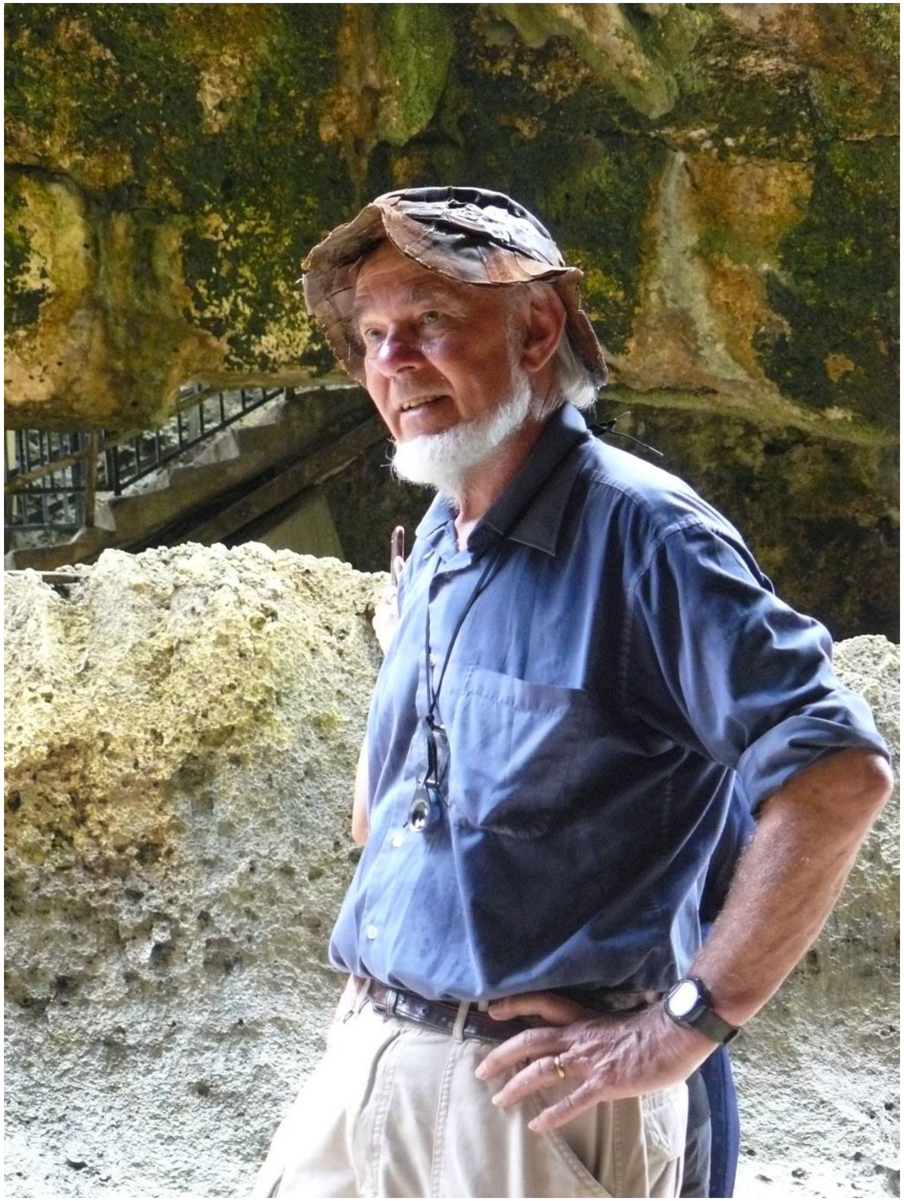
Department of Earth and Planetary Sciences
McGill University

EPSC-220
PRINCIPLES OF GEOCHEMISTRY

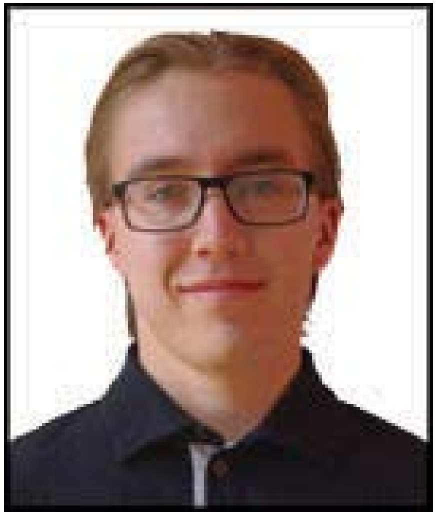
Alfonso Mucci and Anthony Williams-Jones
alfonso.mucci@mcgill.ca; Anthony.Williams-jones@mcgill.ca
Frank Dawson Adams (FDA)- 201/317

http://eps.mcgill.ca/~courses/c220/



Teaching Assistants

William Nesbitt
(william.nesbitt@mail.mcgill.ca),
FDA-131A



AlexanderTimofeev
(alexander.timofeev@mail.mcgill.ca)
FDA-346

Benjamin Keenan
(benjamin.keenan@mail.mcgill.ca)
FDA-349

Tentative Course Outline

Fall term 2017
Lectures: Mondays and Wednesdays 11:35AM – 12:25AM (FDA-315)
Laboratory: Tuesdays 2:35PM- 5:25PM (FDA-211)

Week	***Subject***
1	Introduction -organization (course description and schedule), books, evaluation
1	Origin of elements (AM) -The Big Bang -Cosmic abundances and nucleosynthesis -Terrestrial abundances
2/3	Chemical thermodynamics and phase equilibria (AM) -Thermodynamic systems -Intensive and extensive properties -Equilibrium versus steady state -Reversible and irreversible processes -Metastable equilibrium -Fundamental relationships (DE, DH, DA, DG, C_p) and laws of thermodynamics -Ideal gases
3/4	-Gibbs free energy, chemical potential and the law of mass action (AW-J) -Influence of P and T on free energy and the Clausius-Clapeyron equation -Activity and fugacity
5	The phase rule (AW-J) -Binary phase diagrams
6	Water chemistry (AM) -Acid-base reactions -Redox reactions -Eh-pH diagrams -Complexation reactions -Solubility concept

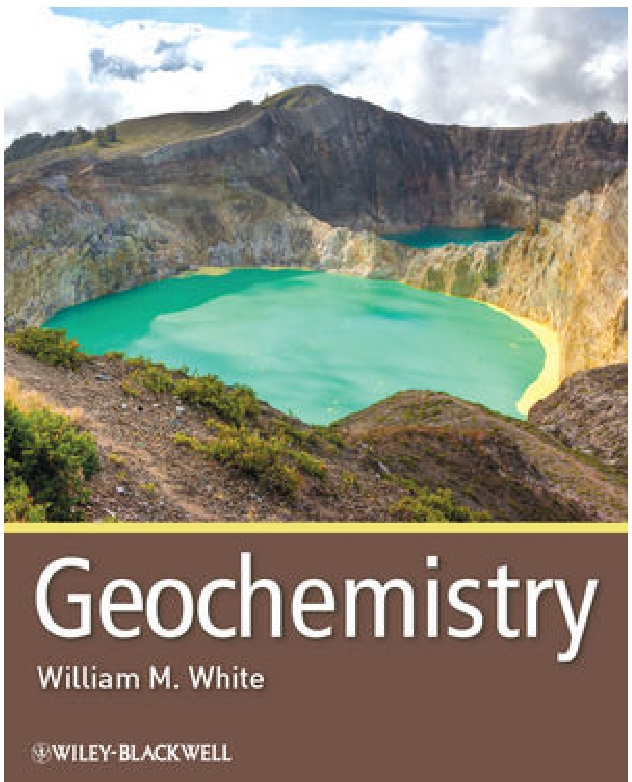
7	Weathering (AM) -Congruent dissolution reactions -Incongruent dissolution reactions -Redox reactions -Soil development	
8/9	Isotope Geochemistry (AW-J) -Stable isotopes -Radiogenic isotopes	
10	Hydrothermal Processes (AW-J) -Fluid-rock interaction. -Black smokers -Geothermal systems -Physico-chemical controls of ore deposition	
11	Elemental cycles (AW-J)	
12/13	Chemical kinetics (AM) -Rate determining step -Elementary reactions -Rate expressions for elementary reactions -Reaction order -Complex reactions -Influence of T on reaction rate, Arrhenius equation -Nucleation and crystal growth	
14	Organic geochemistry (AM) -Terminology -Maturation of organic matter -Hydrocarbons in crude oil	
Evaluation:	Mid-term	30%
	Problem sets/assignments	30%
	Final exam	40%

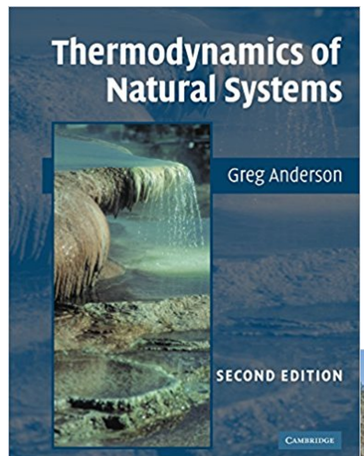
Reference books:

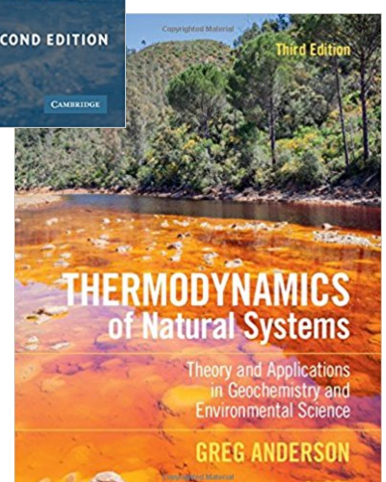
White, William M. (2005) Geochemistry, Wiley-Blackwell, Hoboken, NJ, USA
On line textbook: http://www.imwa.info/geochemistry/http://www.eps.mcgill.ca/~courses/c220

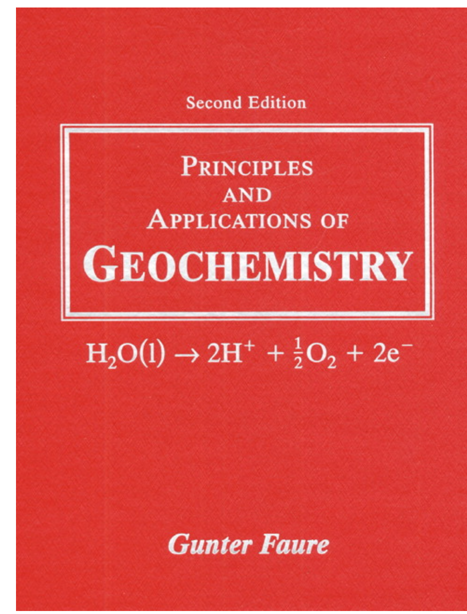
Anderson, G.M (1996) Thermodynamics of Natural Systems, 1st Edition, Wiley & Sons, Toronto, 382 pp.
(2009) Thermodynamics of Natural Systems, 2nd Edition, Wiley & Sons, Toronto, 664 pp.
(2017) Thermodynamics of Natural Systems: Theory and Applications in Geochemistry and Environmental Science , Wiley & Sons, Toronto, 428 pp.

Faure, G. (1991) Principles and Applications of Inorganic Geochemistry, MacMillan Publishing Co., New York, 626pp.

