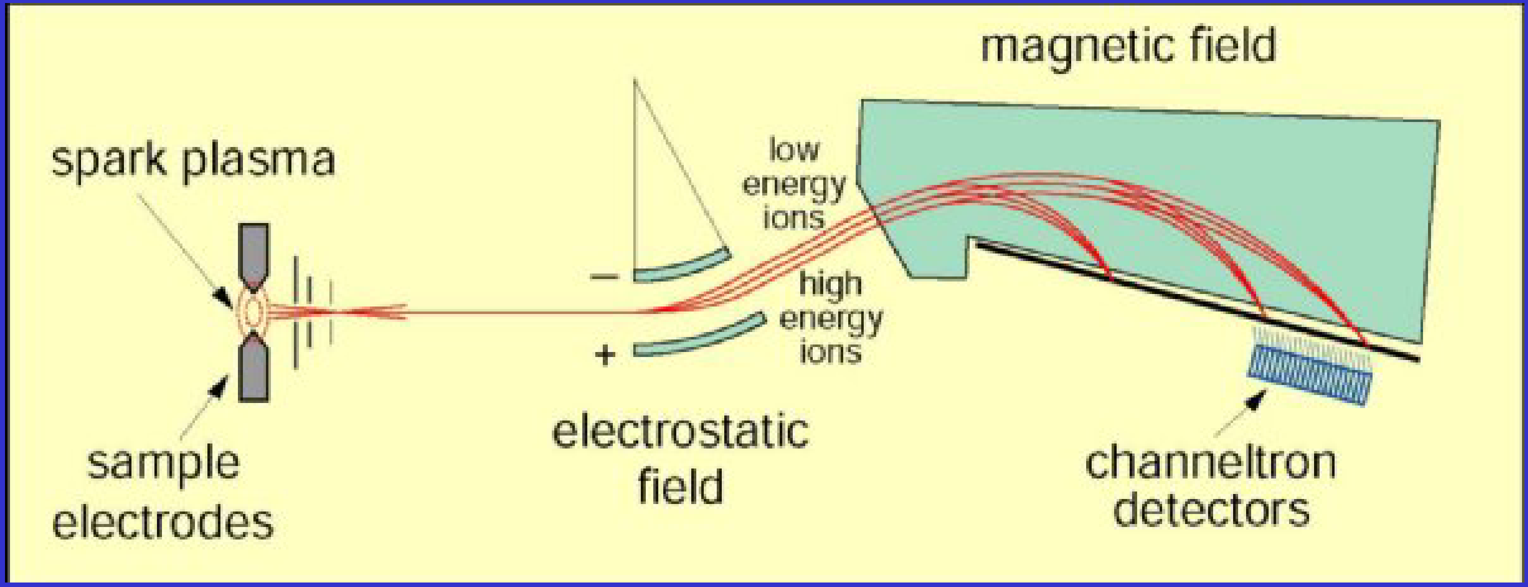
| | |
|---|---|
| $^{20}Ne$ | 90.48% |
| $^{21}Ne$ | 0.27% |
| $^{22}Ne$ | 9.25% |



