Chemistry 531

Chemistry
Of the
Elements

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Chapter 1

Origin of the Elements.

Isotopes and Atomic Weights

Hot Big Bang Theory of Stellar Evolution

Primeval

$\rho = 10^{96}$ g/cc $T = 10^{32}$ K

Nucleus

$T = 10^{31}$ K $t = (Gh/e^5)^{1/2} = 1.33 \times 10^{-43}$ s

gravity separates

$t = 10^{-35}$ s $T = 10^{28}$ K

strong nuclear force separates

$t = 10^{-10}$ s $T = 10^{15}$ K

electromagnetic & weak nuclear forces separate

$t = 6 \times 10^{-6}$ s $T = 1.4 \times 10^{12}$ K

protons & neutrons form from quarks, electrons become stable

$t = 1$ s $T > 10^7$ K

particle|anti-particle annhilations form electromagnetic photons

$t = 10$ s

neutrons; $t_{1/2} = 11.3$ m; decay to protons & electrons

Strong Nuclear Force precipitates homogeneous fusion reactions in Universe

2n + 2p → ${}^{4}_{2}$He 25%

→ ${}^{1}_{1}$H 75%

n + p → ${}^{2}_{1}$D 10^{-3}%

3n + 3p
3n + 4p → ${}^{6,7}_{3}$Li 10^{-6}%

$t = 500$ s

Homogeneous fusion stops as density drops, particles diffuse out of SNF range .

Hot Big Bang Theory of Cosmic Evolution

Readily Explains the following Observations:

- **Light received from distant galaxies is red-shifted– E. Hubble 1929 – Universe is expanding, rate = 1.8 km/s per 10^6 light-years.**

- **Universal Black-Body Radiation – Penzias & Wilson 1973 – $T_{universe}$ = 2.735 K – Dying "ember" of the "Big Bang".**

- **Explanation of the Universal H:He:D ratio – The "Universal Homogeneous Fusion".**

What We Know About the Universe

1) **The Universe is 13.7 billion years old. The shape of space-time is flat, the universe is "flat" I.e. does not curve.**

2) **Protons, neutrons & electrons make up only 4% of the known matter.**

3) **96% of matter is "dark matter" which cannot be seen only inferred by its effect on visible matter in the universe.**

4) **The rate of expansion of the universe 71 km/s per megaparsec. 1 parsec = 3.26 light years = 30.9 x 10^{12} km.**

5) **The rate of expansion of the universe is increasing! Not decreasing.**

6) **A phenomenon called "dark energy", essentially antigravity, pervades the universe causing the increase in the rate of expansion of the universe.**

Cosmic Abundances of the Elements

Empirical Observations:

- **Abundances decrease approximately exponentially as atomic mass increases.**

- **Pronounced peak in abundance at Z = 23-28**

- **D, Li, Be & B are rare relative to H, He, C, N.**

- **Lighter atoms with masses divisible by four are much more abundant than their neighbors. G. Oddo, 1914.**