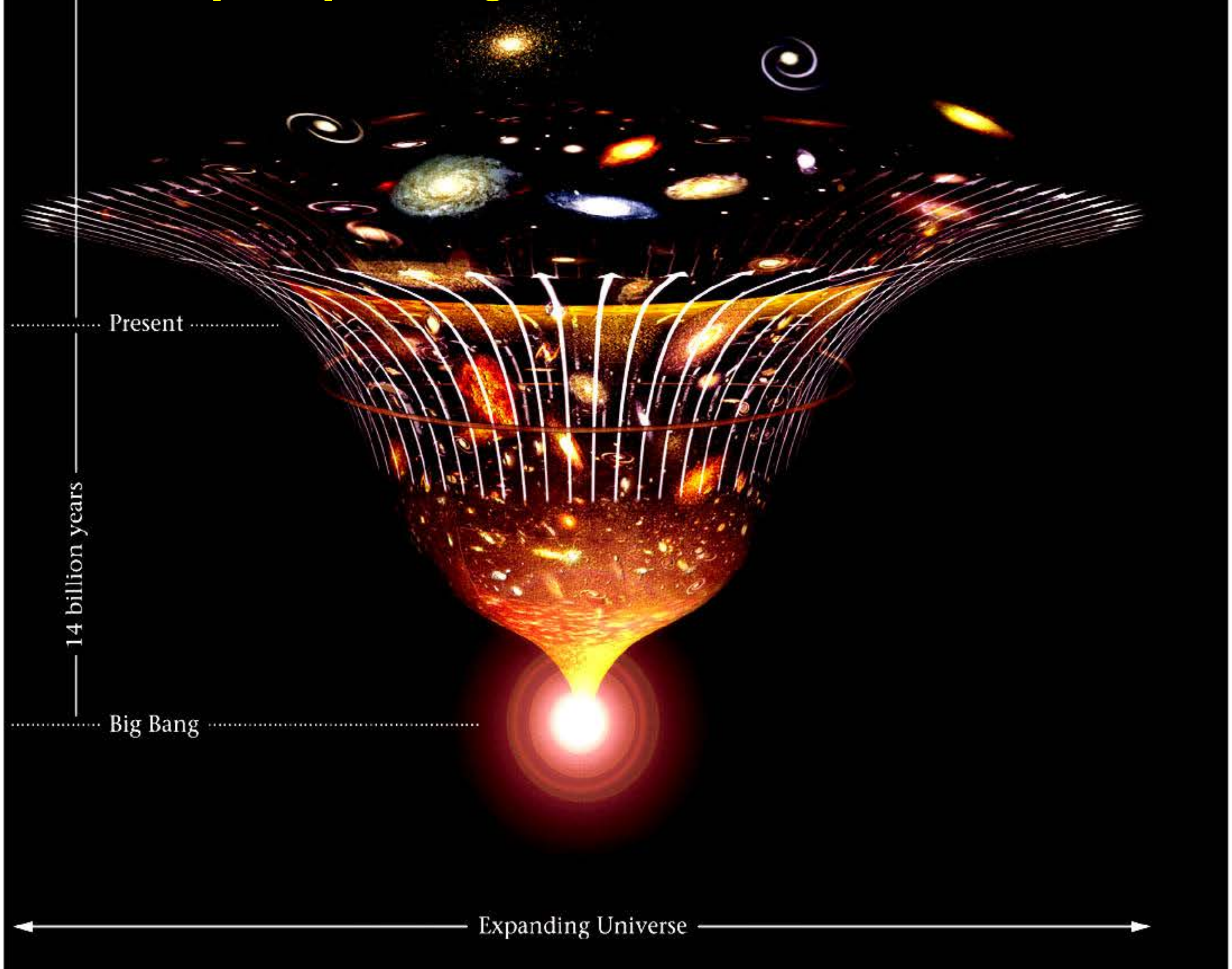




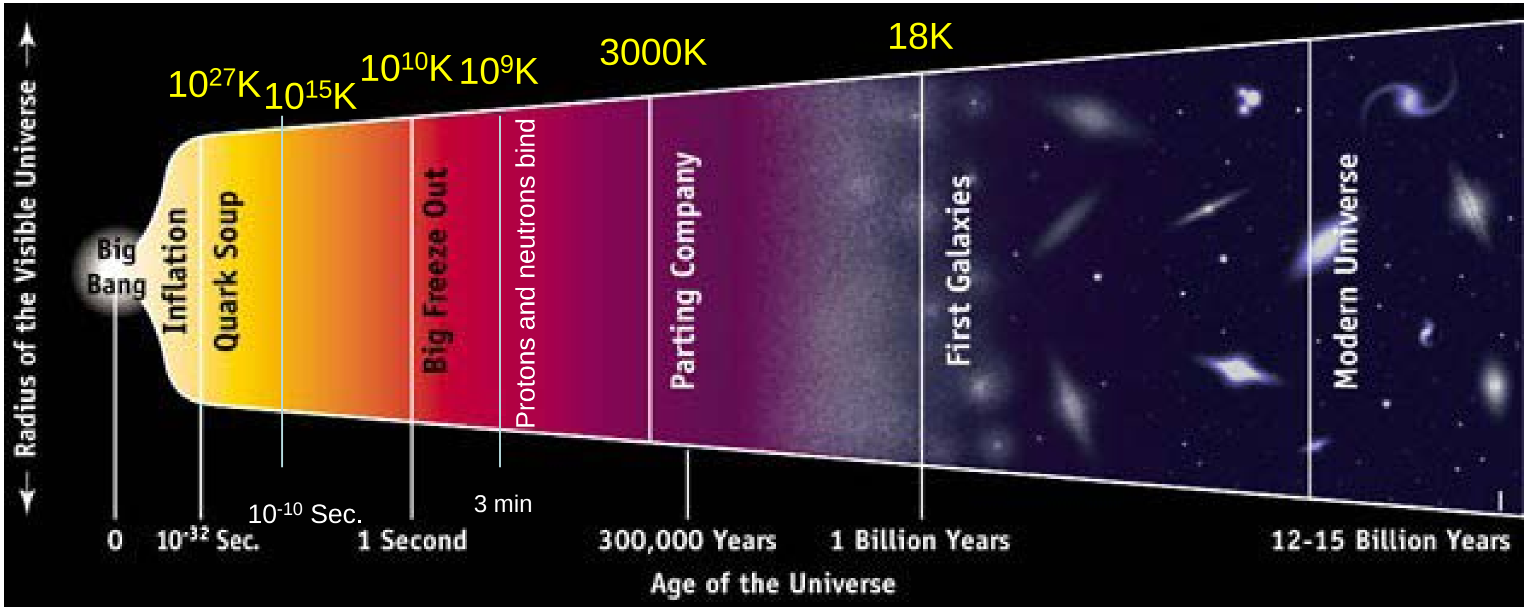


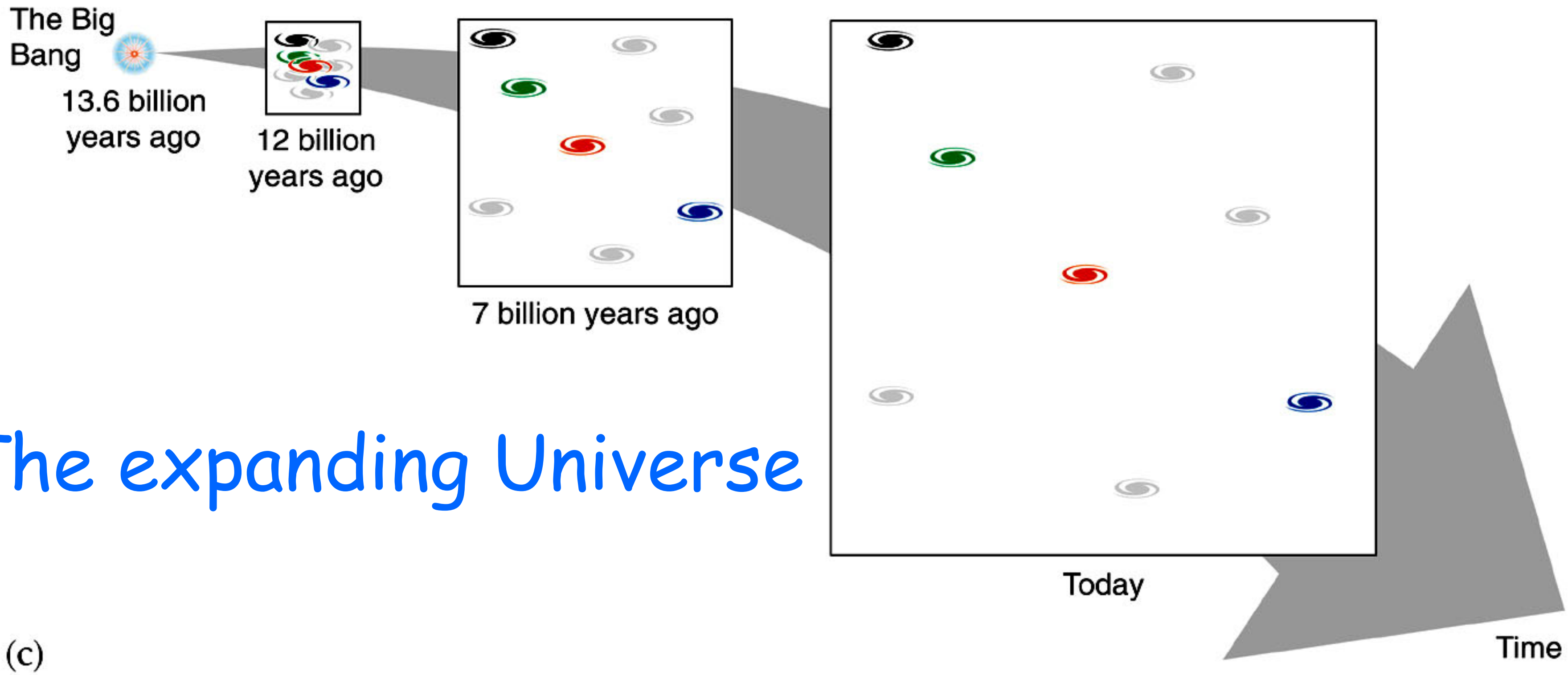


http://eps.mcgill.ca/~courses/c220/

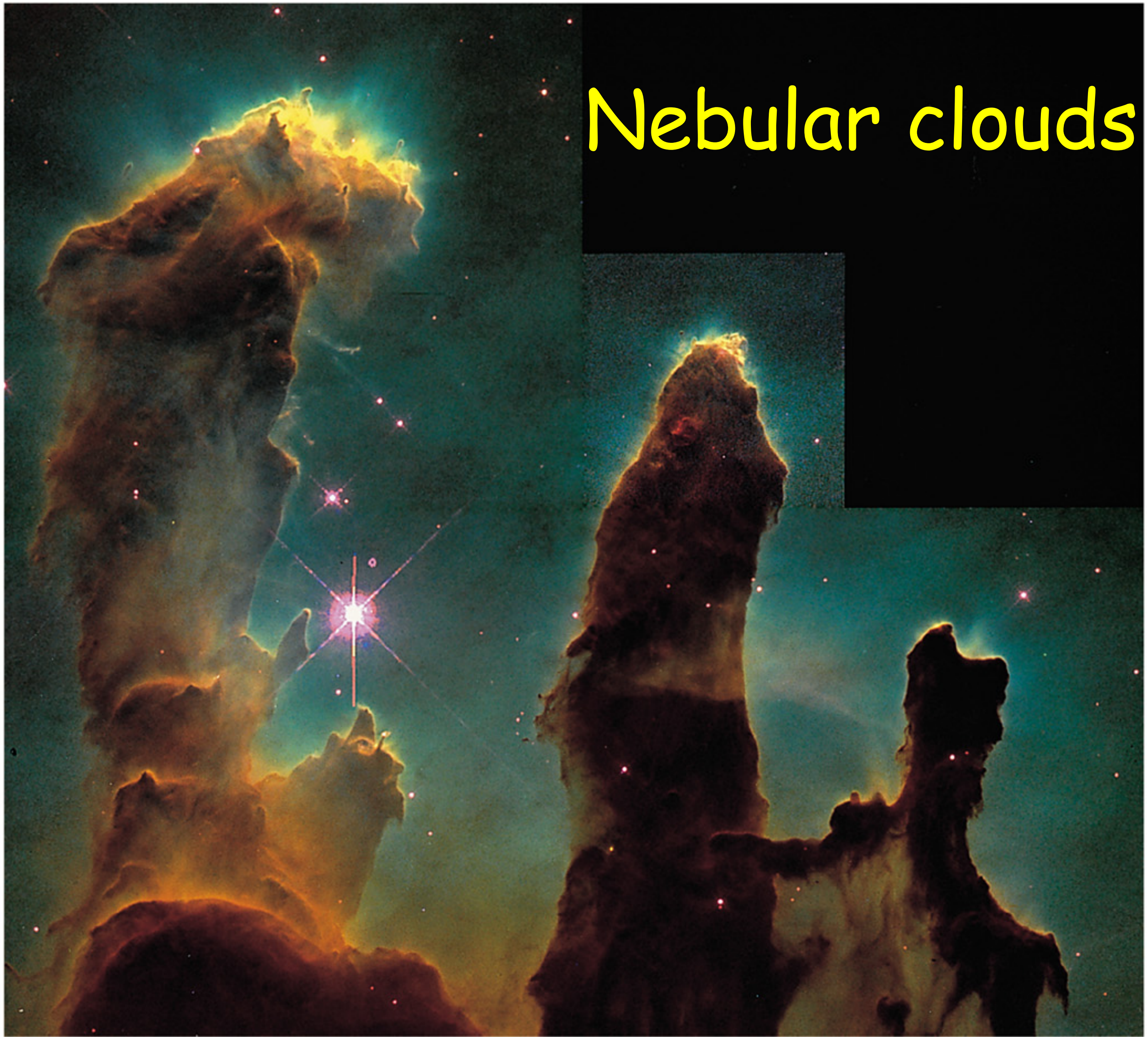


BIG BANG – first proposed by G. Lemaitre (Ph.D. MIT) in 1927



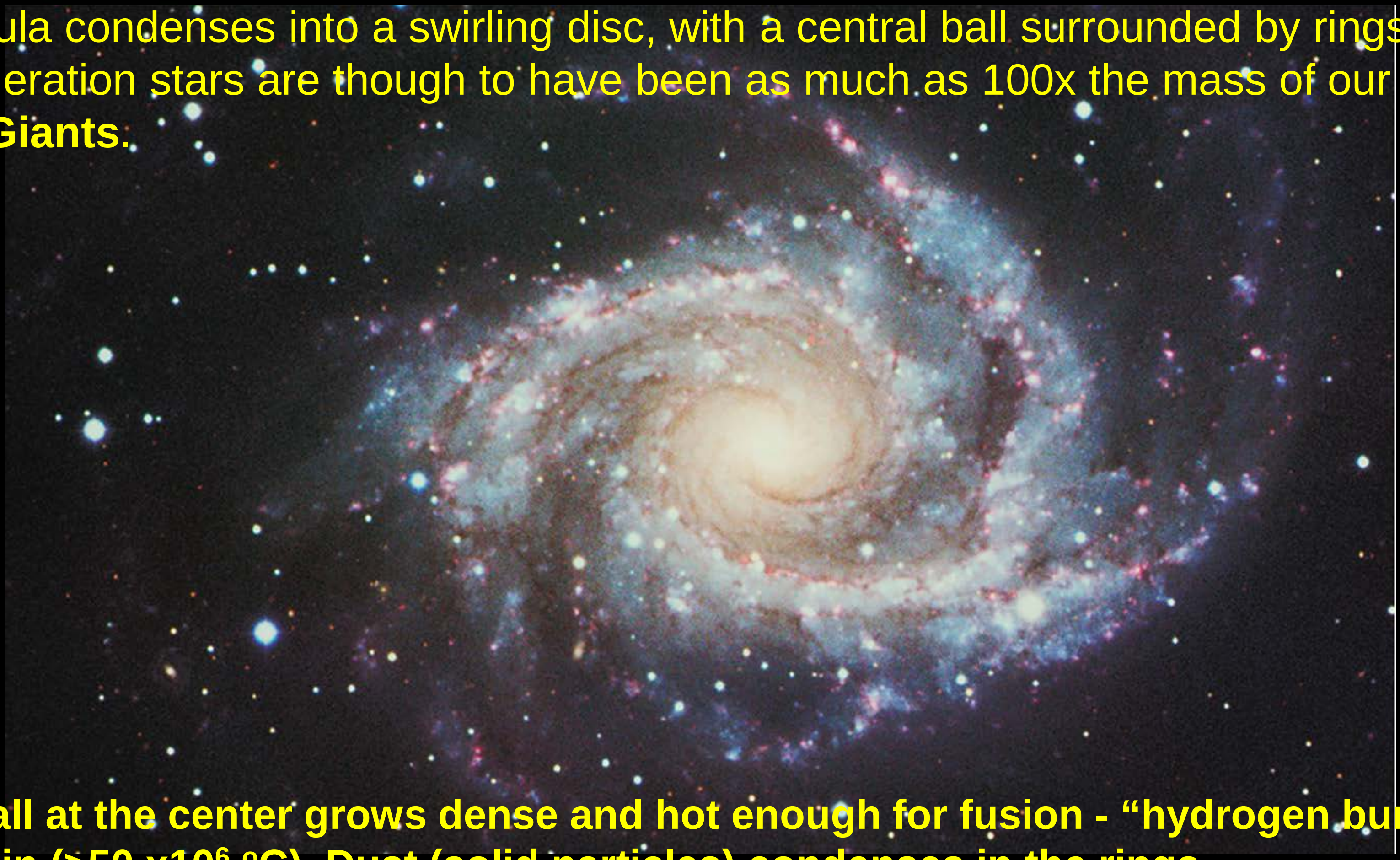


The expanding Universe


Nebular clouds

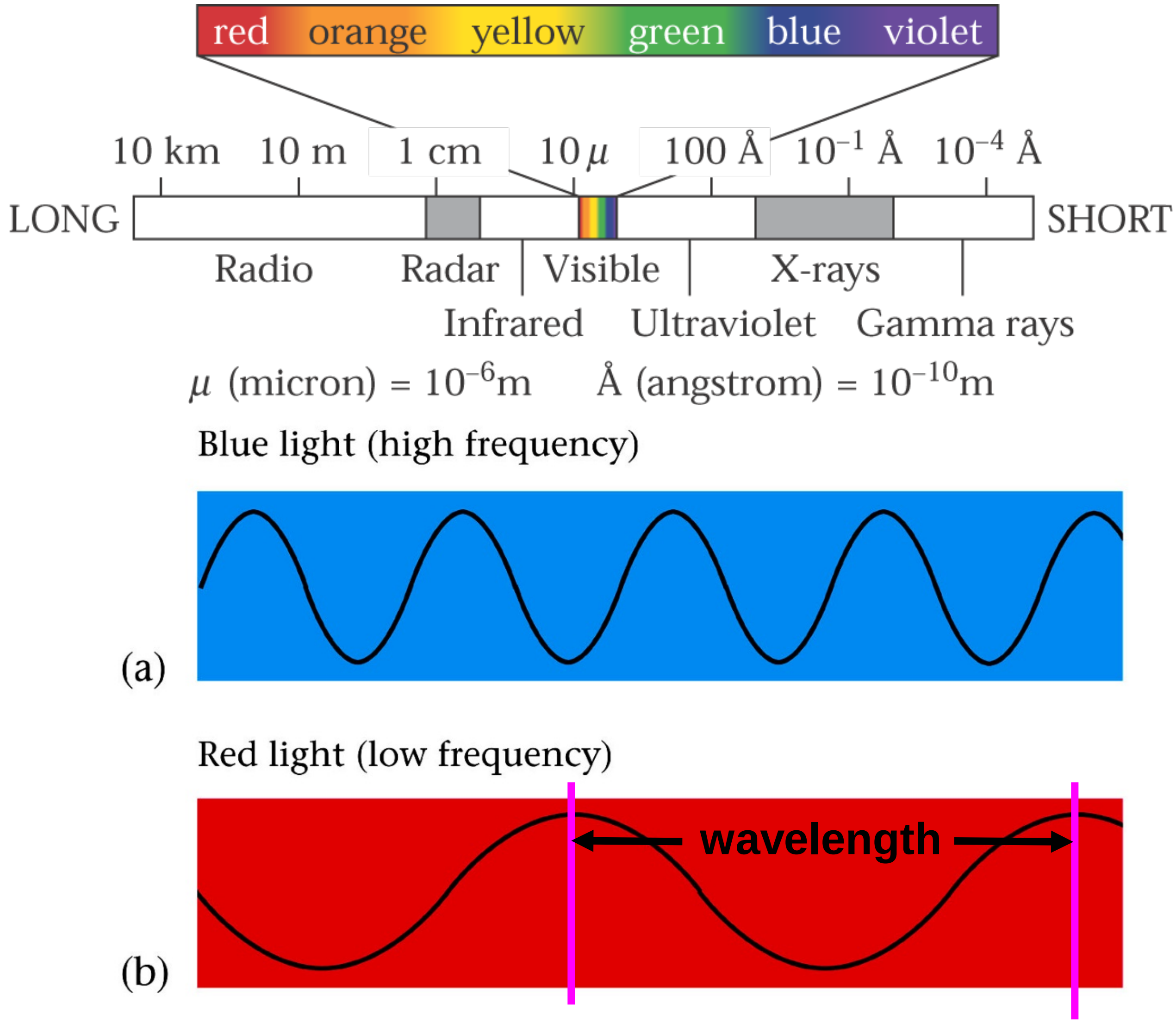
The birth and growth of a star

The nebula condenses into a swirling disc, with a central ball surrounded by rings.
First generation stars are though to have been as much as 100x the mass of our Sun
→ **Red Giants**.



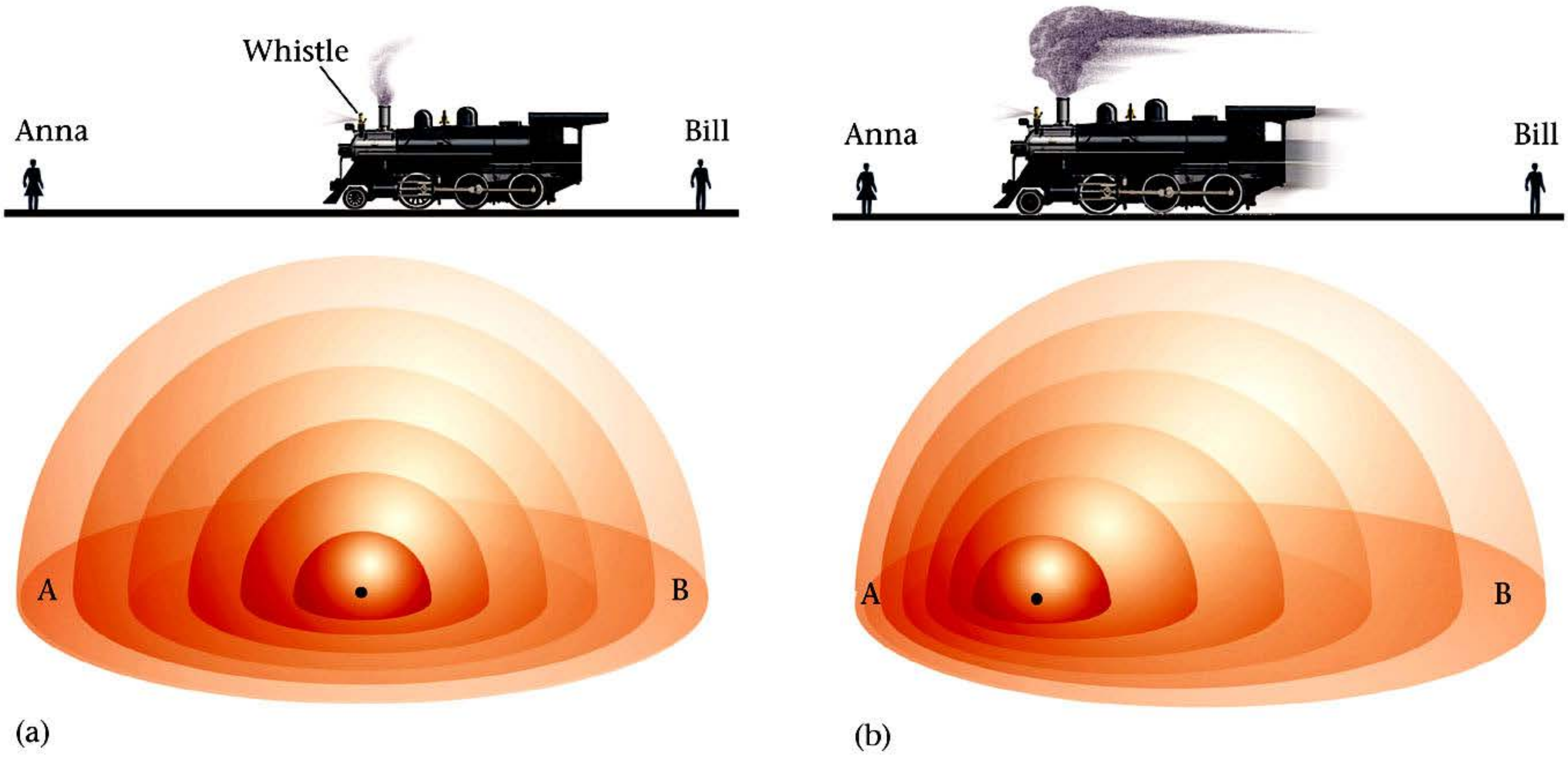
The ball at the center grows dense and hot enough for fusion - "hydrogen burning" - to begin (>50 x10^{6} ^{o}C). Dust (solid particles) condenses in the rings.