# Mass Spectrometry

1. Ionization

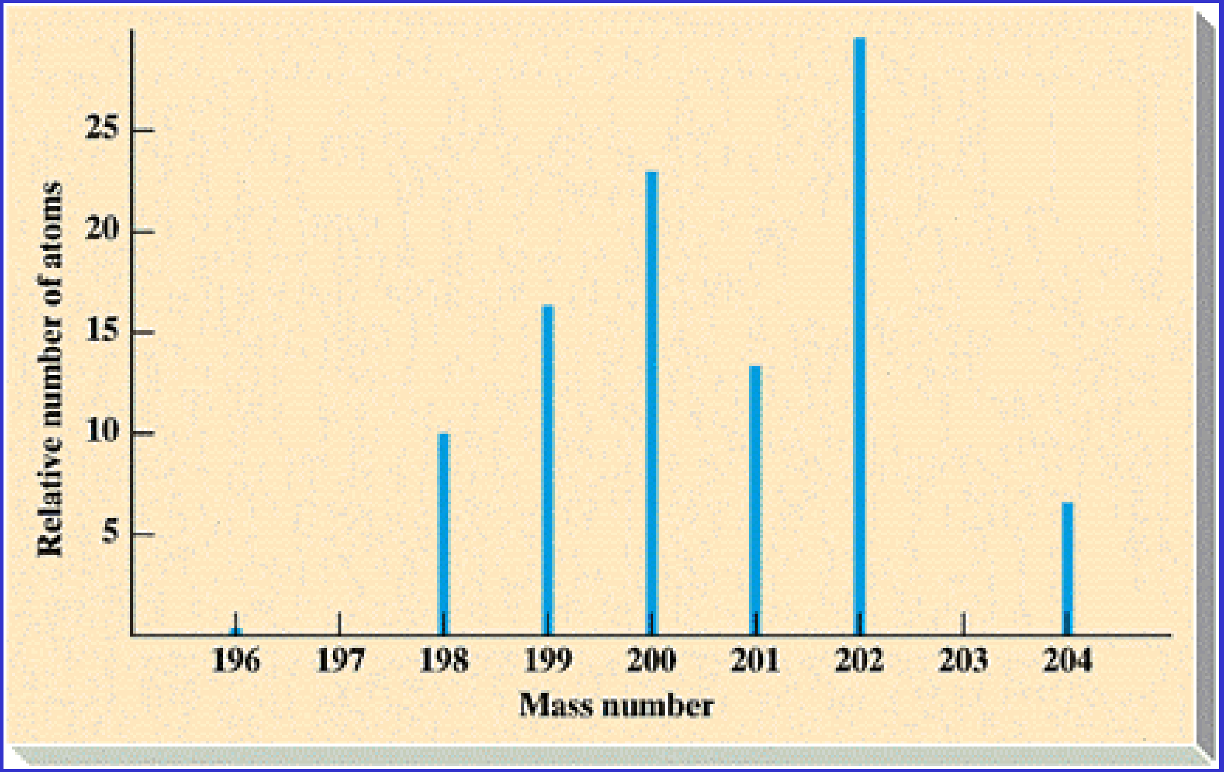
2. Mass separation according to *m/z*



3. Detection

# Mass Spectrum of Hg

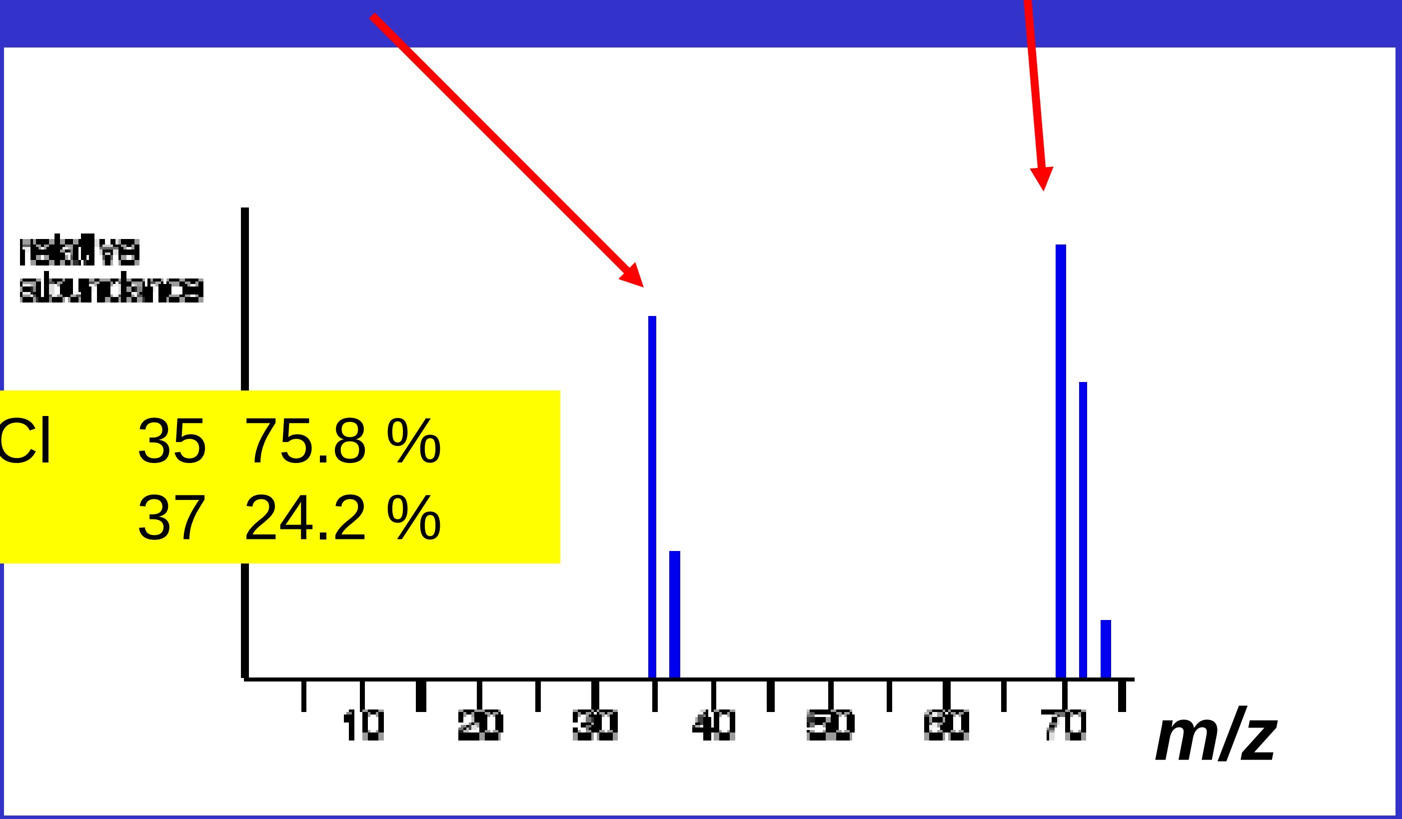
| ${}_{80}^{A}Hg$ | % |
|---|---|
| 196 | 0.146 |
| 198 | 10.02 |
| 199 | 16.84 |
| 200 | 23.13 |
| 201 | 13.22 |
| 202 | 29.80 |
| 204 | 6.850 |



# Mass Spectrum of $Cl_2$

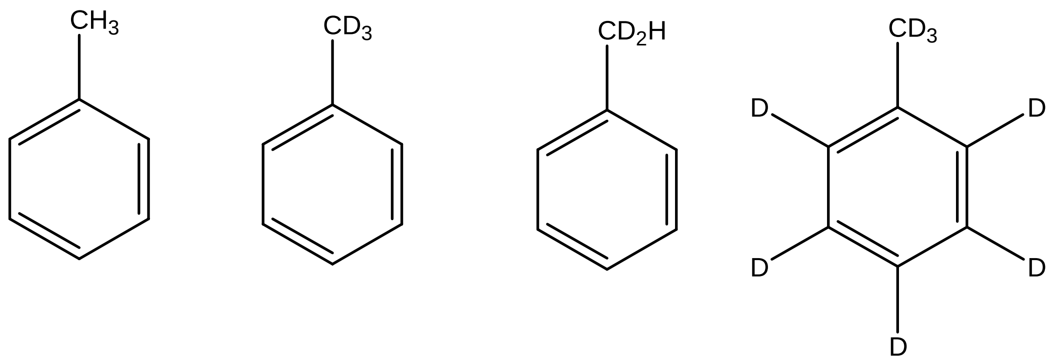
$^{35}Cl^+$ and $^{37}Cl^+$

$(^{35}Cl\text{-}^{35}Cl)^+$ $(^{35}Cl\text{-}^{37}Cl)^+$ $(^{37}Cl\text{-}^{37}Cl)^+$



| | | |
|---|---|---|
| $_{17}Cl$ | 35 | 75.8 % |
| | 37 | 24.2 % |

# Isotopomers



$H_2O$ $D_2O$ HDO $H_2{}^{17}O$ $H_2{}^{18}O$

$H_3C{-}C{\equiv}N$ $D_3C{-}C{\equiv}N$ $D_2HC{-}C{\equiv}N$

$H_3{}^{13}C{-}C{\equiv}N$ $H_3C{-}{}^{13}C{\equiv}N$ $H_3C{-}C{\equiv}{}^{15}N$

# Atomic Mass Unit

**Avogadro's Hypothesis**: Two equal volumes of gas, at the same temperature and pressure, contain the same number of molecules.

The easiest was to measure relative atomic masses of gases

Oxygen weighs 16× more than hydrogen

Oxygen combines with most of the elements, standard O = 16

- **Chemical analysis provides average mass**

O = 16 (mixture of isotopes)

- **Mass spectrometry provides isotope mass**

$^{16}O = 16$

# Atomic Mass Unit

1961 Atomic Mass Unit

compromise between scales based on O = 16 and $^{16}O = 16$,

Atomic Mass Unit based on nuclide $^{12}C$

1 amu = 1 $u$ = 1 $m_u$ = 1 d = 1 (Dalton) = 1/12 of atomic mass of nuclide $^{12}C$

1 amu = $1.6606\ 10^{-27}$ kg

**Mass of 1 atom of $^{12}C$ is 12 amu (by definition)**

**Mass of 1 mol of $^{12}C$ is 12 g  exactely**

(Number of significant figures?)

