

Chemistry 531

**Chemistry
Of the
Elements**

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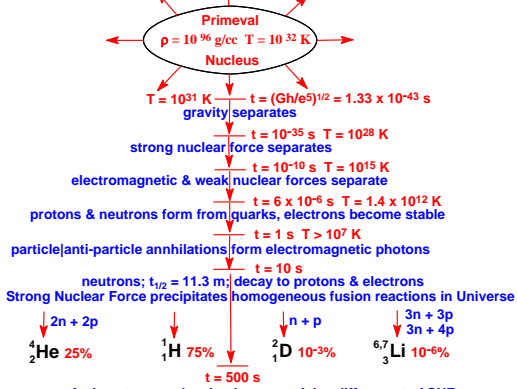
Greenwood & Earnshaw

2nd Edition

Chapter 1

**Origin of the Elements.
Isotopes and Atomic Weights**

Hot Big Bang Theory of Stellar Evolution



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 – $T_{\text{universe}} = 2.735 \text{ K}$ – 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 = 30.9×10^{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.

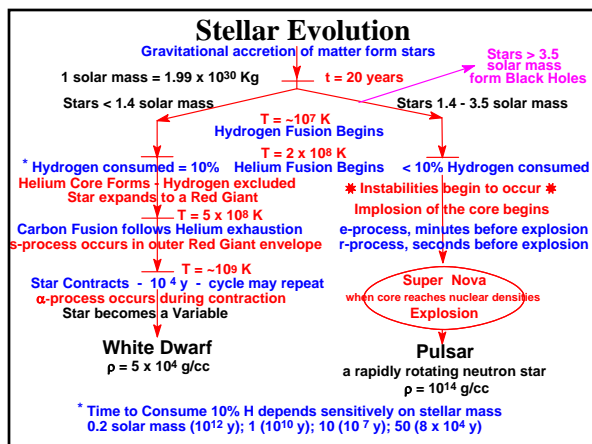
Cosmic Abundances of the Elements

Empirical Observations:

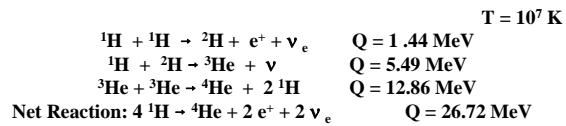
- Atoms with Atomic mass even are more abundant than those of mass odd.
- Atoms of heavy elements tend to be neutron-rich, heavy proton-rich nuclides are rare.
- Double peaked abundances occur at $A = 80, 90$; $A = 130, 138$; and at $A = 196, 208$.

Synthesis of the Elements

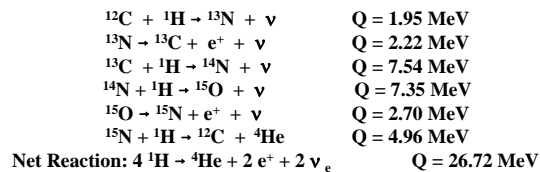
- Exothermic Processes in Stellar Interiors: Successively H, He, C fusion; α -process; e-process.
- Neutron Capture Processes: (slow) s-process; (rapid) r-process.
- Less Common Processes: p-process (proton capture), e-process (thermal equilibration), x-process (spallation, collisionally induced fragmentation).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



Stellar Hydrogen Fusion Reactions

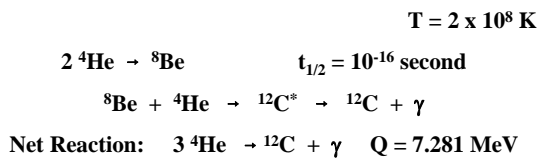


CNO Catalytic Cycle

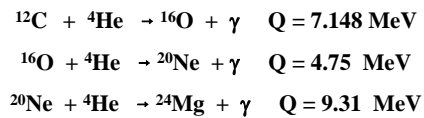


Stellar Helium Fusion

< 1.4 Solar Mass Star becomes a Red Giant

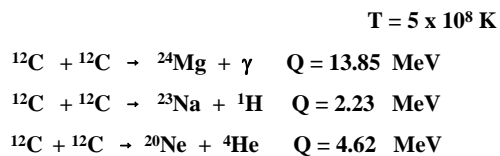


Other Fusion Reactions occur during this period:



Stellar Carbon Fusion

Occurs in aging Red Giants

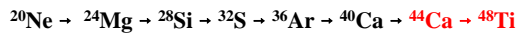
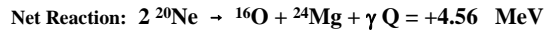
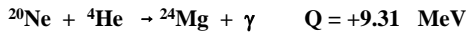
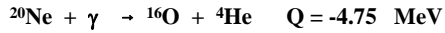


Many other nuclides become possible due to ${}^1\text{H}$ and ${}^4\text{He}$ regeneration.

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



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 $(1.2-2.0) \times 10^{10}$ 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 .

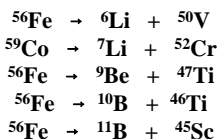
e-Process:

Stars mass > 1.4 solar mass preceding a supernova have $T > 3 \times 10^9$ 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 bypassed by normal thermonuclear processes. *Cosmic Ray induced spallation* (fragmentation) of stable nuclides in interstellar gas, mostly ^1H and ^4He but also Fe, Co, Ni.



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 ^2H .

Li – ^6Li 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).