The expanding Universe



The distance between between successive waves is known as the **wavelength**, whereas the time interval between the passage of each wave through a given point is known as the **frequency**.

DOPPLER EFFECT



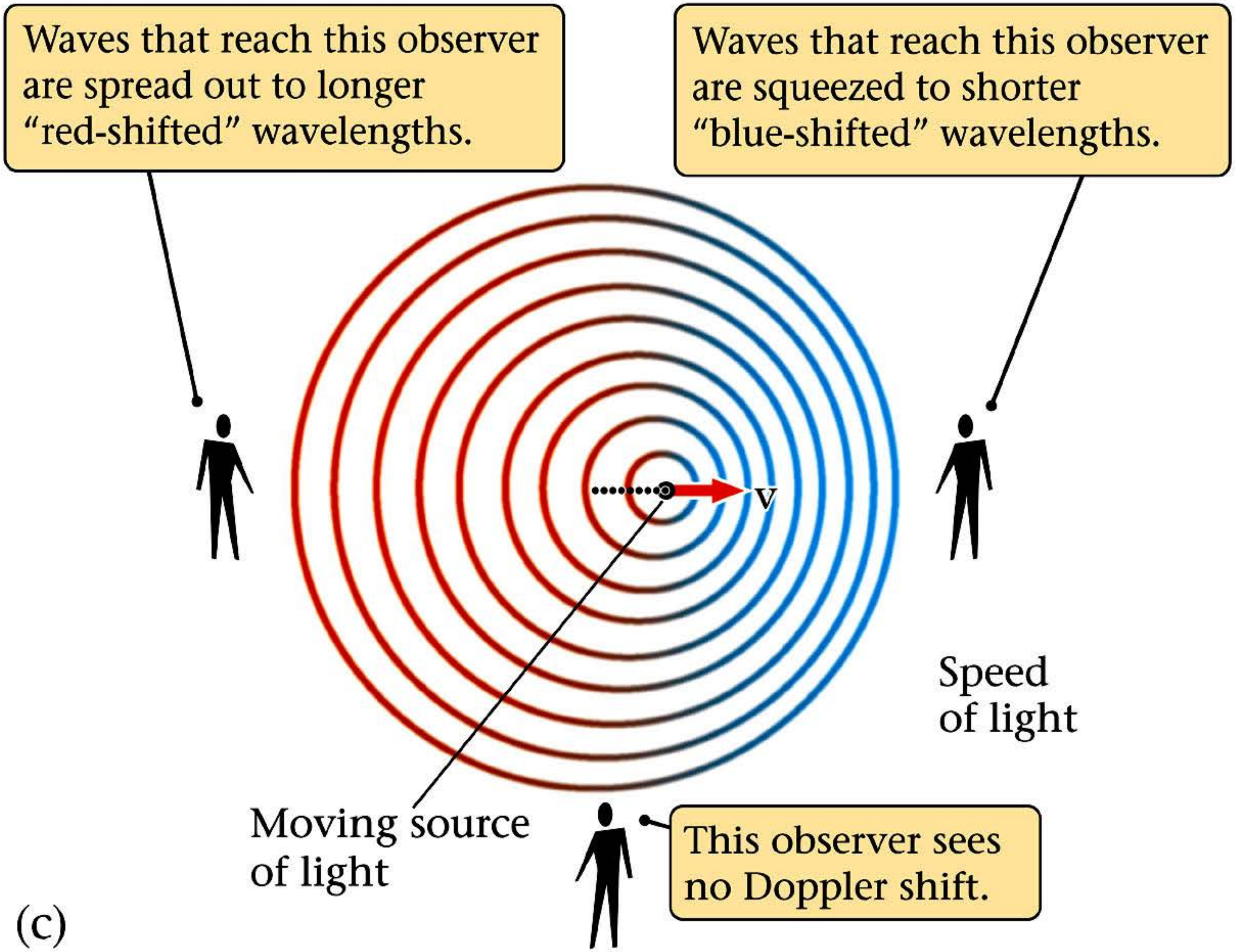
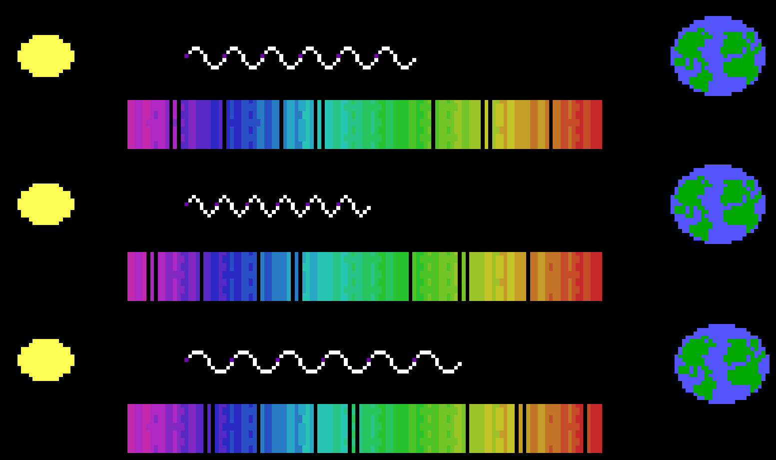

Waves that reach this observer are spread out to longer "red-shifted" wavelengths.
Waves that reach this observer are squeezed to shorter "blue-shifted" wavelengths.
v
Speed of light
Moving source of light
This observer sees no Doppler shift.
(c)

FIGURE 1.7

The expanding Universe

Discovery of Expanding Universe

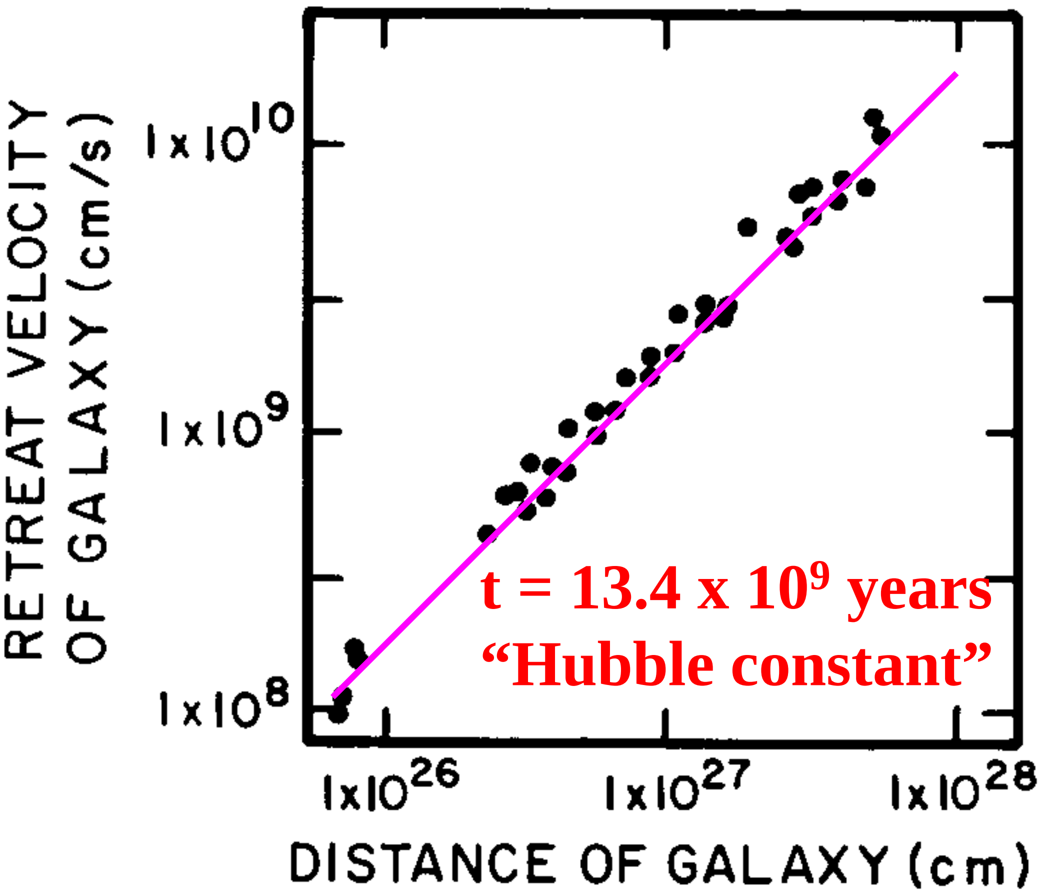
Edwin Hubble



Hydrogen light observed from distant galaxies, shifted to longer wavelengths or towards the red of the light spectrum– “Red Shift”. Hence, hydrogen light spectrum from distant galaxies is recorded on Earth at different wavelengths which are characteristic of the retreat velocity of the galaxy.

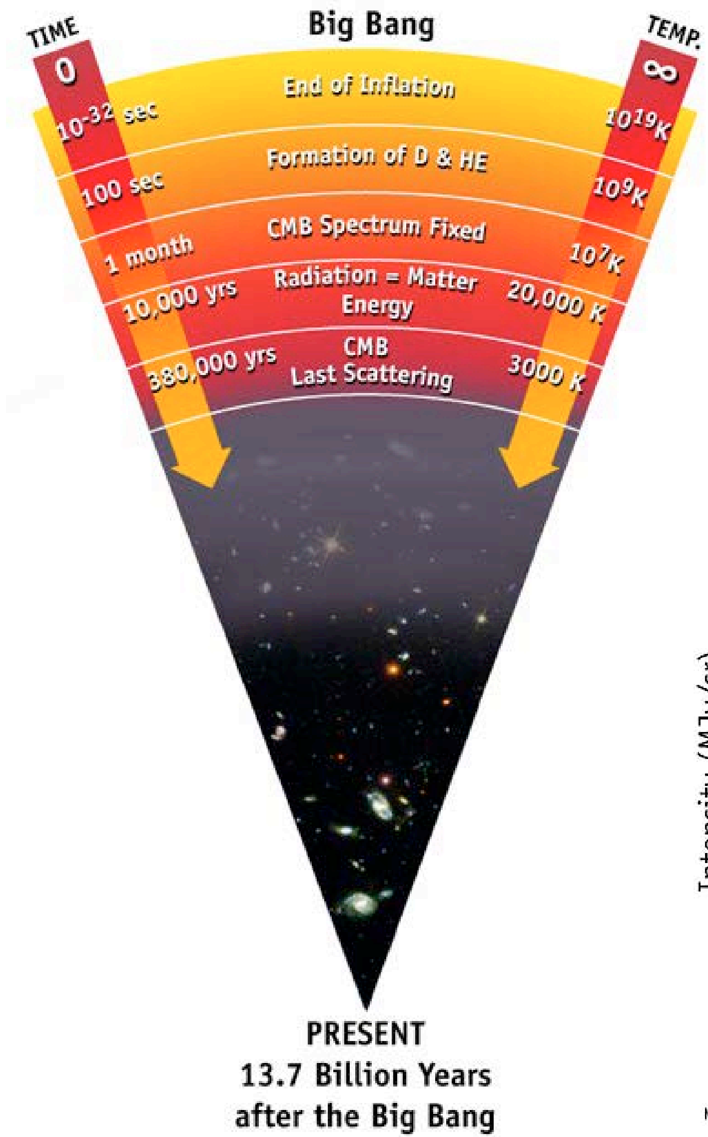
The expanding Universe

Figure 1-7. Relationship between galactic distance and galactic recession velocity: Each point represents a distant galaxy (or cluster of distant galaxies). Since the distances range over a factor of 100, a logarithmic rather than linear scale is used for this graph.

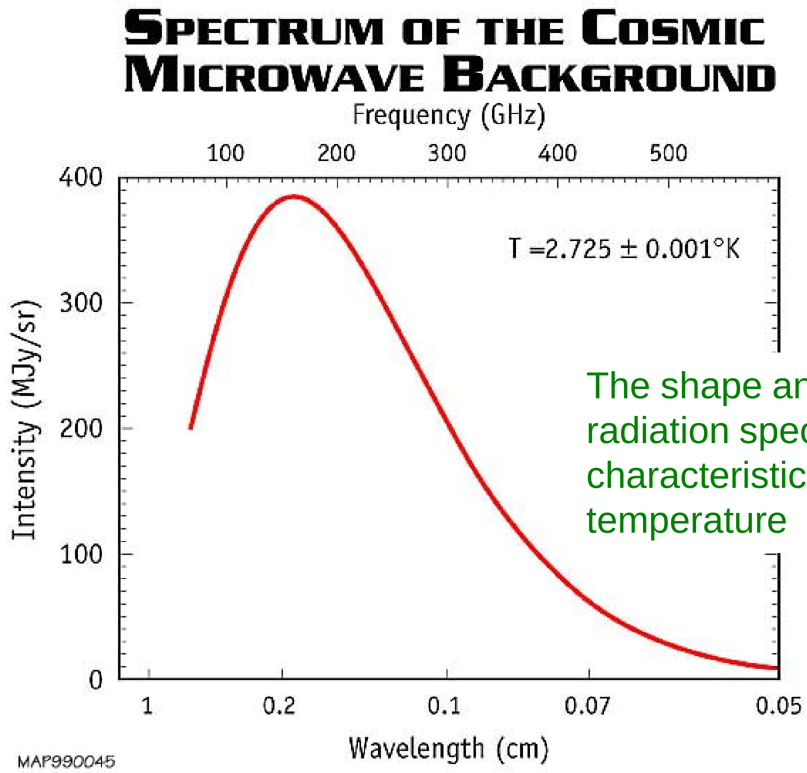


From: W.S. Broecker (1985) How to build a habitable planet

Background radiation from the Big Bang



Arno Penzias
Robert Wilson
1963



The shape and intensity of the radiation spectrum is characteristic of a given temperature

Nucleosynthesis

neutron → electron + proton = é + H^+

$t_{1/2}$ = 12 minutes

H^+ + neutron → Deuterium (D)

2 H^+ + neutrons → Helium (He)

3 H^+ + neutrons → Lithium (Li)

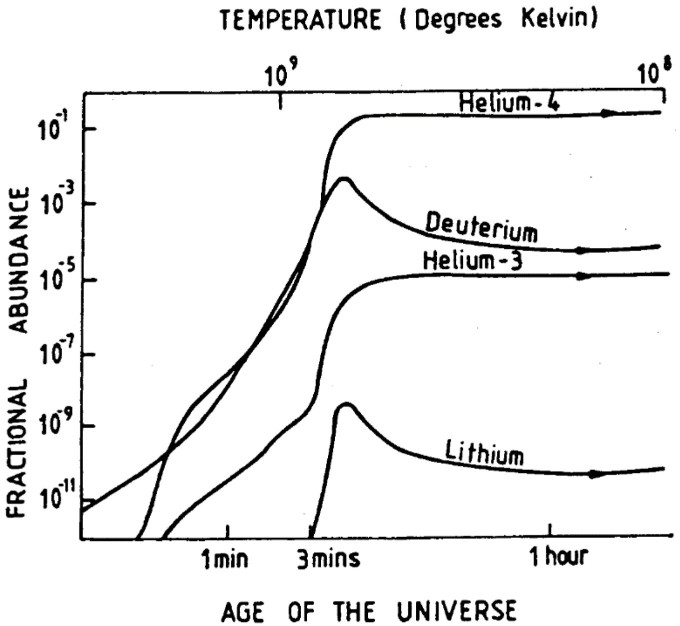
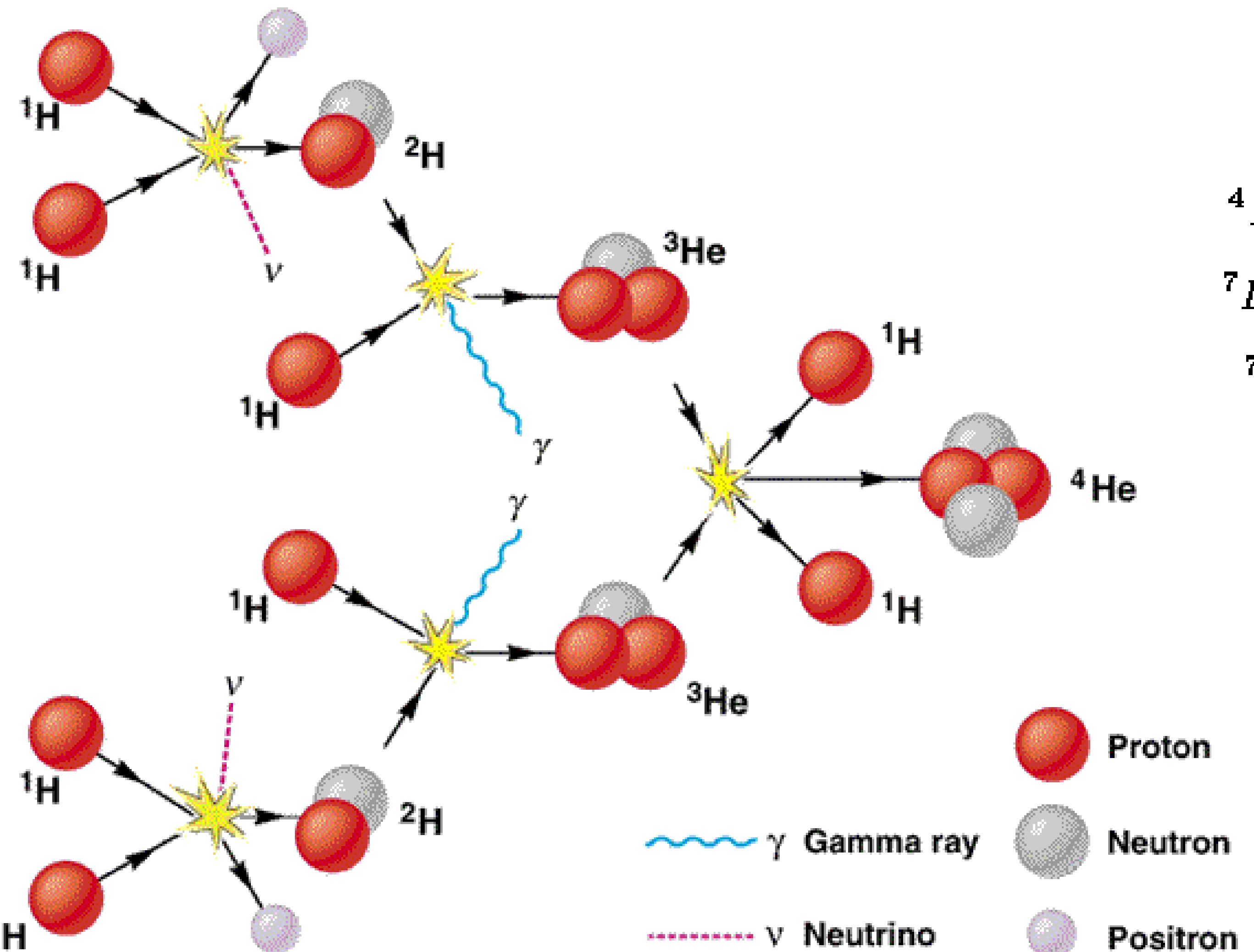