Cosmic Abundances of the Elements

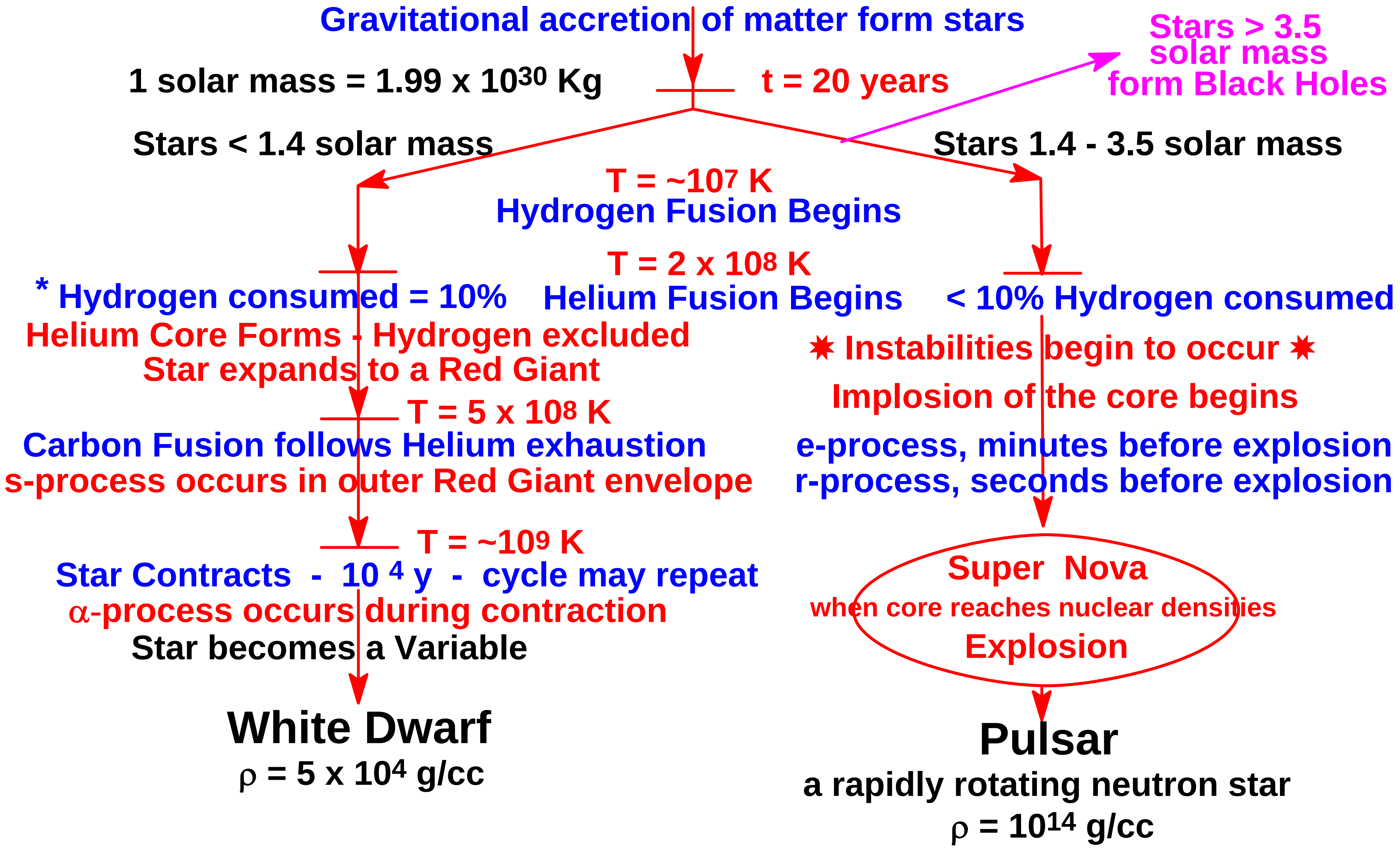
Empirical Observations:

- **Atoms with Atomic mass even are more abundant than those of mass odd.**
- **Atoms of heavy elements tend to be neutron-rich, heavy proton-rich nuclides are rare.**
- **Double peaked abundances occur at A = 80, 90; A = 130, 138; and at A = 196, 208.**

Synthesis of the Elements

- **Exothermic Processes in Stellar Interiors:** Successively H, He, C fusion; α-process; e-process.
- **Neutron Capture Processes:** (slow) s-process; (rapid) r-process.
- **Less Common Processes:** p-process (proton capture), e-process (thermal equilibration), x-process (spallation, collisionally induced fragmentation).
- **Radioactive Decay of Nuclides**

Stellar Evolution



Gravitational accretion of matter form stars

1 solar mass = 1.99 x 10^{30} Kg

t = 20 years

Stars > 3.5 solar mass form Black Holes

Stars < 1.4 solar mass

Stars 1.4 - 3.5 solar mass

T = ~10^7 K
Hydrogen Fusion Begins

T = 2 x 10^8 K
Helium Fusion Begins

* Hydrogen consumed = 10%
Helium Core Forms - Hydrogen excluded
Star expands to a Red Giant

T = 5 x 10^8 K
Carbon Fusion follows Helium exhaustion
s-process occurs in outer Red Giant envelope

T = ~10^9 K
Star Contracts - 10^4 y - cycle may repeat
α-process occurs during contraction
Star becomes a Variable