# Relative Atomic Mass

**Nuclide mass =** mass of a pure isotope

**Average Atomic Mass of element** = average mass of isotopes weighted by their natural abundance = Atomic Weight

**Relative** atomic mass = *m*(A) / amu [dimensionless]

1 amu = 1.6606 $10^{-27}$ kg

$$\boxed{A_r = \frac{m(atomu)}{amu}}$$

**Mass of 1 atom of $^{12}C$ is 12 amu (by definition) = 12 × 1.6606 $10^{-27}$ kg**

**Relative** atomic mass of **$^{12}C$ = 12**

**Mass of 1 mol of $^{12}C$ is 12 g exactely**

# Average Atomic Mass = Atomic Weight

Natural C:

98.892 % $^{12}C$   1.108 % $^{13}C$

Nuclide mass of $^{12}C = 12$ amu

Nuclide mass of $^{13}C = 13.00335$ amu

Atomic Weight of C (weighted average):

$A_w = (0.98892)(12) + (0.01108)(13.00335) = 12.011$ amu

1 amu = $1.6606\ 10^{-27}$ kg

# Average Atomic Mass = Atomic Weight

**Mo, molybden** $A_w = 95.94$

| Mass Number | Nuclide Mass, amu | Abundance, % |
|---|---|---|
| 92 | 91.906808 | 14.84 |
| 94 | 93.905085 | 9.25 |
| 95 | 94.905840 | 15.92 |
| 96 | 95.904678 | 16.68 |
| 97 | 96.906020 | 9.55 |
| 98 | 97.905406 | 24.13 |
| 100 | 99.907477 | 9.63 |

# Average Atomic Mass = Atomic Weight

| Elem. | Nuclides | Z | N | A | Nuclide mass, amu | Abund., % | Atomic weight, amu |
|---|---|---|---|---|---|---|---|
| H | H | 1 | 0 | 1 | 1.007825 | 99.985 | |
| | D | 1 | 1 | 2 | 2.01410 | 0.015 | 1.0079 |
| | T | 1 | 2 | 3 | | | |
| He | $^{3}$He | 2 | 1 | 3 | 3.01603 | 0.00013 | 4.0026 |
| | $^{4}$He | 2 | 2 | 4 | 4.00260 | 99.99987 | |
| B | $^{10}$B | 5 | 5 | 10 | 10.01294 | 19.78 | 10.81 |
| | $^{11}$B | 5 | 6 | 11 | 11.00931 | 80.22 | |
| F | $^{19}$F | 9 | 10 | 19 | 18.99840 | 100 | 18.9984 |

Significant figures

# Molecular Weight

**Calculate $M_r$ for a formula**

$M_r(CO_2) = A_r(C) + 2 \times A_r(O) = 44.01$

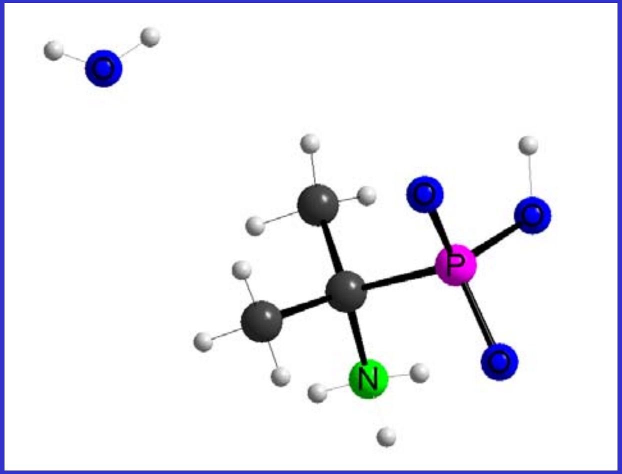
$M_r(CuSO_4.5H_2O) =$

$= A_r(Cu) + A_r(S) + (4 + 5) \times A_r(O) + 10 \times A_r(H)$

$= 249.68$

**Molecular Weight of $CuSO_4.5H_2O$ = 249.68 g $mol^{-1}$**

# Atomic Composition %



$C_3H_{12}O_4PN$

$M_r(C_3H_{12}O_4PN)$ =

= 3 × $A_r$(C) + 12 × $A_r$(H) + 4 × $A_r$(O)

+ 1 × $A_r$(P) + 1 × $A_r$(N) = 157.11

$M_r(C_3H_{12}O_4PN)$ = 157.11 …………100%

3 × $A_r$(C)………………………………22.92%

12 × $A_r$(H)……………………………7.70%

4 × $A_r$(O) ………………………………40.74%

1 × $A_r$(P)………………………………..19.72%

1 × $A_r$(N)……………………………. 8.92%

# Empirical Formula

Calculate empirical formula (stoichiometric) for a compound that consists of 26.58% K, 35.35% Cr and 38.07% O.

= Find stoichiometric coeficients x, y, z in $K_xCr_yO_z$

$$x = \frac{26.58}{39.098} = 0.6798\text{...........}1$$
$$y = \frac{35.35}{51.990} = 0.6799\text{...........}1.0001$$
$$z = \frac{38.07}{15.999} = 2.3795\text{............}3.4998$$

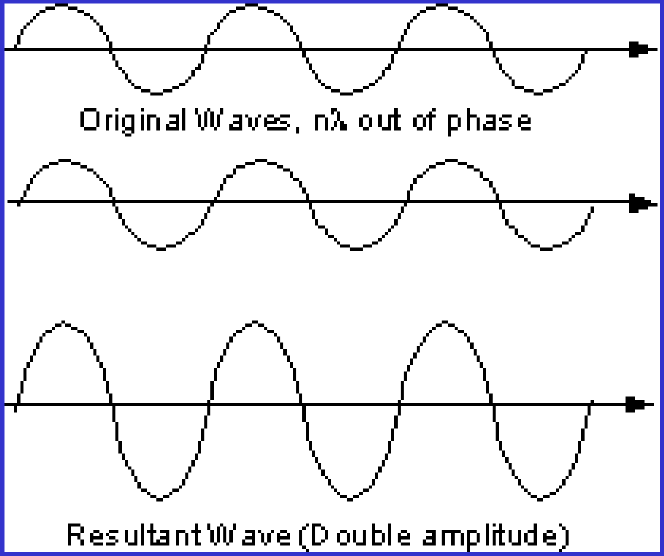
$$n = \frac{m}{A_r}$$

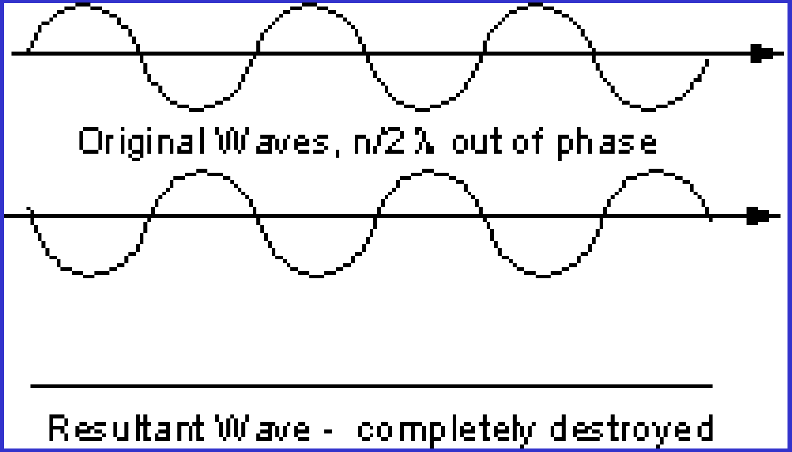
$$K_1Cr_{1.0001}O_{3.4998} \longrightarrow K_2Cr_2O_7$$