FIGURE 3.4
The detailed production of the lightest elements out of protons and neutrons during the first three minutes of the universe's history. The nuclear reactions occur rapidly when the temperature falls below a billion degrees Kelvin. Subsequently, the reactions are shut down, because of the rapidly falling temperature and density of matter in the expanding universe.

From: W.S. Broecker (1985)
How to build a habitable planet

Nucleosynthesis



$$p + n \rightarrow D$$

$$D + D \rightarrow^3 He + n$$

$$D + D \rightarrow^3 H + p$$

$$^4He +^3 H \rightarrow^7 Li + \gamma$$

$$^7Li + p \rightarrow^4 He +^4 He$$

$$^7Be + n \rightarrow^7 Li + p.$$

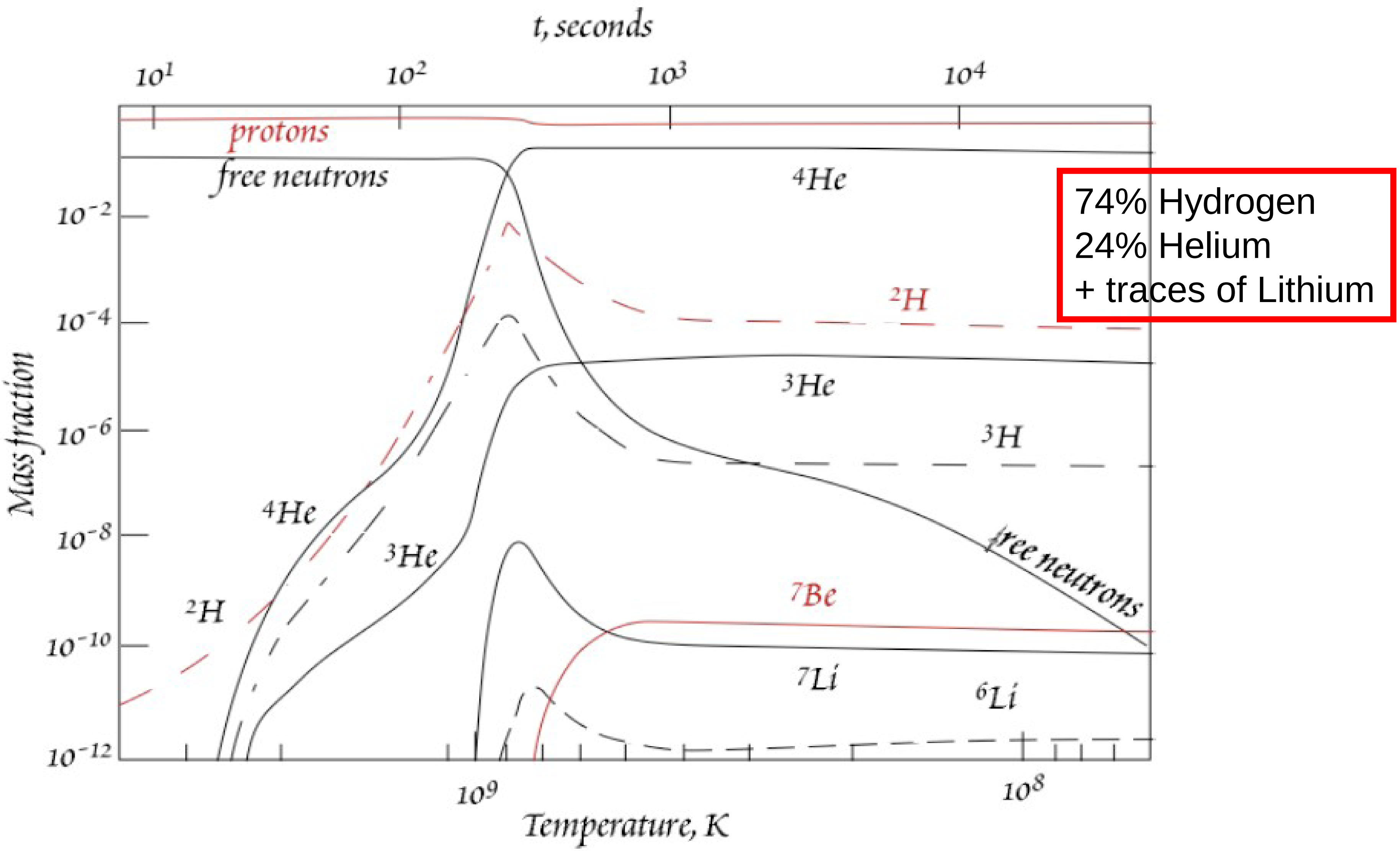
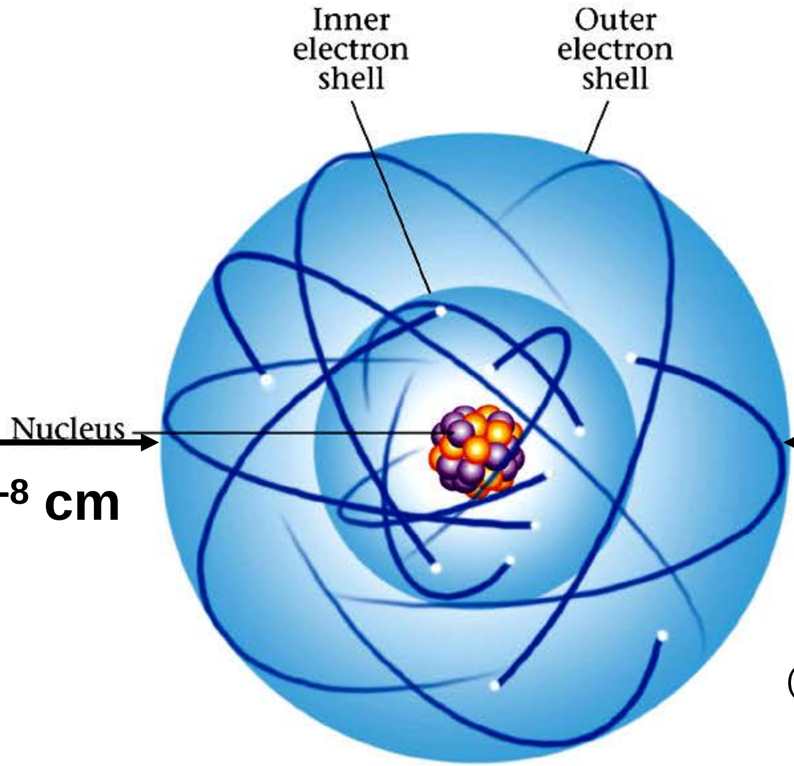


Figure 3. Compositional evolution during cosmological nucleosynthesis. ^{7}Be and ^{3}H are unstable and decay to ^{7}Li and ^{3}He with half-lives of 53 days (4.6 x 10^6 s) and 12.3 years (4 x 10^8 s) respectively. After Ned Wright's Cosmology Tutorial (http://www.astro.ucla.edu/~wright/cosmolog.htm).

Structure of the atom



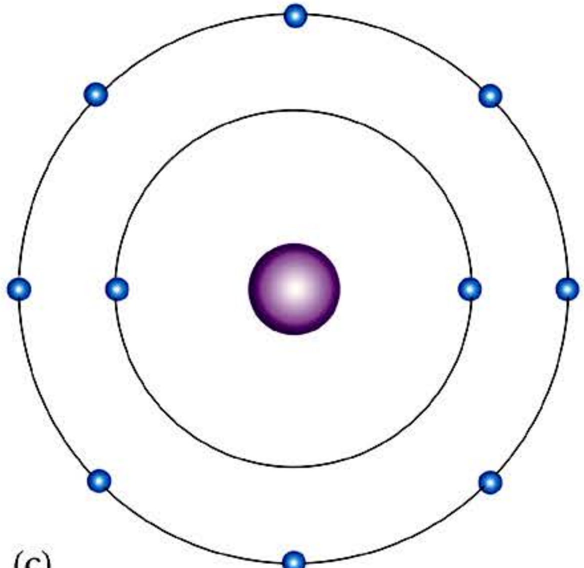
10^{-8} cm

Electron negatively-charged particle

Proton positively-charged particle

Neutron neutral particle (no charge)

(b)



(c)

A neutrally-charged atom will have an equal number of electrons and protons, é = p

protons = atomic number (nature of the atom)
protons + # neutrons = atomic mass

(protons and neutrons are ~1800 times heavier than electrons)

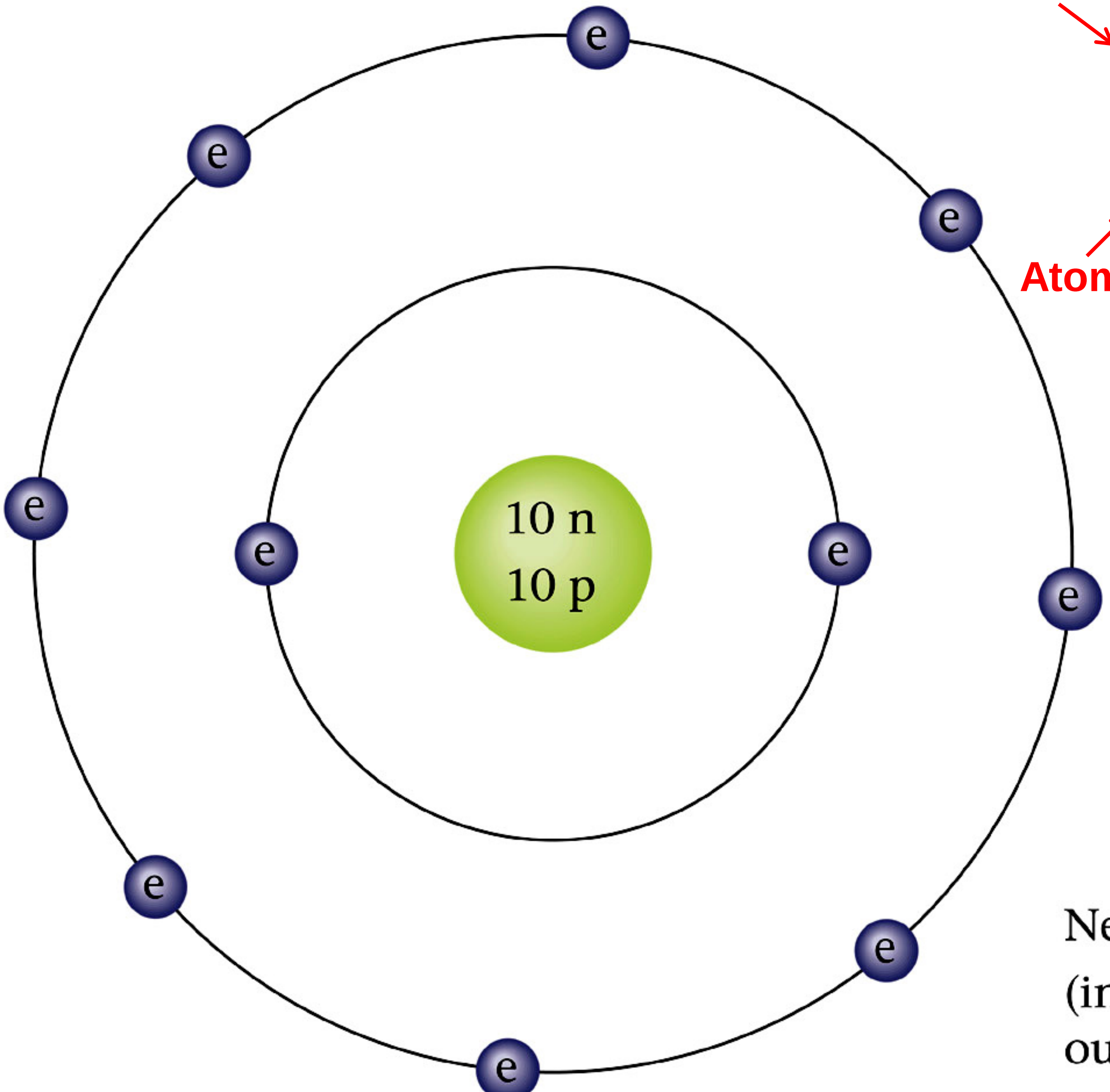
Periodic table of the elements

Symbol / Atomic number / Name / Atomic weight (key: He 2, Helium, 4.002)

Alkali metals · Transition elements (metals) · Nonmetals · Inert gases

H 1 Hydrogen 1.007																	He 2 Helium 4.002
Li 3 Lithium 6.941	Be 4 Beryllium 9.0121											B 5 Boron 10.811	C 6 Carbon 12.011	N 7 Nitrogen 14.006	O 8 Oxygen 15.999	F 9 Fluorine 18.998	Ne 10 Neon 20.179
Na 11 Sodium 22.989	Mg 12 Magnesium 24.305											Al 13 Aluminum 26.981	Si 14 Silicon 28.085	P 15 Phosphorus 30.973	S 16 Sulfur 32.066	Cl 17 Chlorine 35.452	Ar 18 Argon 39.948
K 19 Potassium 39.098	Ca 20 Calcium 40.078	Sc 21 Scandium 44.955	Ti 22 Titanium 47.88	V 23 Vanadium 50.941	Cr 24 Chromium 51.996	Mn 25 Manganese 54.938	Fe 26 Iron 55.847	Co 27 Cobalt 58.933	Ni 28 Nickel 58.693	Cu 29 Copper 63.546	Zn 30 Zinc 65.39	Ga 31 Gallium 69.723	Ge 32 Germanium 72.61	As 33 Arsenic 74.921	Se 34 Selenium 78.96	Br 35 Bromine 79.904	Kr 36 Krypton 83.80
Rb 37 Rubidium 85.467	Sr 38 Strontium 87.62	Y 39 Yttrium 88.905	Zr 40 Zirconium 91.224	Nb 41 Niobium 92.906	Mo 42 Molybdenum 95.94	Tc 43 Technetium 98.907	Ru 44 Ruthenium 101.07	Rh 45 Rhodium 102.905	Pd 46 Palladium 106.42	Ag 47 Silver 107.868	Cd 48 Cadmium 112.411	In 49 Indium 114.82	Sn 50 Tin 118.710	Sb 51 Antimony 121.757	Te 52 Tellurium 127.60	I 53 Iodine 126.904	Xe 54 Xenon 131.29
Cs 55 Cesium 132.905	Ba 56 Barium 137.327	La 57 Lanthanum 138.905	Hf 72 Hafnium 178.49	Ta 73 Tantalum 180.947	W 74 Tungsten 183.85	Re 75 Rhenium 186.207	Os 76 Osmium 190.2	Ir 77 Iridium 192.22	Pt 78 Platinum 195.08	Au 79 Gold 196.966	Hg 80 Mercury 200.59	Tl 81 Thallium 204.383	Pb 82 Lead 207.2	Bi 83 Bismuth 208.980	Po 84 Polonium 208.982	At 85 Astatine 209.987	Rn 86 Radon 222.017
Fr 87 Francium 223.019	Ra 88 Radium 226.025	Ac 89 Actinium 227.027															