White Dwarf
ρ = 5 x 10^4 g/cc

< 10% Hydrogen consumed
✷ Instabilities begin to occur ✷
Implosion of the core begins
e-process, minutes before explosion
r-process, seconds before explosion

Super Nova
when core reaches nuclear densities
Explosion

Pulsar
a rapidly rotating neutron star
ρ = 10^{14} g/cc

* Time to Consume 10% H depends sensitively on stellar mass
0.2 solar mass (10^{12} y); 1 (10^{10} y); 10 (10^7 y); 50 (8 x 10^4 y)

Stellar Hydrogen Fusion Reactions

T = 10^7 K

$^1H + {}^1H \rightarrow {}^2H + e^+ + \nu_e$ Q = 1 .44 MeV

$^1H + {}^2H \rightarrow {}^3He + \nu$ Q = 5.49 MeV

$^3He + {}^3He \rightarrow {}^4He + 2\,{}^1H$ Q = 12.86 MeV

Net Reaction: $4\,{}^1H \rightarrow {}^4He + 2\,e^+ + 2\,\nu_e$ Q = 26.72 MeV

CNO Catalytic Cycle

$^{12}C + {}^1H \rightarrow {}^{13}N + \nu$ Q = 1.95 MeV

$^{13}N \rightarrow {}^{13}C + e^+ + \nu$ Q = 2.22 MeV

$^{13}C + {}^1H \rightarrow {}^{14}N + \nu$ Q = 7.54 MeV

$^{14}N + {}^1H \rightarrow {}^{15}O + \nu$ Q = 7.35 MeV

$^{15}O \rightarrow {}^{15}N + e^+ + \nu$ Q = 2.70 MeV

$^{15}N + {}^1H \rightarrow {}^{12}C + {}^4He$ Q = 4.96 MeV

Net Reaction: $4\,{}^1H \rightarrow {}^4He + 2\,e^+ + 2\,\nu_e$ Q = 26.72 MeV

Stellar Helium Fusion

< 1.4 Solar Mass Star becomes a Red Giant

$T = 2 \times 10^{8}$ K

$2\ {}^{4}He \rightarrow {}^{8}Be$ $\quad t_{1/2} = 10^{-16}$ **second**

$${}^{8}Be + {}^{4}He \rightarrow {}^{12}C^{*} \rightarrow {}^{12}C + \gamma$$

Net Reaction: $3\ {}^{4}He \rightarrow {}^{12}C + \gamma \quad Q = 7.281\ \text{MeV}$

Other Fusion Reactions occur during this period:

$${}^{12}C + {}^{4}He \rightarrow {}^{16}O + \gamma \quad Q = 7.148\ \text{MeV}$$

$${}^{16}O + {}^{4}He \rightarrow {}^{20}Ne + \gamma \quad Q = 4.75\ \text{MeV}$$

$${}^{20}Ne + {}^{4}He \rightarrow {}^{24}Mg + \gamma \quad Q = 9.31\ \text{MeV}$$

Stellar Carbon Fusion

Occurs in aging Red Giants

$T = 5 \times 10^{8}$ K

$^{12}C + ^{12}C \rightarrow ^{24}Mg + \gamma \quad Q = 13.85$ MeV

$^{12}C + ^{12}C \rightarrow ^{23}Na + ^{1}H \quad Q = 2.23$ MeV

$^{12}C + ^{12}C \rightarrow ^{20}Ne + ^{4}He \quad Q = 4.62$ MeV

Many other nuclides become possible due to ^{1}H and ^{4}He regeneration.

Stellar α-Process

Contracting Red Giants

During contraction temperatures reach 10^9 K, gamma radiations reach very high energies. Time spent in this phase 10^2 to 10^4 years

$^{20}\text{Ne} + \gamma \rightarrow {}^{16}\text{O} + {}^{4}\text{He} \qquad Q = -4.75 \text{ MeV}$

$^{20}\text{Ne} + {}^{4}\text{He} \rightarrow {}^{24}\text{Mg} + \gamma \qquad Q = +9.31 \text{ MeV}$

Net Reaction: $2\,{}^{20}\text{Ne} \rightarrow {}^{16}\text{O} + {}^{24}\text{Mg} + \gamma \quad Q = +4.56 \text{ MeV}$