# Diffraction

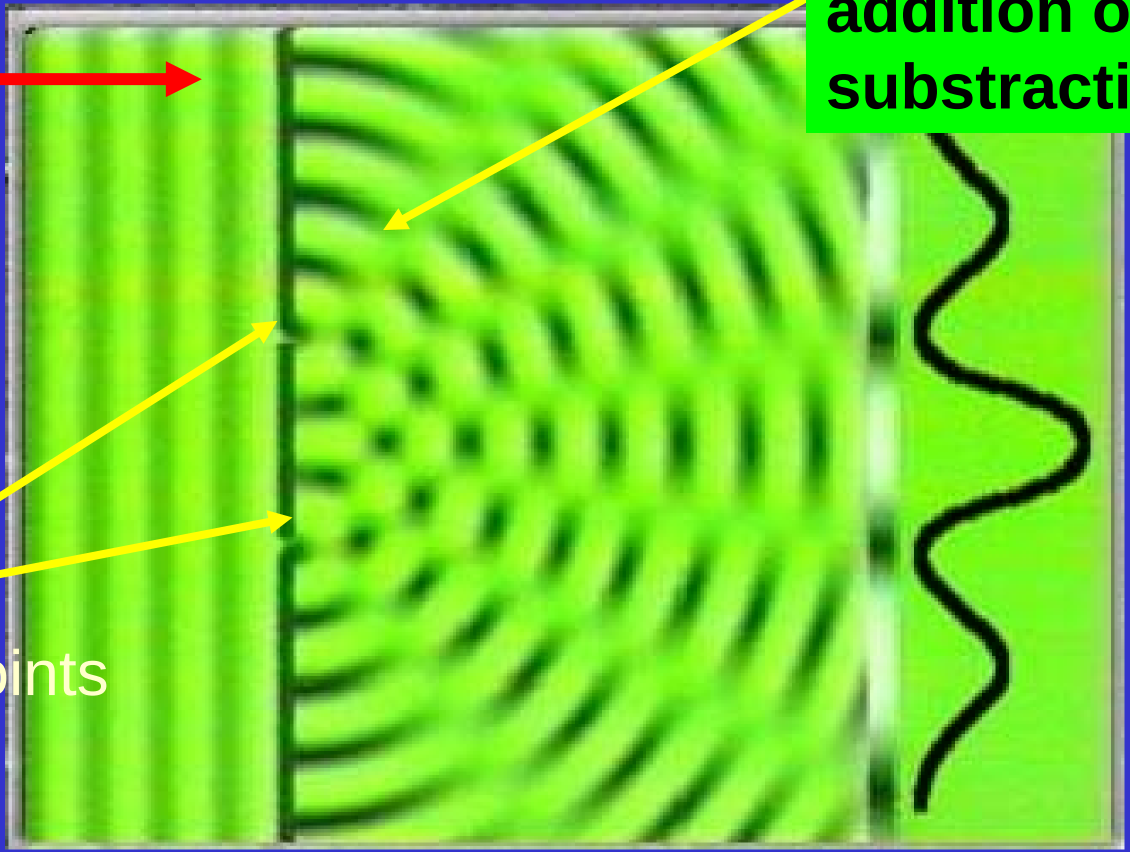
Spectroscopy – energy levels, transitions, selection rules, interpretation provides information on bonding parameters

Diffraction – purely geometrical phenomenon, depends on positions of diffracting atoms and radiation wavelength provides direct info on atomic positions





# Diffraction



**Spherical waves interference = addition or substraction**

Wave progression

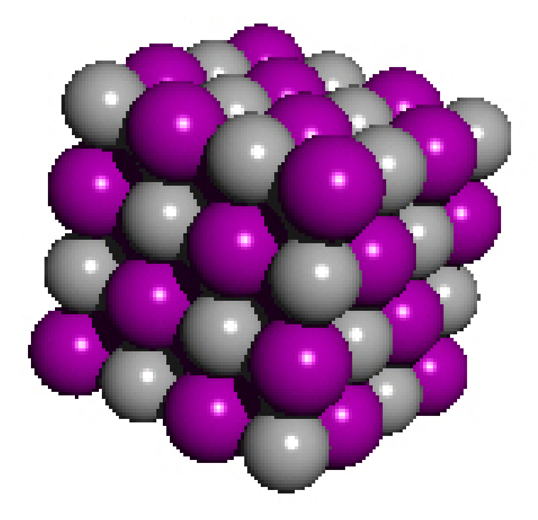
Diffracting points

Grid

# Diffraction

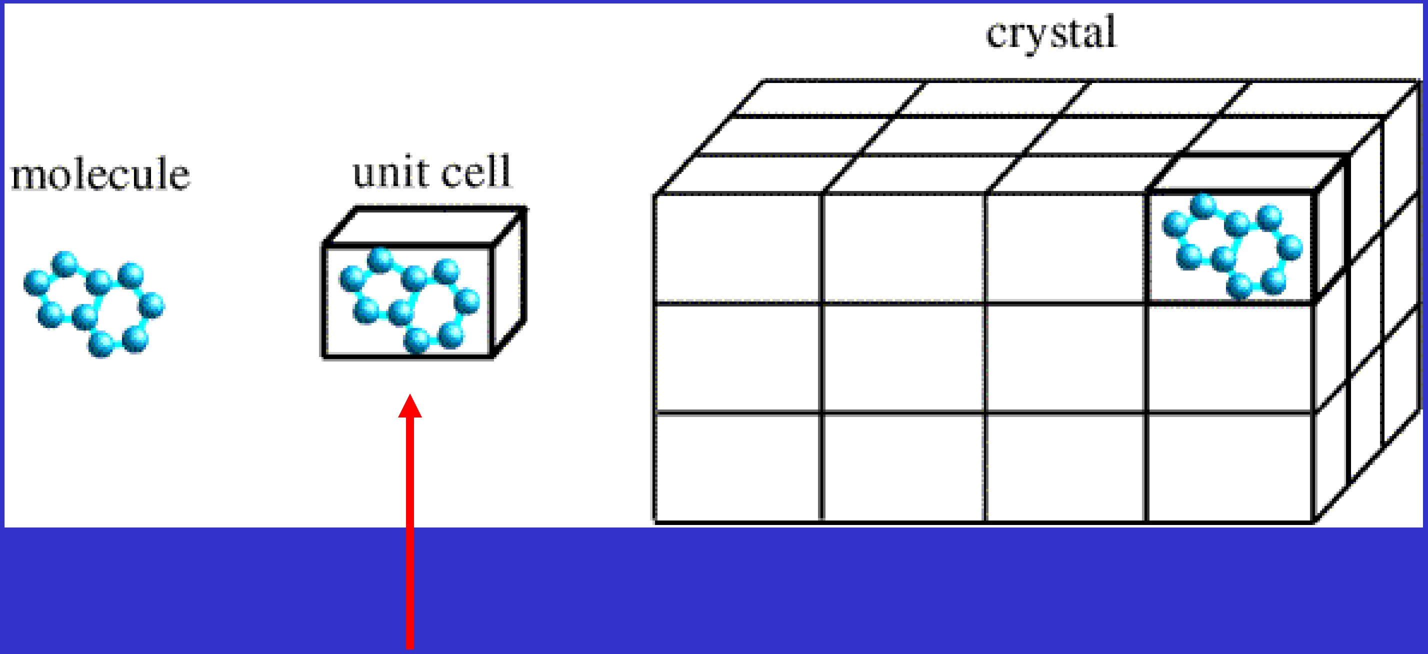
1912 Diffraction experiment

Natural grid = a crystal,  e.g. LiF, regular arrangement of atoms. Interplanar distances (Å) are comparable with X-ray radiation wavelength