Ce 58 Cerium 140.115	Pr 59 Praseodymium 140.907	Nd 60 Neodymium 144.24	Pm 61 Promethium 144.912	Sm 62 Samarium 150.36	Eu 63 Europium 151.965	Gd 64 Gadolinium 157.25	Tb 65 Terbium 158.925	Dy 66 Dysprosium 162.50	Ho 67 Holmium 164.930	Er 68 Erbium 167.26	Tm 69 Thulium 168.934	Yb 70 Ytterbium 173.04	Lu 71 Lutetium 174.967
Th 90 Thorium 232.038	Pa 91 Protactinium 231.035	U 92 Uranium 238.028	Np 93 Neptunium 237.048	Pu 94 Plutonium 244.064	Am 95 Americium 243.061	Cm 96 Curium 247.070	Bk 97 Berkelium 247.070	Cf 98 Californium 251.079	Es 99 Einsteinium 252.083	Fm 100 Fermium 257.095	Md 101 Mendelevium 258.10	No 102 Nobelium 259.100	Lr 103 Lawrencium 262.11



Atomic mass

$^{20}_{10}\mathrm{Ne}$

Atomic number

Neon atom
(inner shell has $2e^-$,
outer shell has $8e^-$)

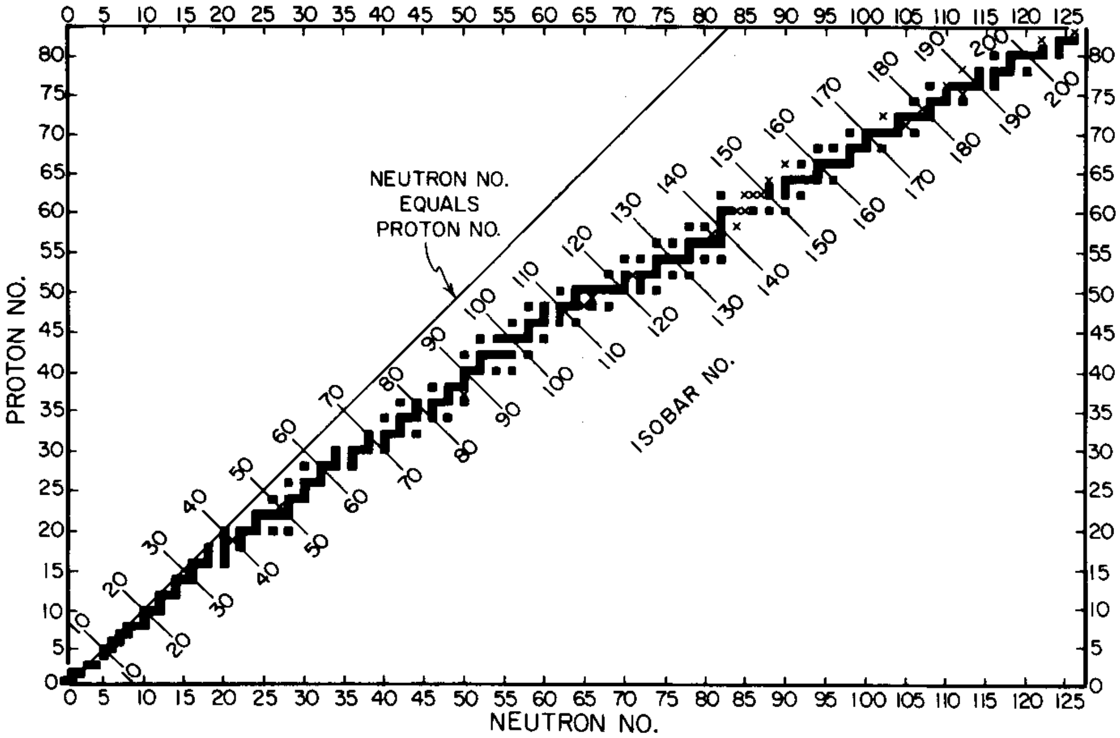
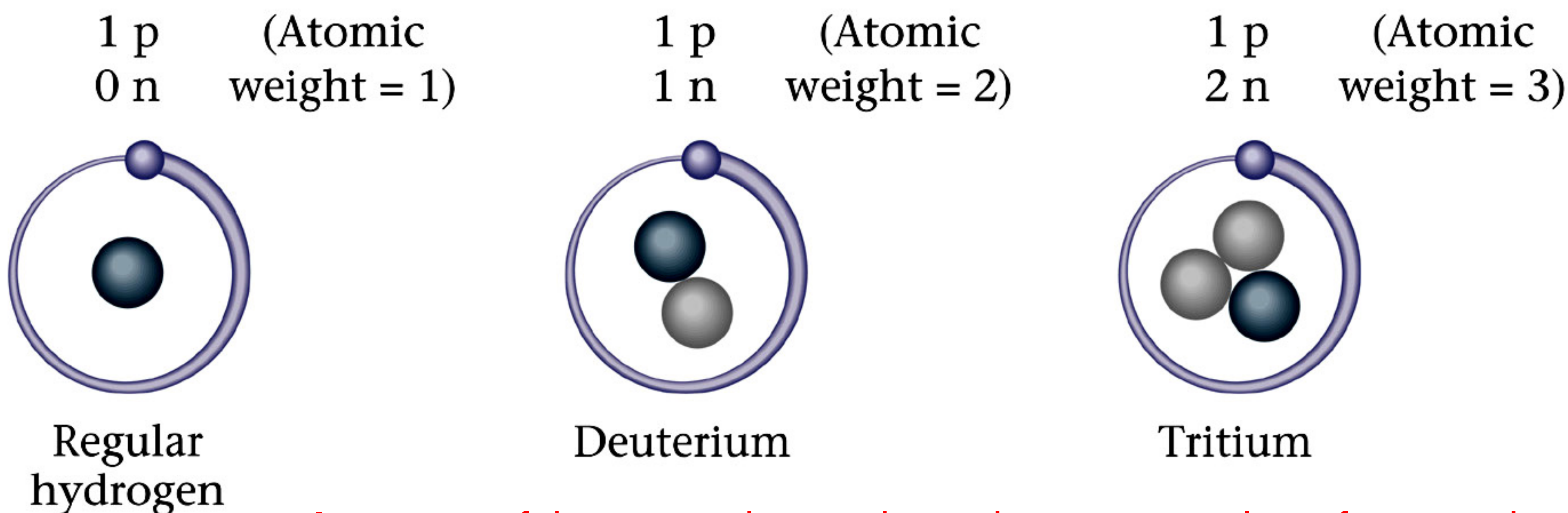


Figure 2-2. Stable nuclide configurations: The squares represent stable combinations of neutrons and protons. The x's represent radioactive nuclides whose half-lives are so long that they survive billions of years after their formation in stars. All the remaining combinations are radioactive with half-lives sufficiently short that they are no longer present in the solar system. Nuclides lying along the same horizontal line (i.e., those with the same proton number) are referred to as isotopes. Those falling along the same vertical line (i.e., those with the same number of neutrons) are referred to as isotones. Those falling along the same diagonal line (i.e., those with the same number of nuclear particles) are called isobars. The diagram terminates with the heaviest stable nuclide (^{209}Bi).

From: W.S. Broecker (1985) How to build a habitable planet

The three isotopes of hydrogen

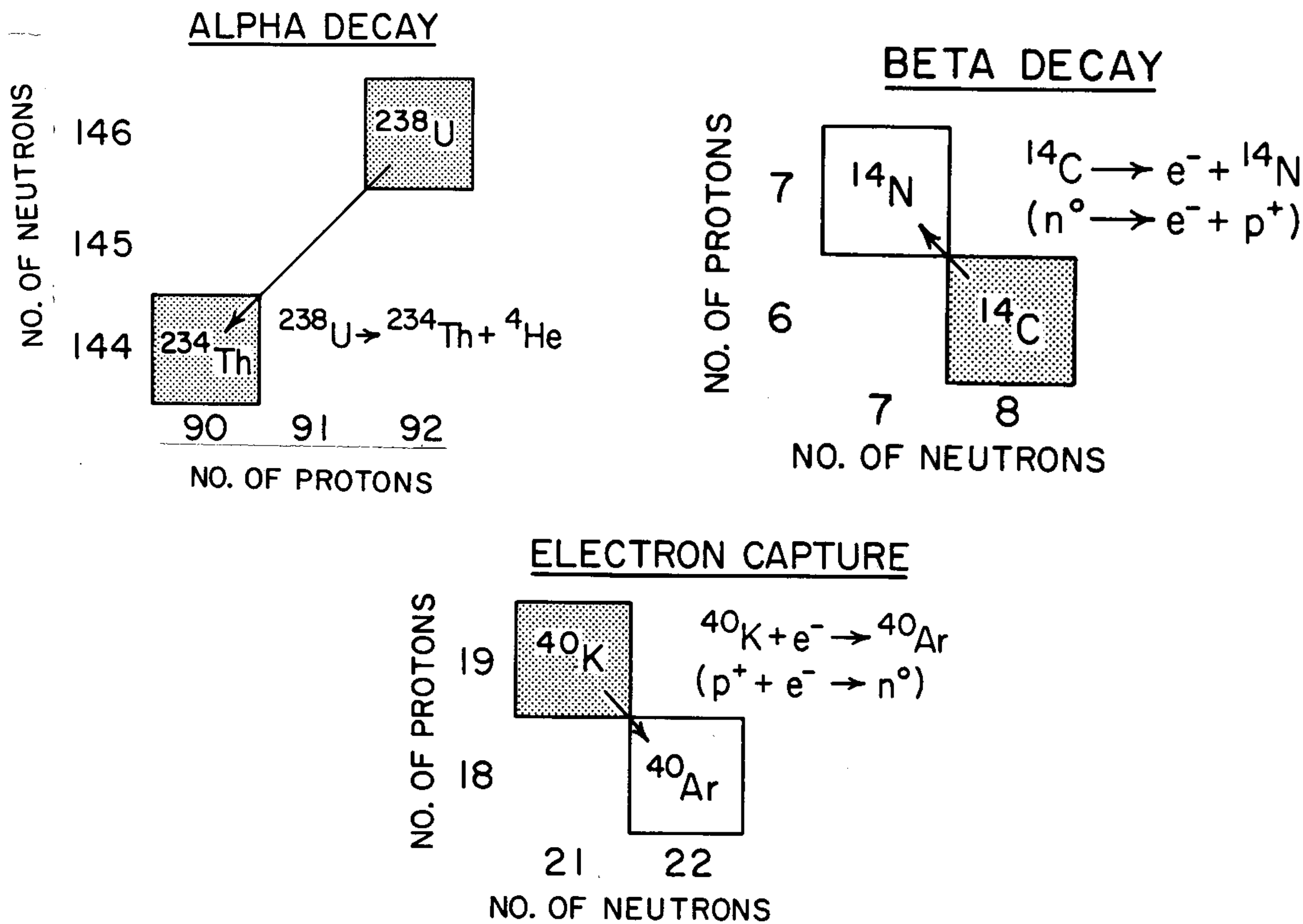


(Protium)

Isotopes of the same element have the same number of protons but different numbers of neutrons in their nucleus, hence different mass.

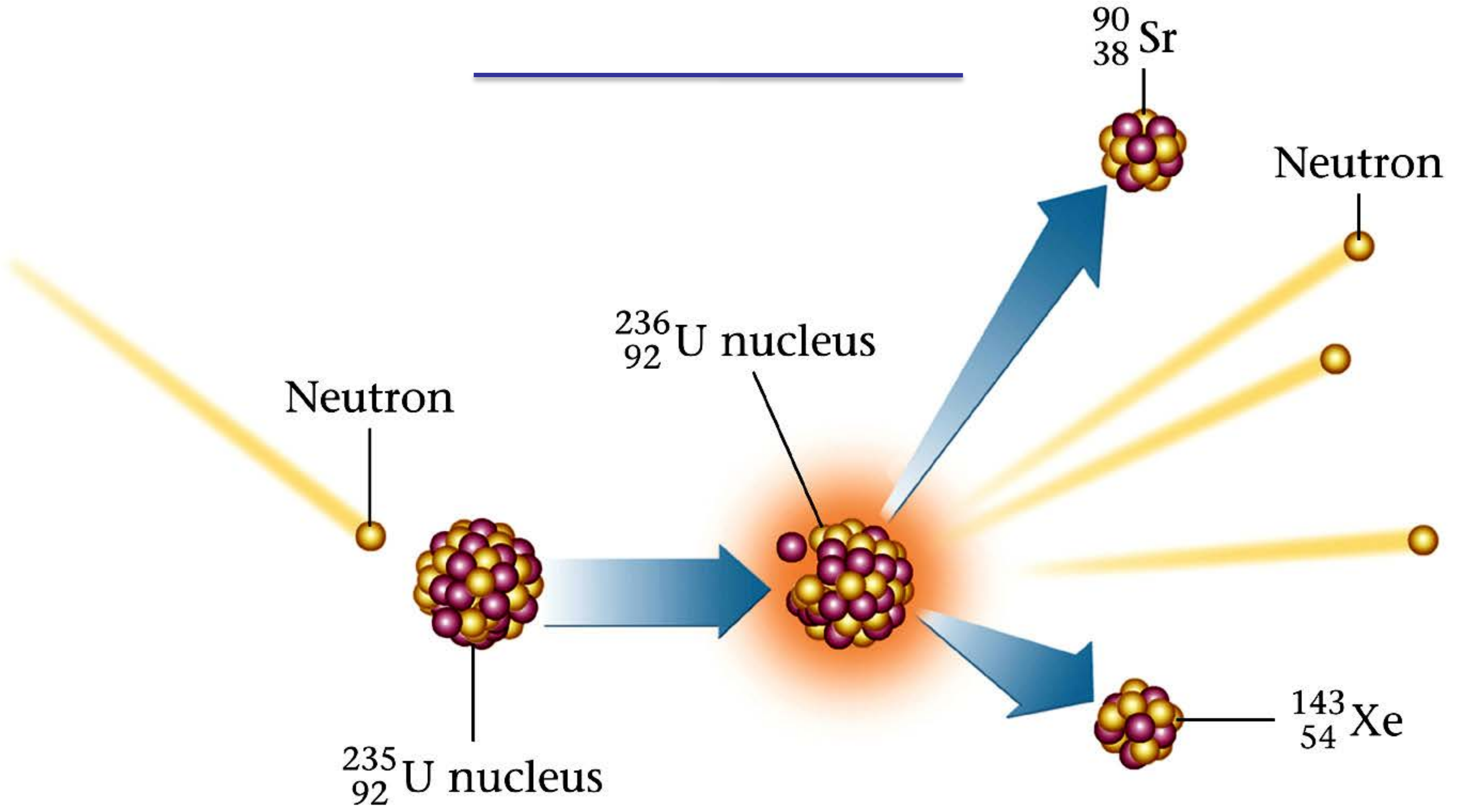
Radio-isotopes have an unstable combination of protons and neutrons in the nucleus and undergo **radioactive decay**

Three most common modes of radioactive decay



From: W.S. Broecker (1985) How to build a habitable planet

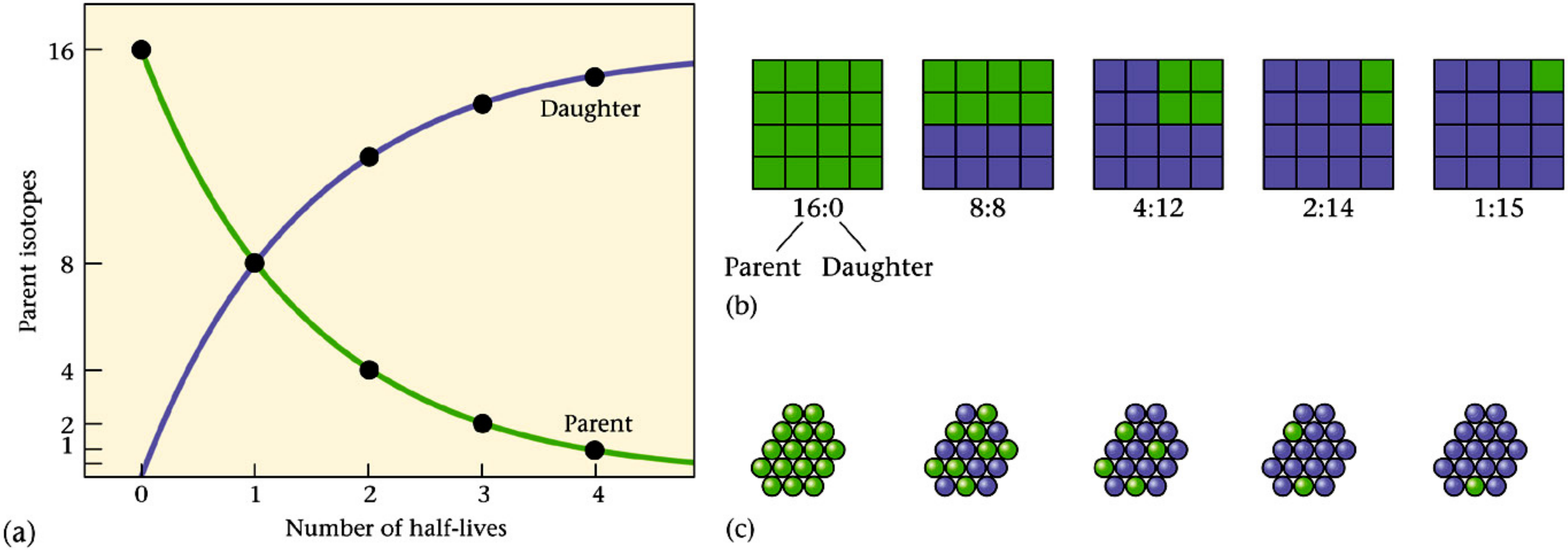
Fission



$^{90}_{38}Sr$
Neutron
$^{236}_{92}U$ nucleus
Neutron
$^{235}_{92}U$ nucleus
$^{143}_{54}Xe$