$^{20}\text{Ne} \rightarrow {}^{24}\text{Mg} \rightarrow {}^{28}\text{Si} \rightarrow {}^{32}\text{S} \rightarrow {}^{36}\text{Ar} \rightarrow {}^{40}\text{Ca} \rightarrow {}^{44}\text{Ca} \rightarrow {}^{48}\text{Ti}$

8.4 0.78 1.00 0.39 0.14 0.052 0.0011 0.0019

Neutron Capture Processes

S-Process

Neutron capture occurring outside core of pulsating red giants over 10^7 years. Nuclides made by repeated, single neutron capture followed by β decay; most isotopes: A= 63-209 and A = 23-46 (non- α-process)

The relative abundances of elements are determined by their *neutron capture cross-sections*. Nuclides build up by resisting further reactions. The *magic numbers*: 2, 8, 20, 28, 50, 82, 126 are configurations which have *minimum neutron capture cross-sections.*

Neutron Capture Processes

R-Process:

Neutron capture occurring in 1.4-3.5 solar mass stars during catastrophic events such as *supernovas*. Nuclides build up by rapid capture of 100-200 neutrons until a *minimum neutron capture cross-section* precipitates a cascade of beta decays until the zone of stability is reached..

This is thought to be the major path for the formation of ^{232}Th, ^{235}U and ^{238}U which occurred over time beginning with the formation of our galaxy about (1.2-2.0) x 10^{10} years ago.

Less Common Processes

p-Process:

Either (p,γ) occurring in second generation stars, or (γ,n) occurring during or immediately preceding a supernova. Process accounts for lesser abundant, proton-rich isotopes having even mass numbers between ^{74}Se and ^{106}Hg, exceptions are ^{113}In and ^{115}Sn.

e-Process:

Stars mass > 1.4 solar mass preceding a supernova have T > 3 x 10^9 K. Many processes occur in which nuclides equilibrate to more stable species. Explains cosmic abundances of nuclides ^{22}Ti to ^{29}Cu.

Less Common Processes

x-Process:

An *extra-stellar* process important in explaining the existence of stable isotopes of Li, Be, B which are by-passed by normal thermonuclear processes. *Cosmic Ray* induced *spallation* (fragmentation) of stable nuclides in interstellar gas, mostly ^{1}H and ^{4}He but also Fe, Co, Ni.

$$^{56}\mathrm{Fe} \rightarrow {}^{6}\mathrm{Li} + {}^{50}\mathrm{V}$$

$$^{59}\mathrm{Co} \rightarrow {}^{7}\mathrm{Li} + {}^{52}\mathrm{Cr}$$

$$^{56}\mathrm{Fe} \rightarrow {}^{9}\mathrm{Be} + {}^{47}\mathrm{Ti}$$

$$^{56}\mathrm{Fe} \rightarrow {}^{10}\mathrm{B} + {}^{46}\mathrm{Ti}$$

$$^{56}\mathrm{Fe} \rightarrow {}^{11}\mathrm{B} + {}^{45}\mathrm{Sc}$$

Maximum Abundance **Exist** **Over-abundant**

Atomic Weights

Mean Relative Atomic Mass: A centrally important "constant" in the development of chemistry as a quantitative science.

Precision greatest for monoisotopic elements: Be, F, Na, Al, P, Sc, Mn, Co, As, Y, Nb, Rh, I, Cs, Pr, Tb, Ho, Tm, Au, Bi

Elements with 99+% abundance have good precision for a given sample: H, He, N, O, Ar, V, La, Ta

Precision limited by natural (B, S, Pb) and artificial (Li, B, U) isotopic enrichment/depletion: H, He, Li, B, C, N, O, Si, S, Ar, Cu, Sr, Pb

Atomic Weight Variation

A growing problem for chemists:

H – Contamination by samples enriched in ^{2}H.

Li – ^{6}Li depletion by nuclear industry.

B – ^{10}B depletion by nuclear medicine industry.

Kr, Ne – "Milked" from nuclear reactors and sold commercially.

Pb – Isolated from geologically distinct ores can vary from near 204 to 208: ^{208}Pb (^{232}Th); ^{207}Pb (^{235}U); ^{206}Pb (^{238}U).