Max von Laue
(1879-1960)
NP in Physics 1914

# Crystal

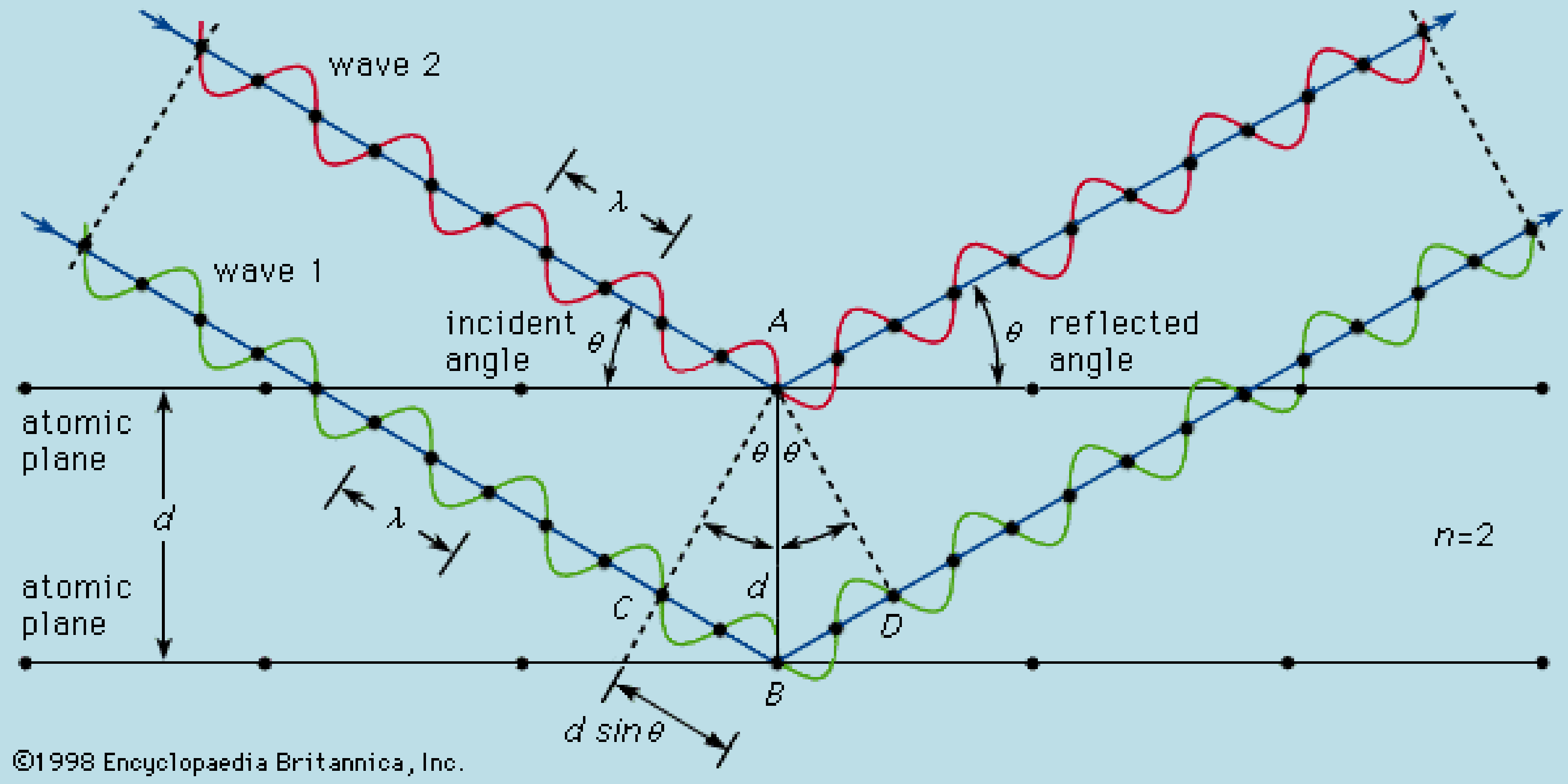


Unit cell

# Bragg's Law

**$2\, d \sin\theta = n\,\lambda$**

W. Henry and W. Lawrence Bragg
NP in Physics 1915



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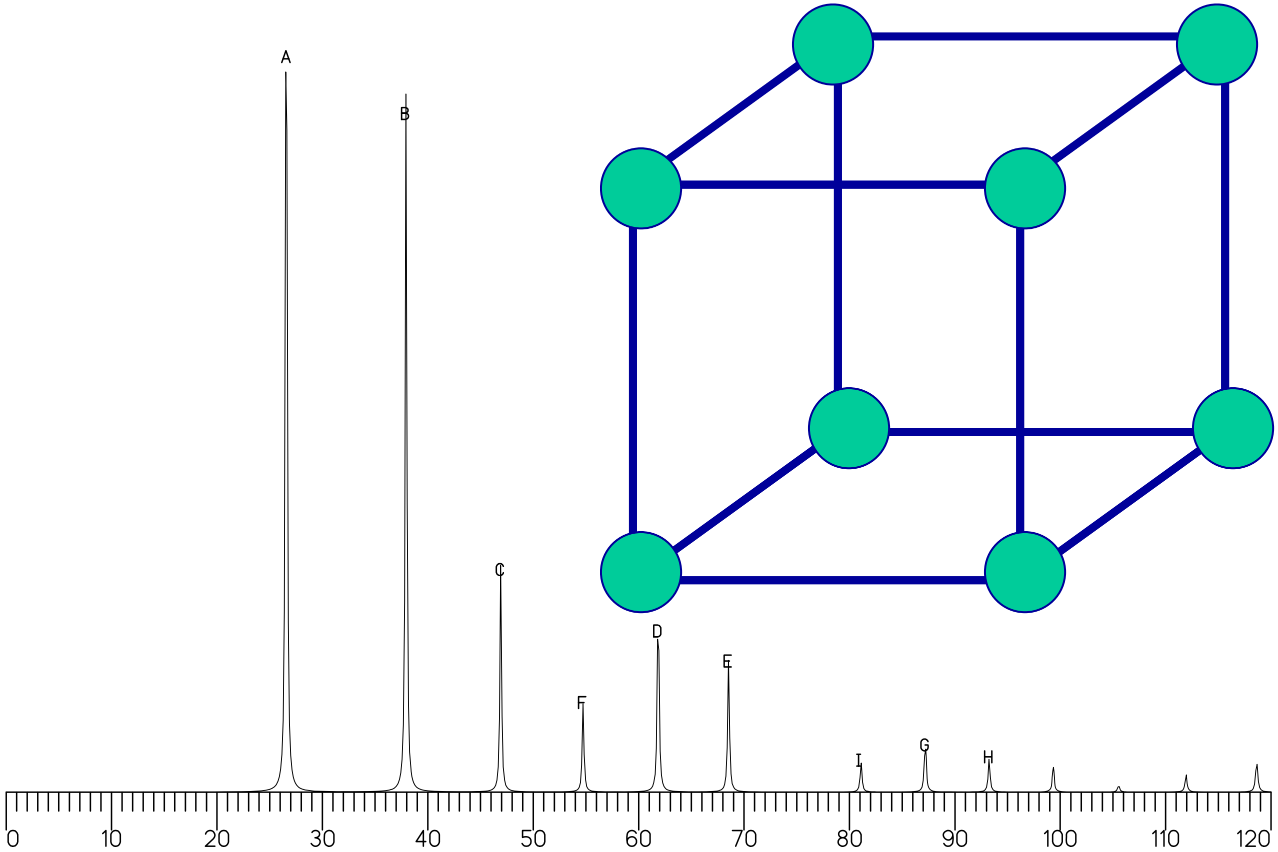
# Powder X-Ray Diffraction Analysis - Po