Rate of radioactive decay

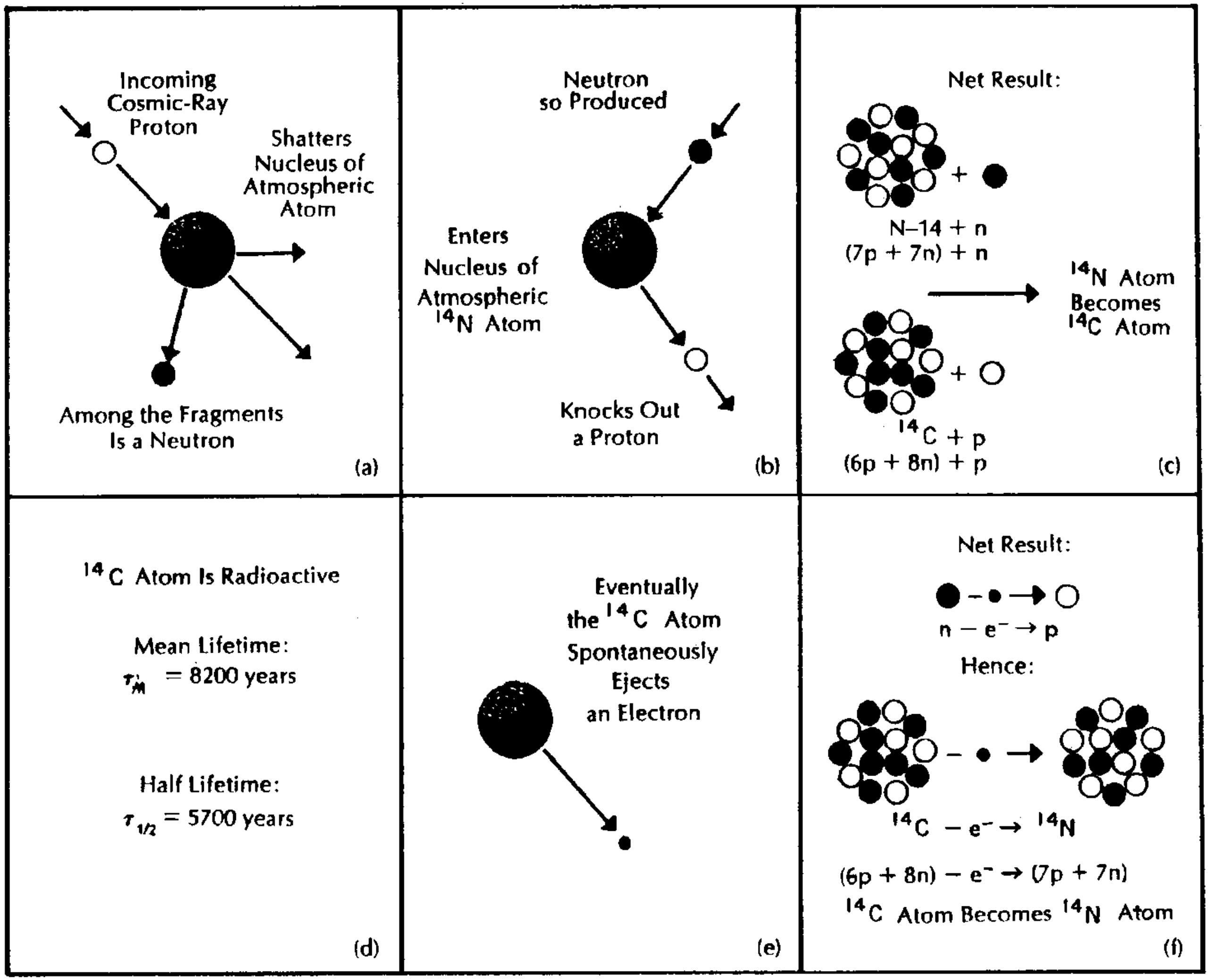
The rates at which radio-isotopes decay are inherent properties of the isotope and are unaffected by changes in temperature, pressure or geological processes.



Rate = k [A]

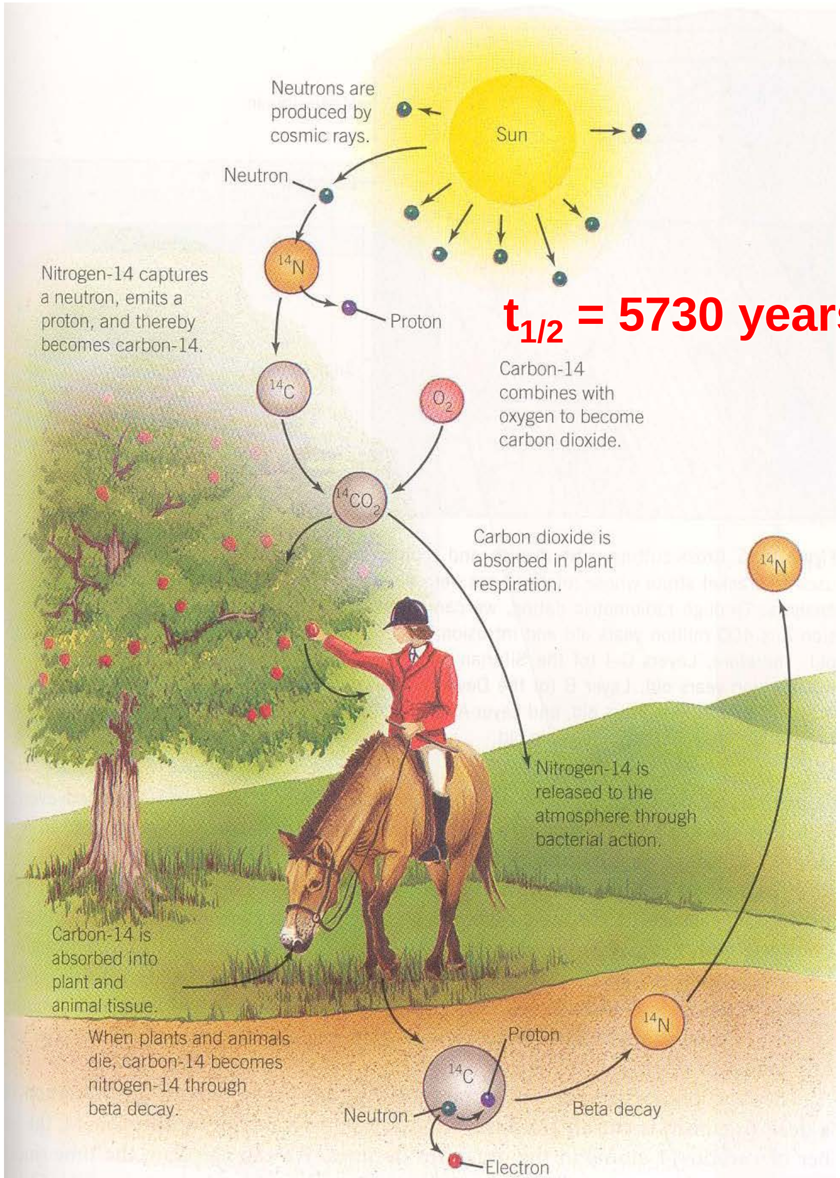
$k = \ln 2/t_{1/2} = 0.693/t_{1/2}$

The "life cycle" of the carbon-14 atom



From: Broecker and Peng (1982) Tracer in the Sea

Radiometric dating



$t_{1/2}$ = 5730 years

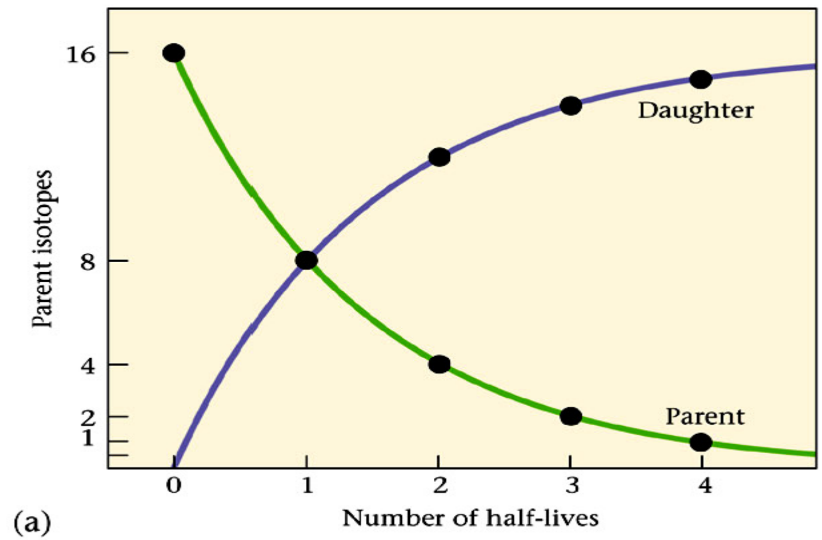


TABLE 12.1 Isotopes Used in the Radiometric Dating of Rocks

Parent → Daughter	Half-Life (years)	Minerals in which the Isotopes Occur
$^{147}Sm \rightarrow ^{143}Nd$	106 billion	Garnets, micas
$^{87}Rb \rightarrow ^{87}Sr$	48.8 billion	Potassium-bearing minerals (mica, feldspar, hornblende)
$^{238}U \rightarrow ^{206}Pb$	4.5 billion	Uranium-bearing minerals (zircon, apatite, uraninite)
$^{40}K \rightarrow ^{40}Ar$	1.3 billion	Potassium-bearing minerals (mica, feldspar, hornblende)
$^{235}U \rightarrow ^{207}Pb$	713 million	Uranium-bearing minerals (zircon, uraninite, apatite)

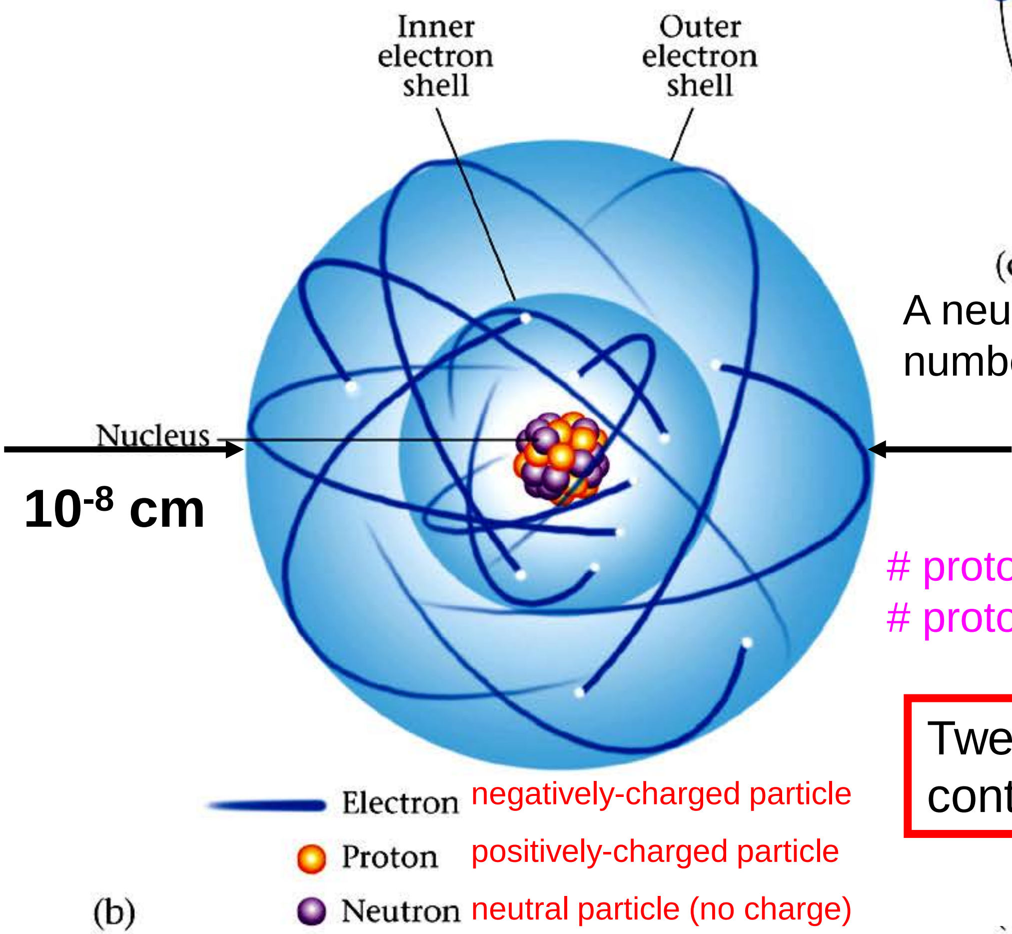
Sm = samarium, Nd = neodymium, Rb = rubidium, Sr = strontium, U = uranium, Pb = lead, K = potassium, Ar = argon

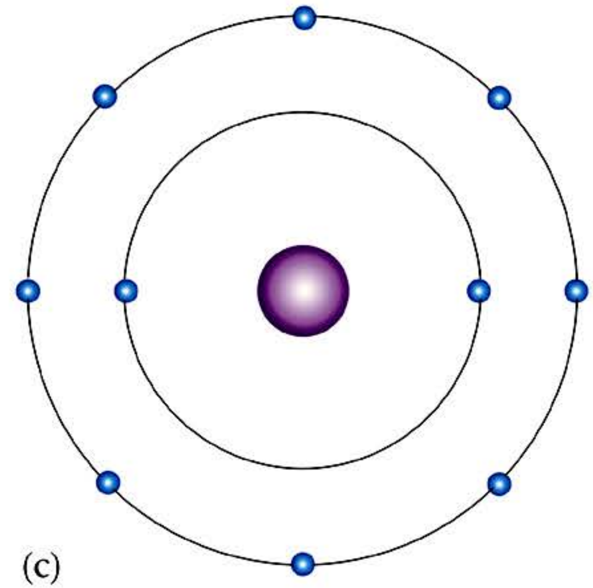
Uranium and Thorium decay series

Element	U-238 Series							Th-232 Series					U-235 Series				
Neptunium																	
Uranium	U-238 4.47×10^9 yrs		U-234 2.48×10^5 yrs										U-235 7.04×10^8 yrs				
Protactinium		Pa-234 1.18 min												Pa-231 3.25×10^4 yrs			
Thorium	Th-234 24.1 days		Th-230 7.52×10^4 yrs					Th-232 1.40×10^{10} yrs		Th-228 1.91 yrs			Th-231 25.5 hrs		Th-227 18.7 days		
Actinium									Ac-228 6.13 hrs					Ac-227 21.8 yrs			
Radium			Ra-226 1.62×10^3 yrs					Ra-228 5.75 yrs		Ra-224 3.66 days					Ra-223 11.4 days		
Francium																	
Radon			Rn-222 3.82 days							Rn-220 55.6 sec					Rn-219 3.96 sec		
Astatine																	
Polonium			Po-218 3.05 min		Po-214 1.64×10^{-4} sec		Po-210 138 days			Po-216 0.15 sec	64 %	Po-212 3.0×10^{-7} sec			Po-215 1.78×10^{-3} sec		
Bismuth				Bi-214 19.7 min		Bi-210 5.01 days					Bi-212 60.6 min					Bi-211 2.15 min	
Lead			Pb-214 26.8 min		Pb-210 22.3 yrs		Pb-206 stable lead (isotope)			Pb-212 10.6 hrs	36%	Pb-208 stable lead (isotope)			Pb-211 36.1 min		Pb-207 stable lead (isotope)
Thallium											Tl-208 3.05 min					Tl-207 4.77 min	

From: Broecker and Peng (1982) Tracer in the Sea

Structure of the atom



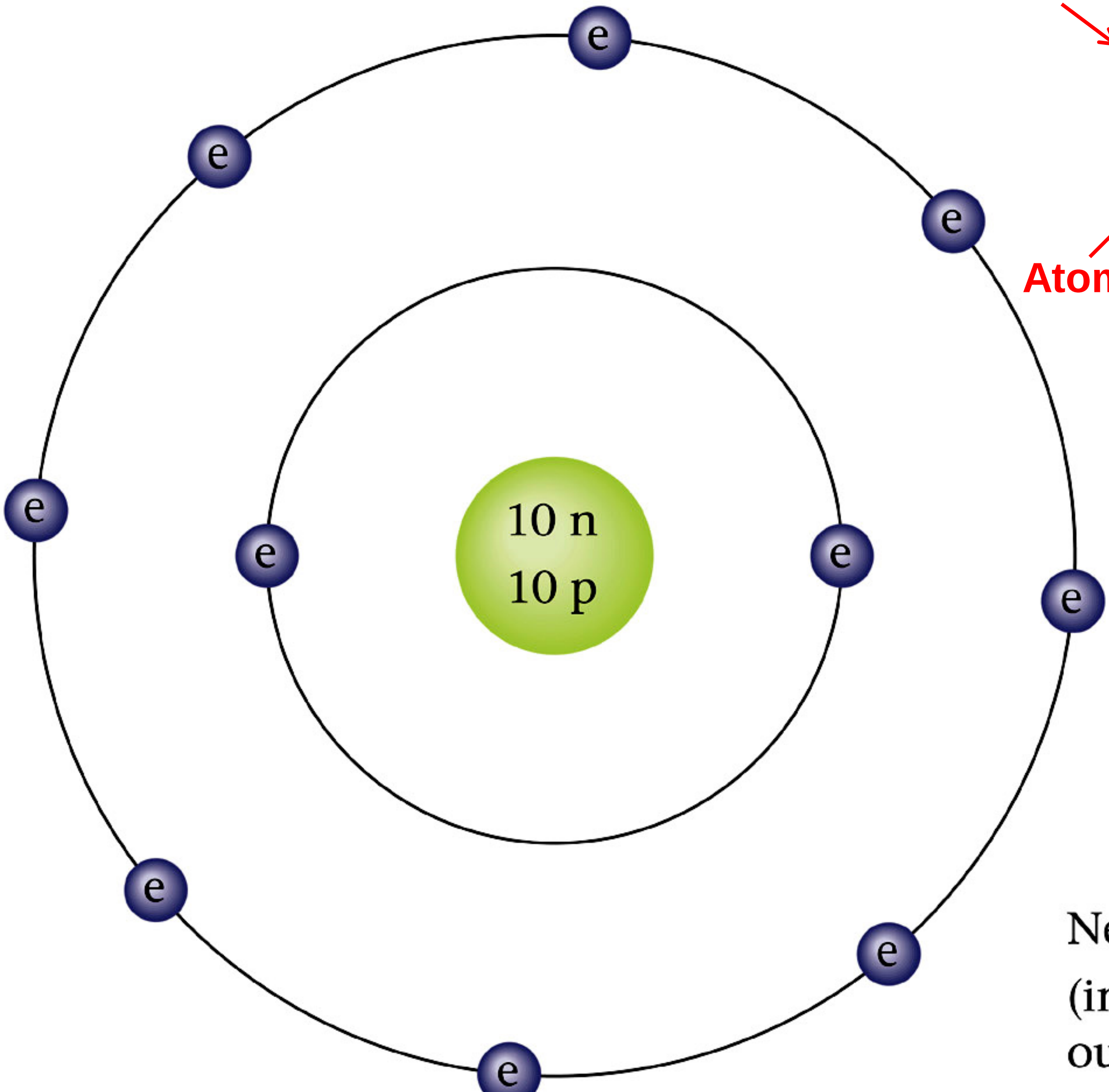


A neutrally-charged atom will have an equal number of electrons and protons, n = p

protons = atomic number (nature of the atom)

protons + # neutrons = atomic mass

Twelve grams of carbon (1.8 cc) contain 6.023 x 10^{23} atoms of carbon.



Atomic mass

$^{20}_{10}\mathrm{Ne}$

Atomic number

Neon atom
(inner shell has $2e^-$,
outer shell has $8e^-$)

Periodic table of the elements

Alkali metals

Symbol | He 2 Helium 4.002 | Atomic number, Name, Atomic weight

Nonmetals

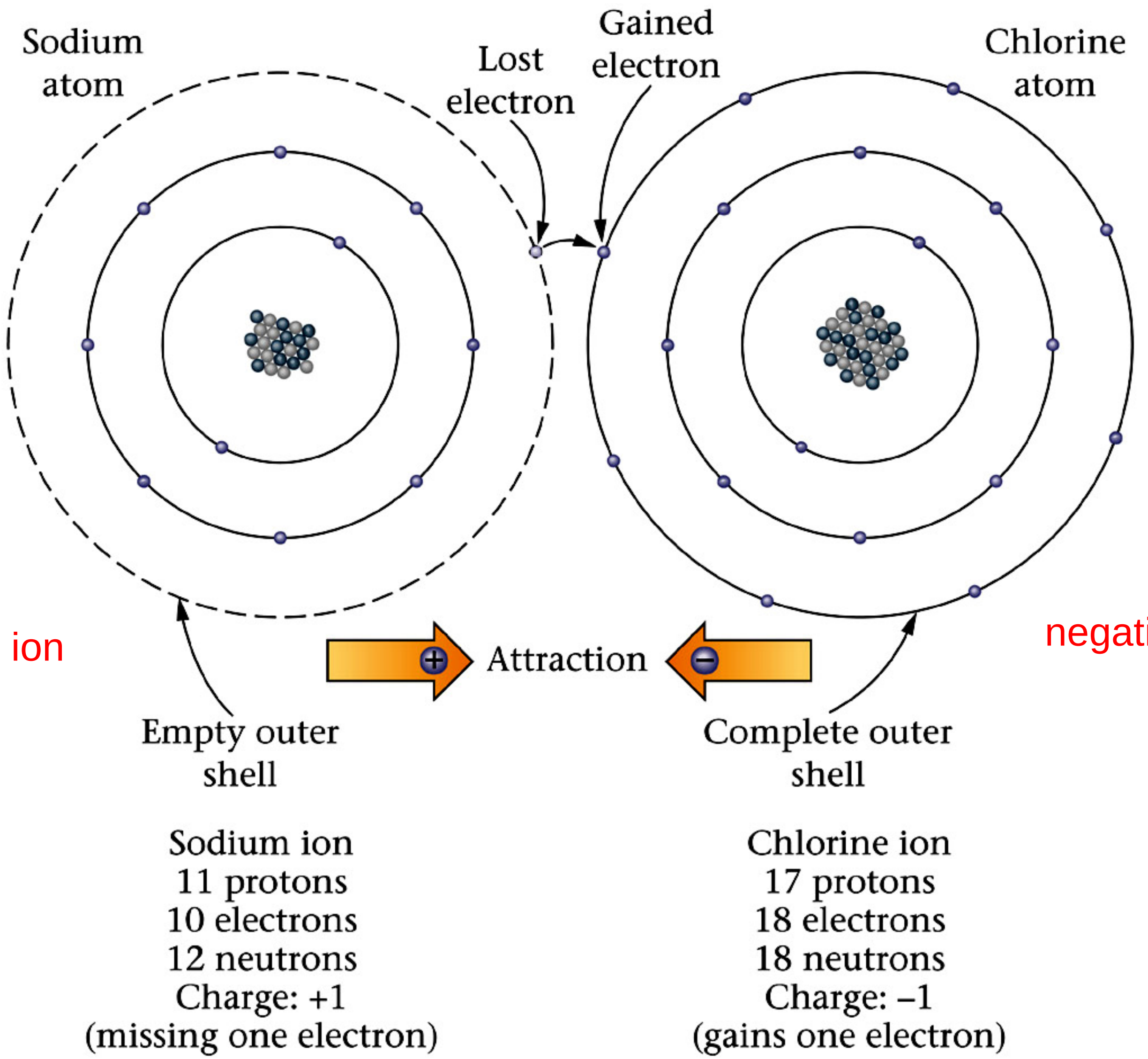
Transition elements (metals)

Inert gases

H 1 Hydrogen 1.007																	He 2 Helium 4.002
Li 3 Lithium 6.941	Be 4 Beryllium 9.0121											B 5 Boron 10.811	C 6 Carbon 12.011	N 7 Nitrogen 14.006	O 8 Oxygen 15.999	F 9 Fluorine 18.998	Ne 10 Neon 20.179
Na 11 Sodium 22.989	Mg 12 Magnesium 24.305											Al 13 Aluminum 26.981	Si 14 Silicon 28.085	P 15 Phosphorus 30.973	S 16 Sulfur 32.066	Cl 17 Chlorine 35.452	Ar 18 Argon 39.948
K 19 Potassium 39.098	Ca 20 Calcium 40.078	Sc 21 Scandium 44.955	Ti 22 Titanium 47.88	V 23 Vanadium 50.941	Cr 24 Chromium 51.996	Mn 25 Manganese 54.938	Fe 26 Iron 55.847	Co 27 Cobalt 58.933	Ni 28 Nickel 58.693	Cu 29 Copper 63.546	Zn 30 Zinc 65.39	Ga 31 Gallium 69.723	Ge 32 Germanium 72.61	As 33 Arsenic 74.921	Se 34 Selenium 78.96	Br 35 Bromine 79.904	Kr 36 Krypton 83.80
Rb 37 Rubidium 85.467	Sr 38 Strontium 87.62	Y 39 Yttrium 88.905	Zr 40 Zirconium 91.224	Nb 41 Niobium 92.906	Mo 42 Molybdenum 95.94	Tc 43 Technetium 98.907	Ru 44 Ruthenium 101.07	Rh 45 Rhodium 102.905	Pd 46 Palladium 106.42	Ag 47 Silver 107.868	Cd 48 Cadmium 112.411	In 49 Indium 114.82	Sn 50 Tin 118.710	Sb 51 Antimony 121.757	Te 52 Tellurium 127.60	I 53 Iodine 126.904	Xe 54 Xenon 131.29
Cs 55 Cesium 132.905	Ba 56 Barium 137.327	La 57 Lanthanum 138.905	Hf 72 Hafnium 178.49	Ta 73 Tantalum 180.947	W 74 Tungsten 183.85	Re 75 Rhenium 186.207	Os 76 Osmium 190.2	Ir 77 Iridium 192.22	Pt 78 Platinum 195.08	Au 79 Gold 196.966	Hg 80 Mercury 200.59	Tl 81 Thallium 204.383	Pb 82 Lead 207.2	Bi 83 Bismuth 208.980	Po 84 Polonium 208.982	At 85 Astatine 209.987	Rn 86 Radon 222.017
Fr 87 Francium 223.019	Ra 88 Radium 226.025	Ac 89 Actinium 227.027															

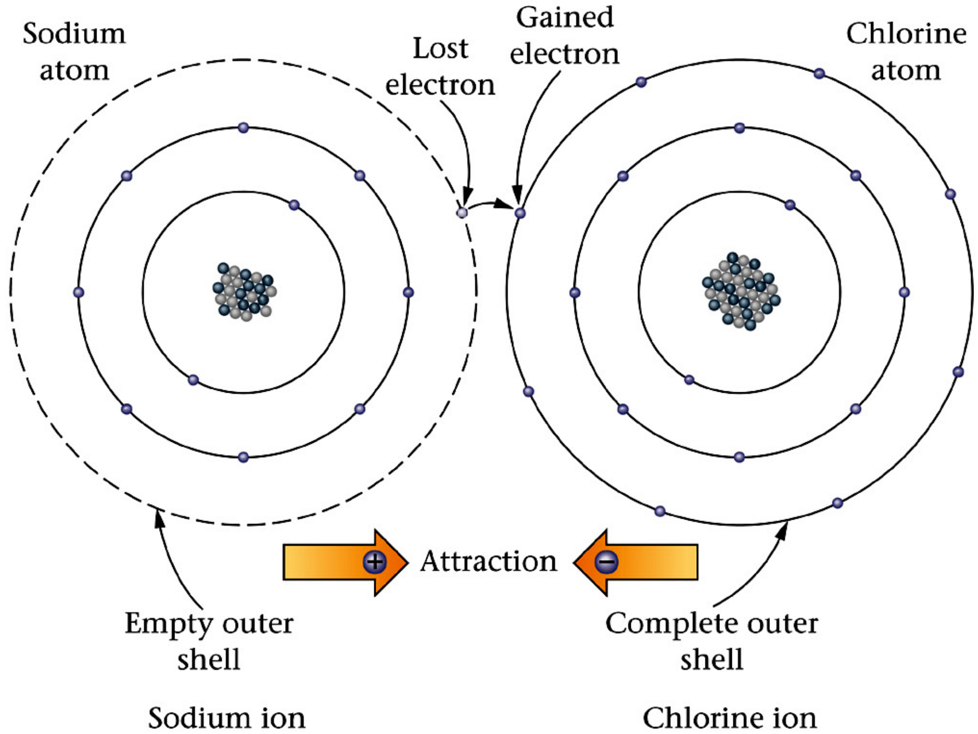
Ce 58 Cerium 140.115	Pr 59 Praseodymium 140.907	Nd 60 Neodymium 144.24	Pm 61 Promethium 144.912	Sm 62 Samarium 150.36	Eu 63 Europium 151.965	Gd 64 Gadolinium 157.25	Tb 65 Terbium 158.925	Dy 66 Dysprosium 162.50	Ho 67 Holmium 164.930	Er 68 Erbium 167.26	Tm 69 Thulium 168.934	Yb 70 Ytterbium 173.04	Lu 71 Lutetium 174.967
Th 90 Thorium 232.038	Pa 91 Protactinium 231.035	U 92 Uranium 238.028	Np 93 Neptunium 237.048	Pu 94 Plutonium 244.064	Am 95 Americium 243.061	Cm 96 Curium 247.070	Bk 97 Berkelium 247.070	Cf 98 Californium 251.079	Es 99 Einsteinium 252.083	Fm 100 Fermium 257.095	Md 101 Mendelevium 258.10	No 102 Nobelium 259.100	Lr 103 Lawrencium 262.11