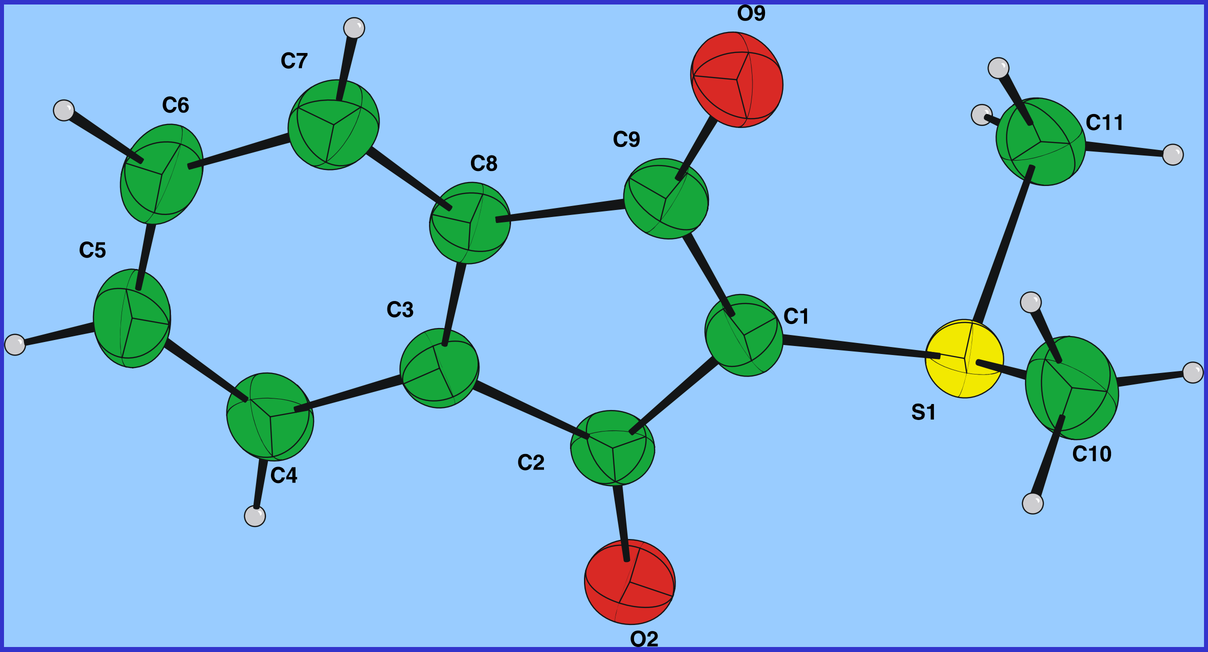
LIST OF THE 9 HIGHEST PEAKS

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A. | 0 | 0 | 1 | 26.568 | 100.000 | B. | 0 | 1 | 1 | 37.926 | 90.986 | C. | 1 | 1 | 1 | 46.920 | 29.478 |
| D. | 0 | 1 | 2 | 61.849 | 21.193 | E. | 1 | 1 | 2 | 68.524 | 17.139 | F. | 0 | 0 | 2 | 54.726 | 11.524 |
| G. | 1 | 2 | 2 | 87.202 | 5.825 | H. | 0 | 1 | 3 | 93.243 | 4.237 | I. | 0 | 2 | 2 | 81.112 | 3.779 |

# X-Ray Diffraction Structure Analysis

# X-Ray Diffraction Structure Analysis

Maps of electron density
Positions of atoms in the unit cell
Bond lengths and angles
Vibrations



# NMR – Nuclear Magnetic Resonance

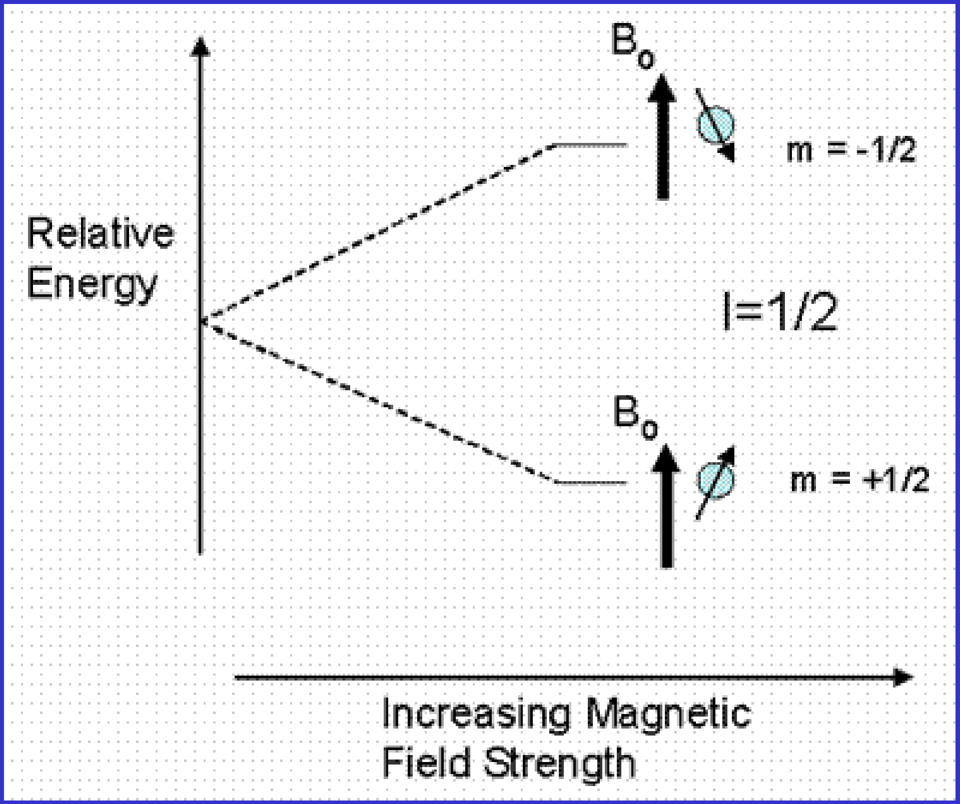
Nuclear spin, I

I = 0 : $^{12}C$, $^{16}O$ – even-even (Z/N)