Ions and the Ionic Bond

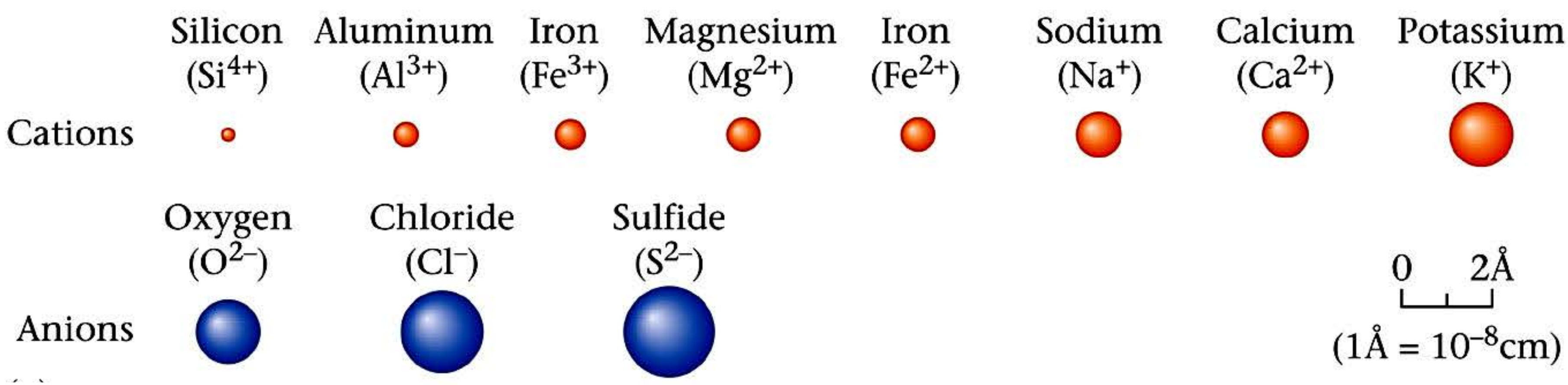


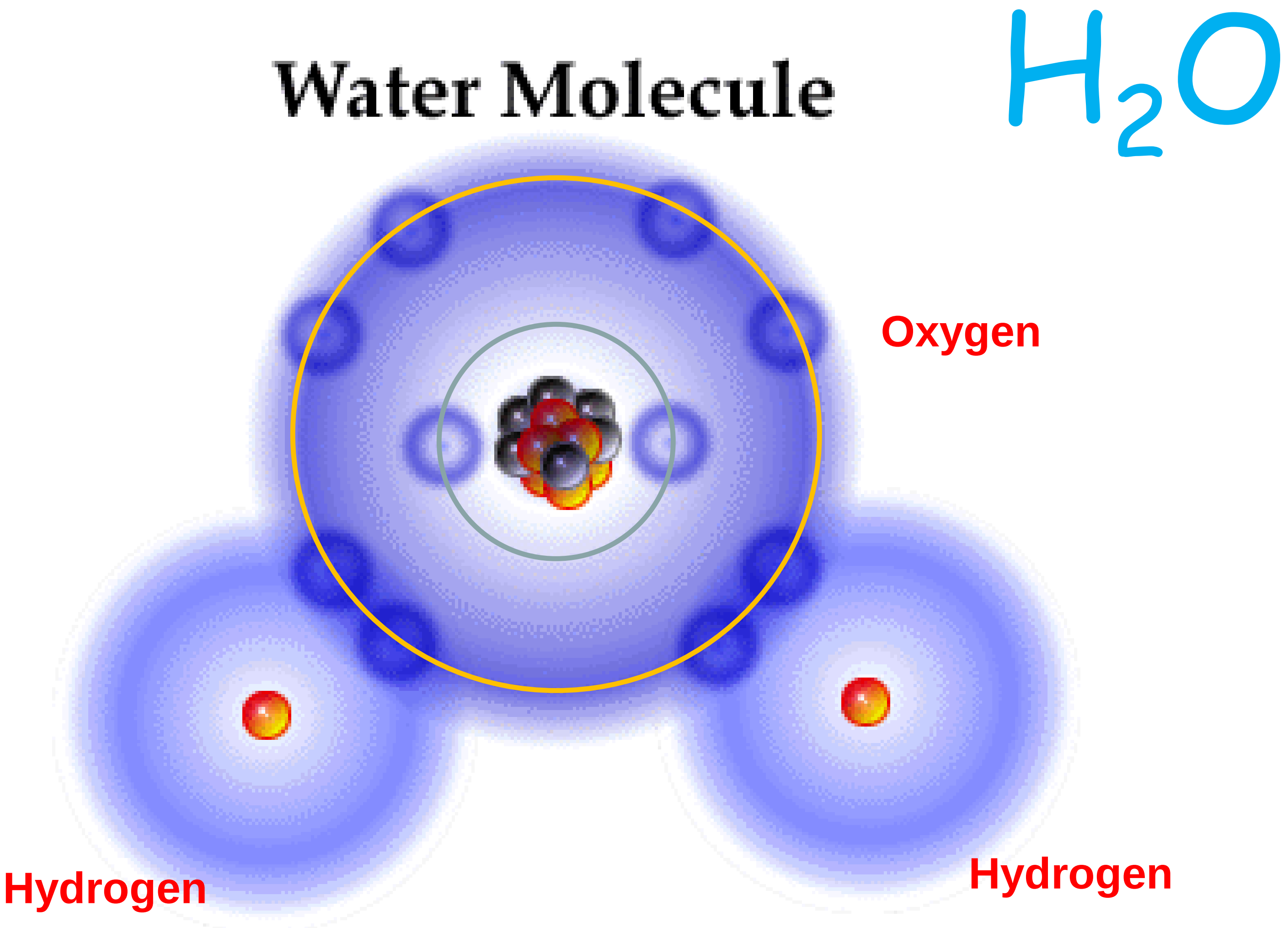
CATION
positively-charged ion

ANION
negatively-charged ion



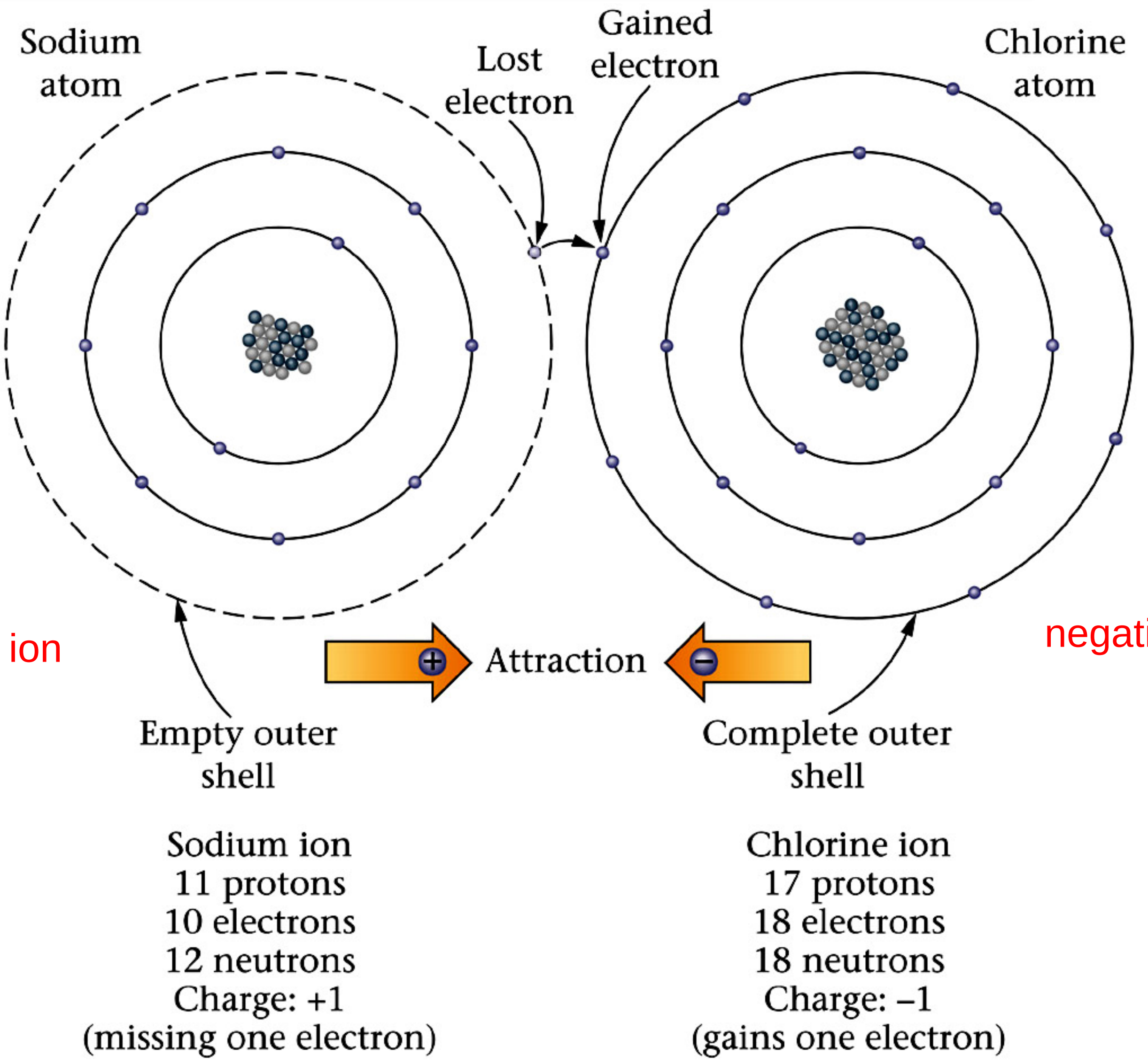
Relative size of ions




Water Molecule
H_2O
Oxygen
Hydrogen
Hydrogen

Ions and the Ionic Bond

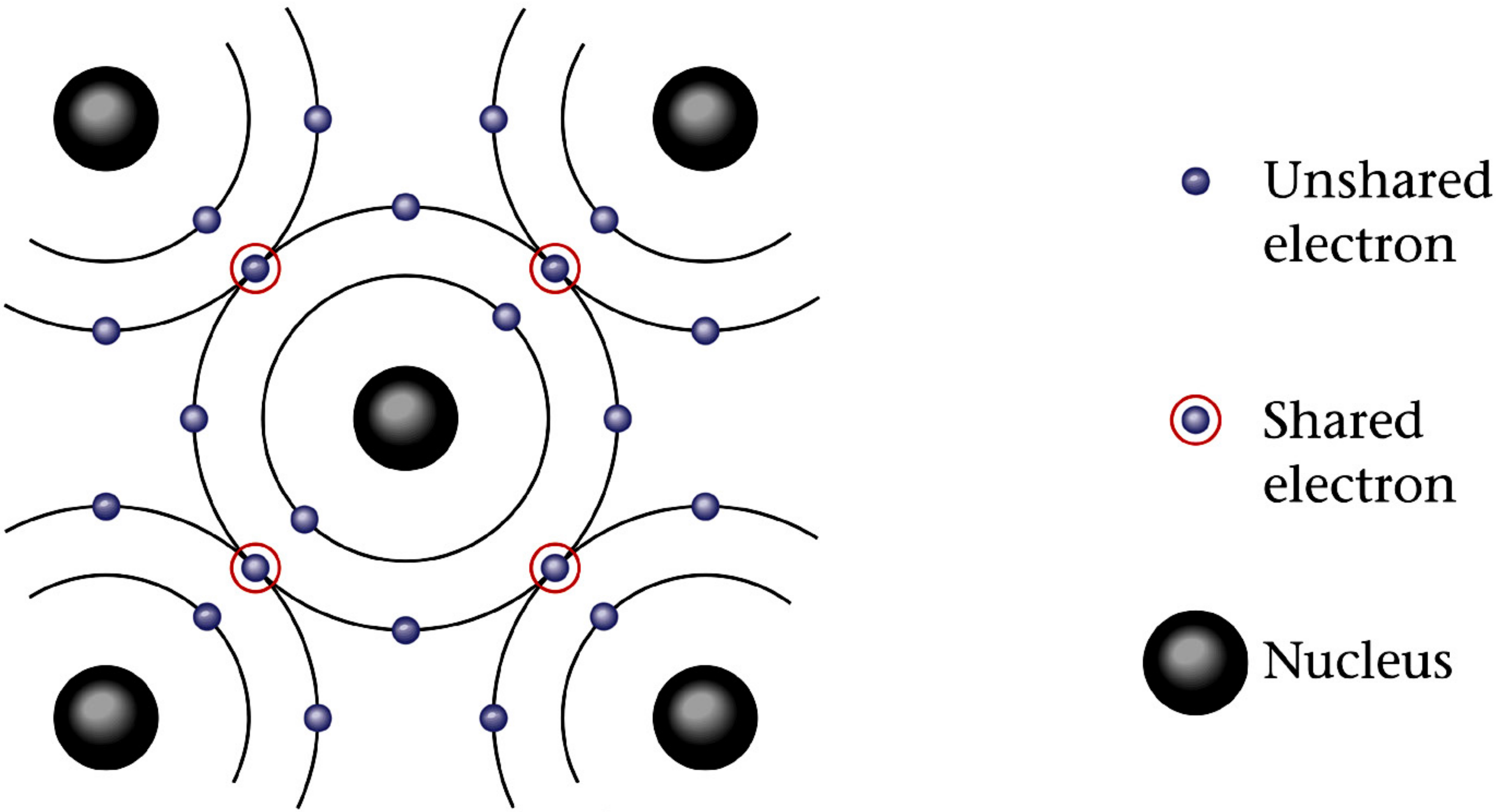
(hard-sphere interactions)



CATION
positively-charged ion

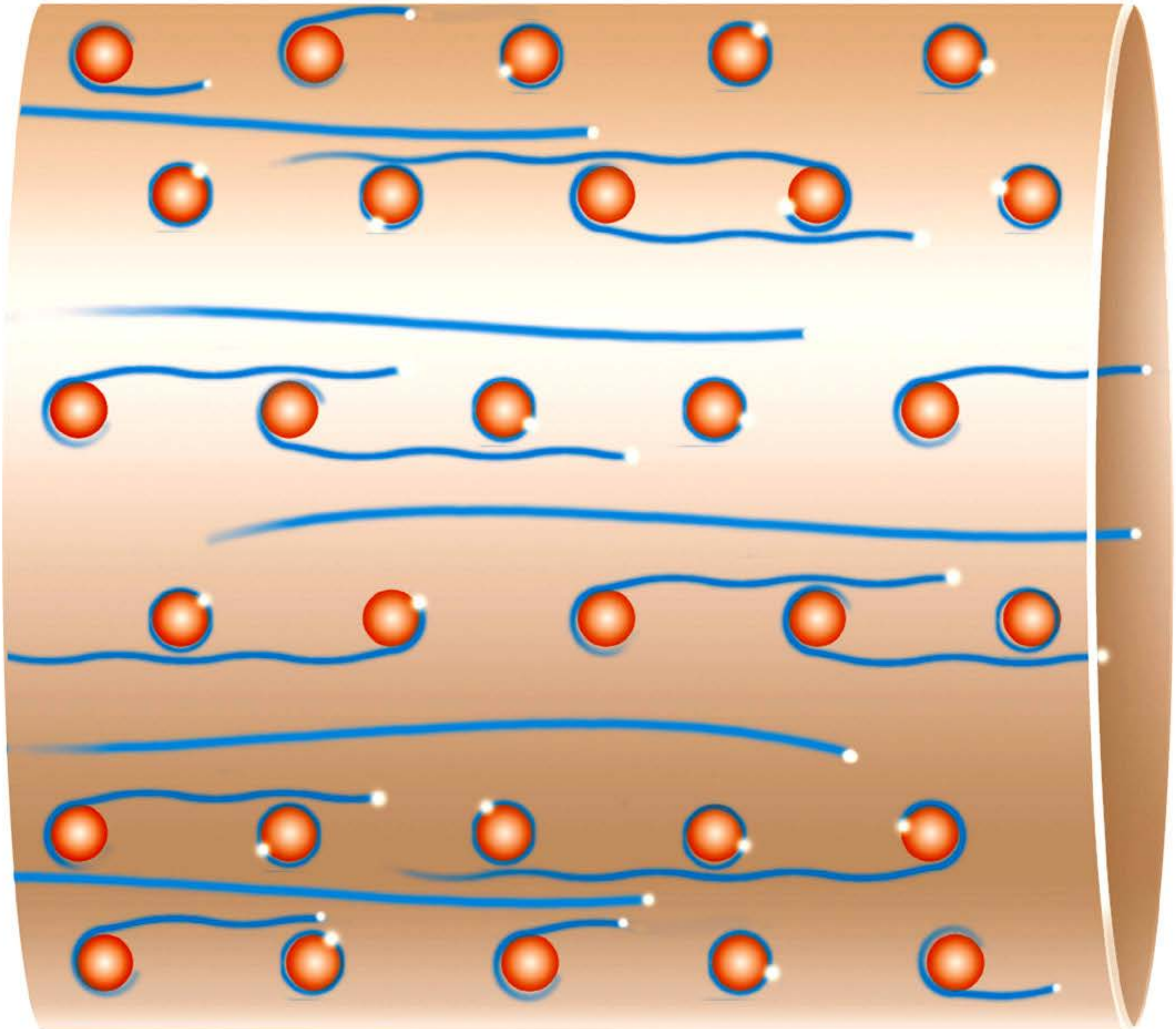
ANION
negatively-charged ion

Covalent Bond
(soft-sphere interactions)



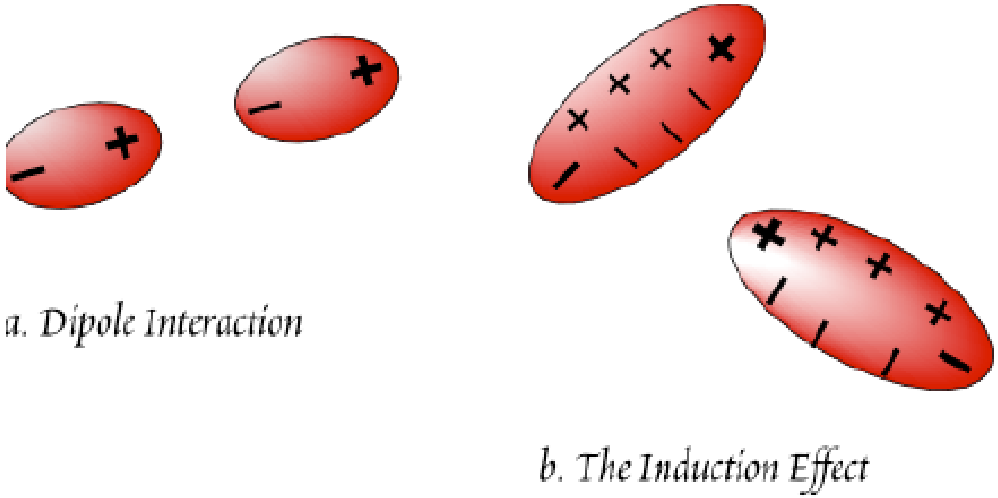
Metallic Bond

(the electrons in the valence/outer shells move easily from atom to atom)

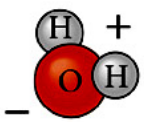


Bonds resulting from the polarity of molecules

(molecules for which there are internal electron density gradients)



Bonds resulting from the polarity of molecules



A polar water molecule

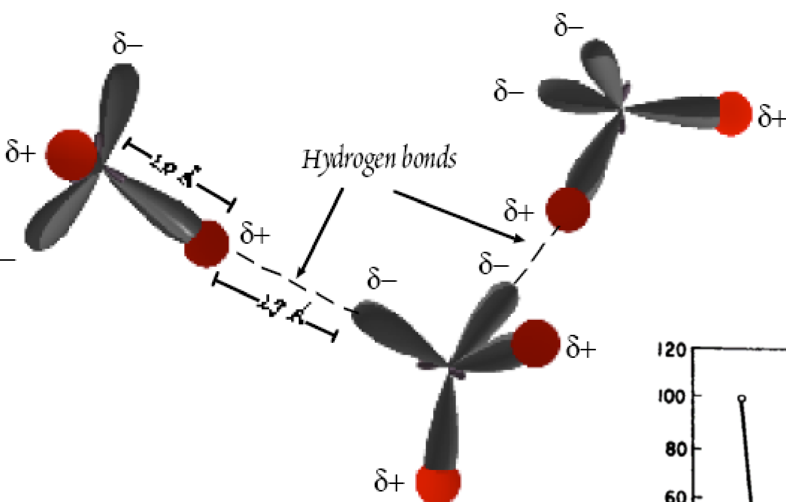
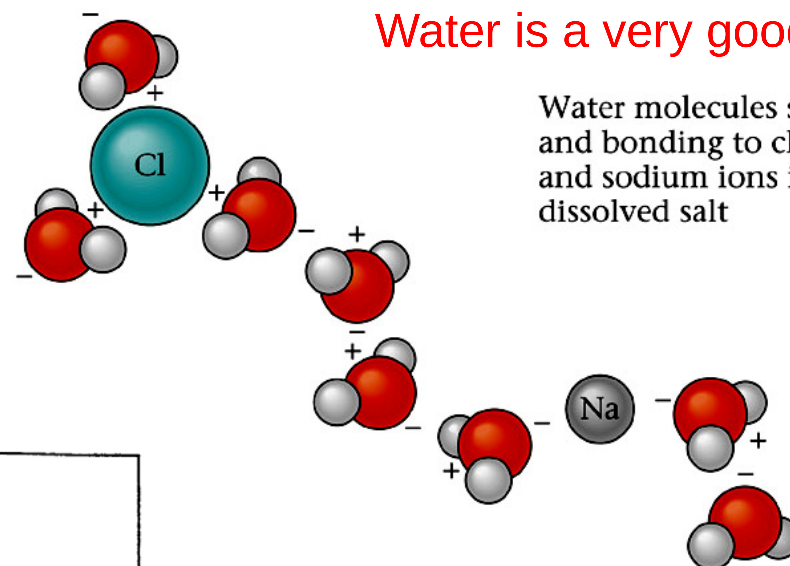
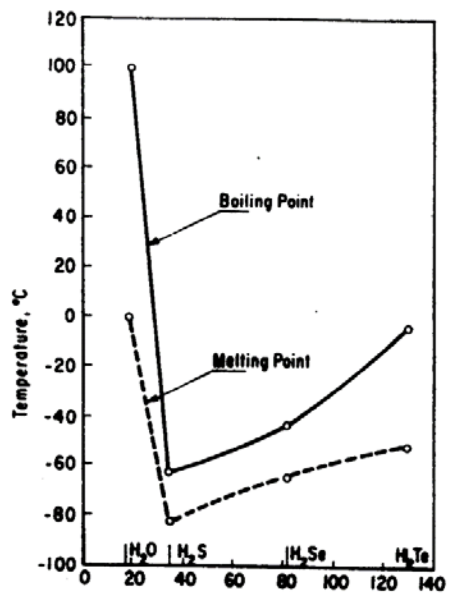


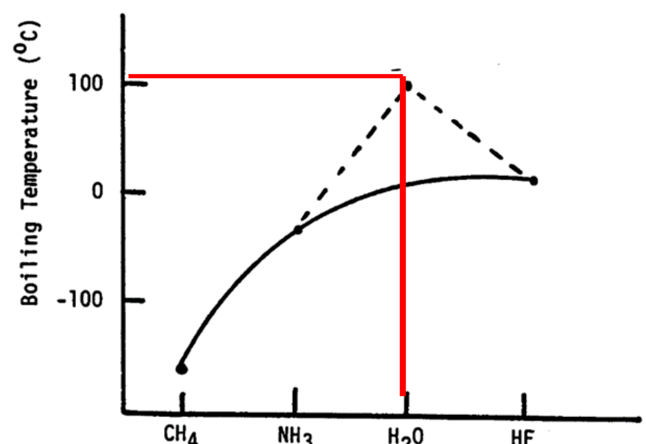
FIGURE a.12

Water is a very good solvent



Water molecules surrounding and bonding to chlorine and sodium ions in dissolved salt





States of matter