I = ½ : n, p, $^{13}C$, $^{1}H$, $^{31}P$, $^{19}F$, $^{29}Si$

I > ½ : D, $^{27}Al$, $^{14}N$

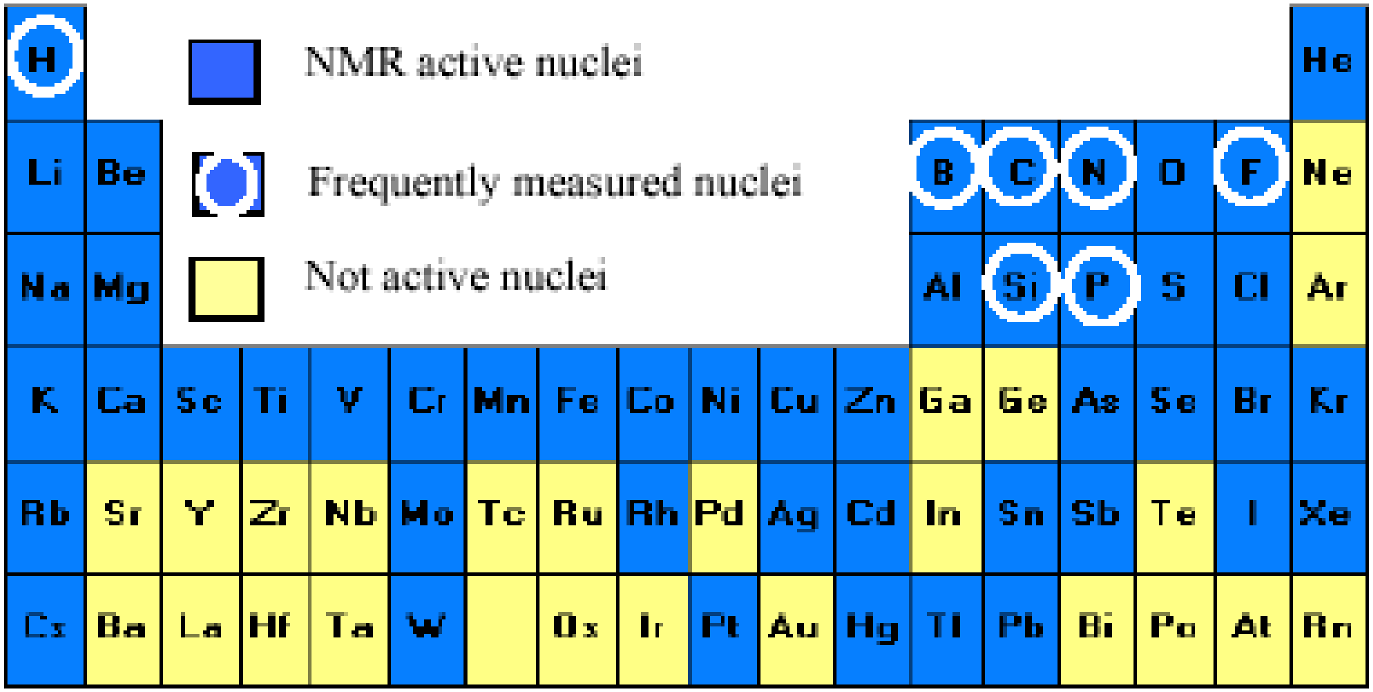
# Proton (I = ½) in Magnetic Field



Difference in energy levels

Magnetic Field Intensity $B_0$

## Periodic Table of the Elements



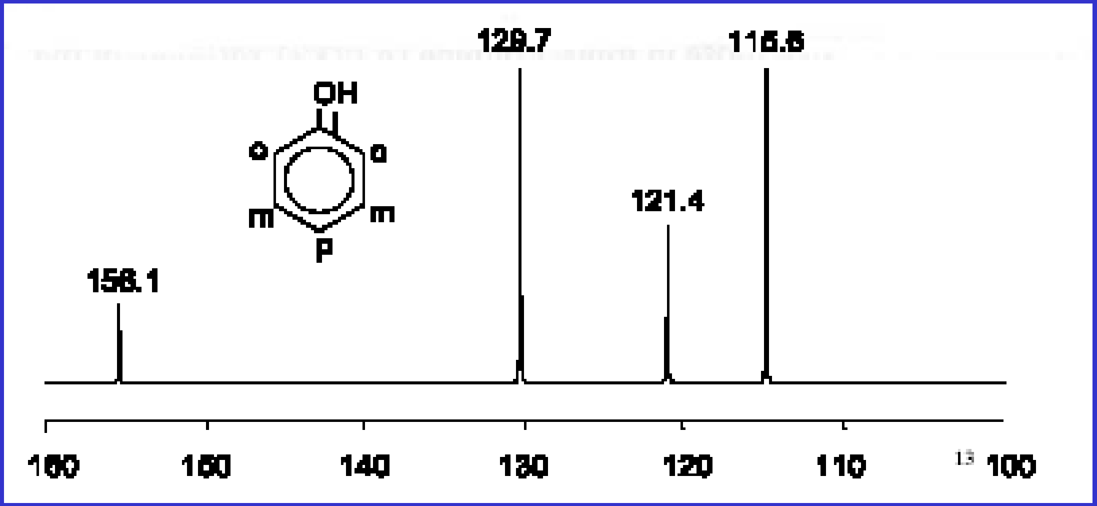
| *I* | Nuclide | *I* | Nuclide |
|---|---|---|---|
| 0 | $^{12}$C, $^{16}$O | 3/2 | $^{11}$B, $^{23}$Na, $^{35}$Cl, $^{37}$Cl |
| 1/2 | $^{1}$H, $^{13}$C, $^{15}$N, $^{19}$F, $^{29}$Si, $^{31}$P | 5/3 | $^{17}$O, $^{27}$Al |
| 1 | $^{2}$H, $^{14}$N | 3 | $^{10}$B |

# NMR – Nuclear Magnetic Resonance

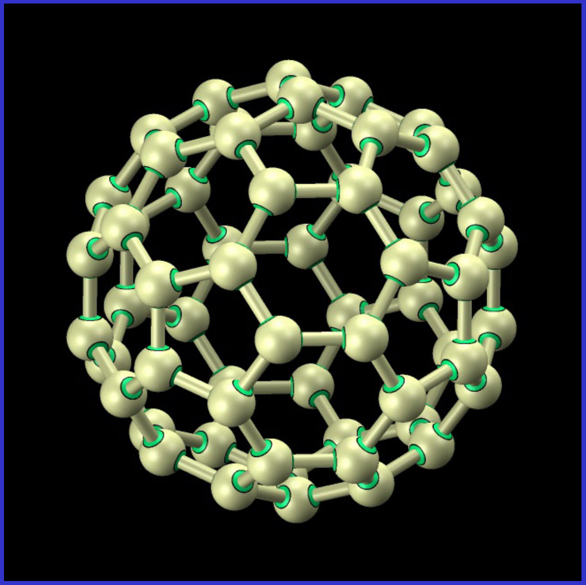
Can distinquish:

- Geometrically and thus also chemically different atoms in a molecule
- Intensities of signals correspond to the number of nuclei
- Interactions (signal splitting) provide fragment connectivity in a molecule

**$^{13}$C NMR**



# NMR – Nuclear Magnetic Resonance

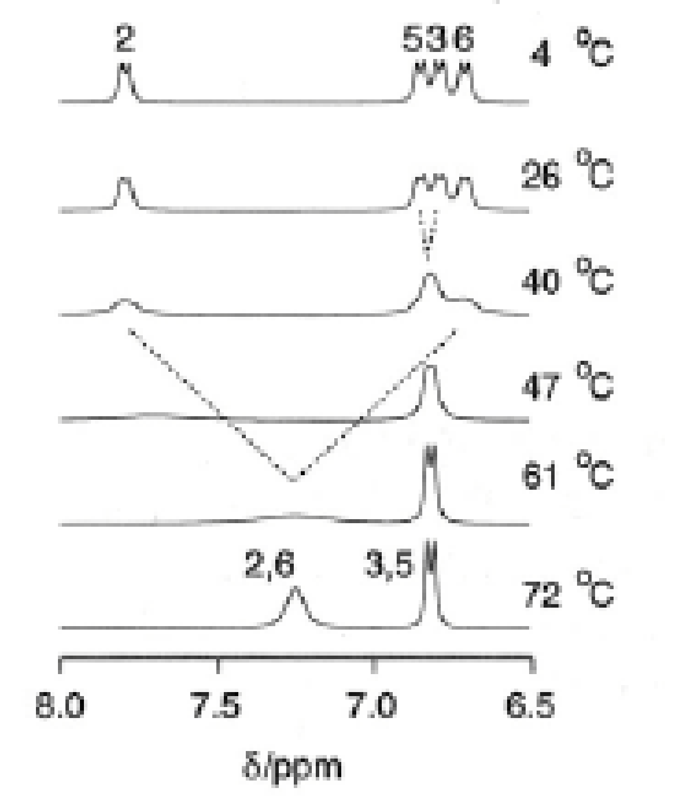


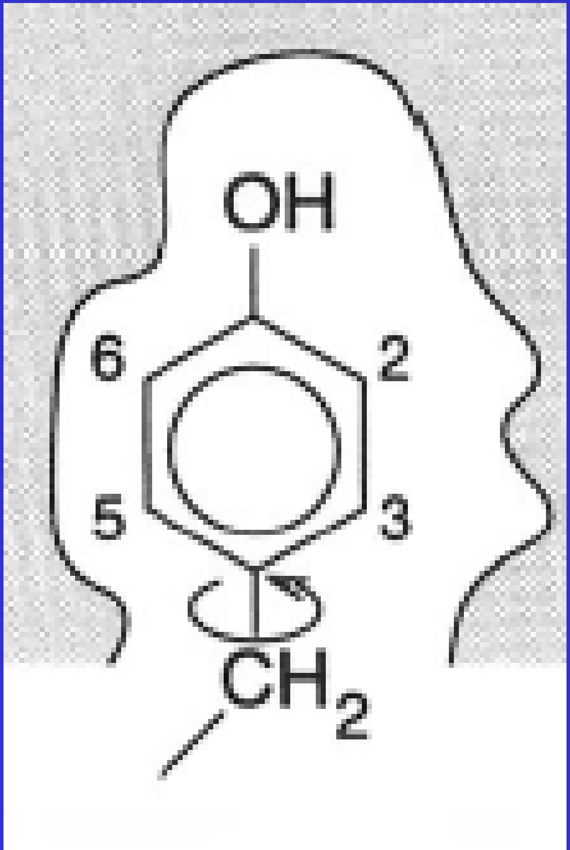
$C_{60}$ – highly symmetrical molecule, all atoms are geometrically and thus also chemically **identical**.

Only one signal in its $^{13}C$ NMR spectrum

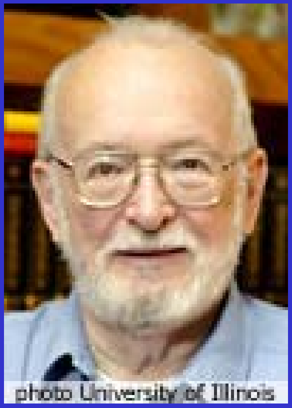
# NMR – Nuclear Magnetic Resonance

Molecular dynamics as a function of temperature

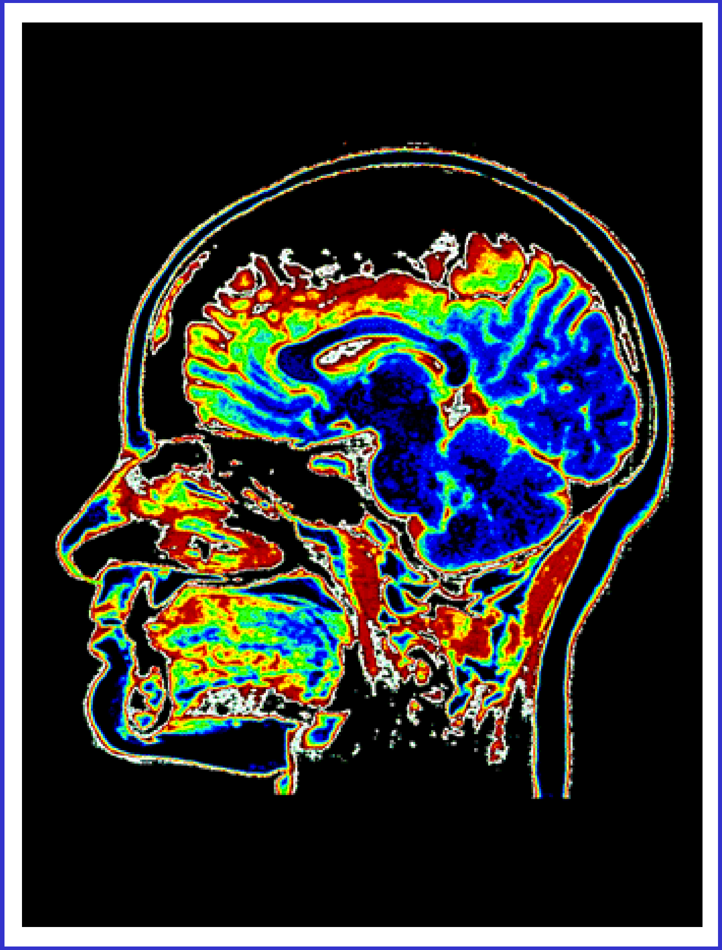


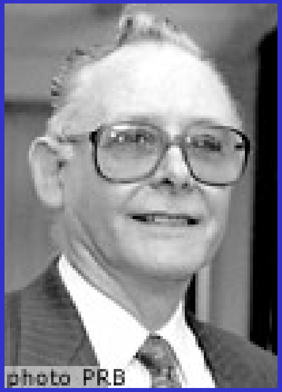


# MRI - Magnetic Resonance Imaging



Paul C. Lauterbur
(1929)





Sir Peter Mansfield
(1933)

NP in physiology and medicine 2003