

																1	2										
																H	He										
3	4															5	6	7	8	9	10						
Li	Be															B	C	N	O	F	Ne						
11	12															13	14	15	16	17	18						
Na	Mg															Al	Si	P	S	Cl	Ar						
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36										
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Cu	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr										
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54										
Rb	Sr	Y	Zr	Nb	Mu	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe										
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72										
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn										
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104										
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uun	Uun																
88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105										
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr														

1

Origin of the Elements. Isotopes and Atomic Weights

1.1 Introduction

This book presents a unified treatment of the chemistry of the elements. At present 112 elements are known, though not all occur in nature: of the 92 elements from hydrogen to uranium all except technetium and promethium are found on earth and technetium has been detected in some stars. To these elements a further 20 have been added by artificial nuclear syntheses in the laboratory. Why are there only 90 elements in nature? Why do they have their observed abundances and why do their individual isotopes occur with the particular relative abundances observed? Indeed, we must also ask to what extent these isotopic abundances commonly vary in nature, thus causing variability in atomic weights and possibly jeopardizing the classical means of determining chemical composition and structure by chemical analysis.

Theories abound, and it is important at all times to distinguish carefully between what has been experimentally established, what is a useful model for suggesting further experiments, and

what is a currently acceptable theory which interprets the known facts. The tentative nature of our knowledge is perhaps nowhere more evident than in the first few sections of this chapter dealing with the origin of the chemical elements and their present isotopic composition. This is not surprising, for it is only in the last few decades that progress in this enormous enterprise has been made possible by discoveries in nuclear physics, astrophysics, relativity and quantum theory.

1.2 Origin of the Universe

At present, the most widely accepted theory for the origin and evolution of the universe to its present form is the "hot big bang".⁽¹⁾ It is supposed that all the matter in the universe

¹ J. SILK, *The Big Bang: The Creation and Evolution of the Universe*, 2nd edn., W. H. Freeman, New York, 1989, 485 pp. J. D. BARROW and J. SILK, *The Left Hand of Creation: The Origin and Evolution of the Expanding Universe*, Heinemann, London, 1984, 256 pp. E. W. KOLB and M. S. TURNER, *The Early Universe*, Addison-Wesley, Redwood City, CA, 1990, 547 pp.

was once contained in a primeval nucleus of immense density ($\sim 10^{96} \text{ g cm}^{-3}$) and temperature ($\sim 10^{32} \text{ K}$) which, for some reason, exploded and distributed radiation and matter uniformly throughout space. As the universe expanded it cooled; this allowed the four main types of force to become progressively differentiated, and permitted the formation of various types of particle to occur. Nothing scientific can be said about the conditions obtaining at times shorter than the Planck time, $t_P [(Gh/c^5)^{1/2} = 1.33 \times 10^{-43} \text{ s}]$ at which moment the forces of gravity and electromagnetism, and the weak and strong nuclear forces were all undifferentiated and equally powerful. At 10^{-43} s after the big bang ($T = 10^{31} \text{ K}$) gravity separated as a distinct force, and at 10^{-35} s (10^{28} K) the strong nuclear force separated from the still combined electro-weak force. These are, of course, inconceivably short times and unimaginably high temperatures: for example, it takes as long as 10^{-24} s for a photon (travelling at the speed of light) to traverse a distance equal to the diameter of an atomic nucleus. When a time interval of 10^{-10} s had elapsed from the big bang the temperature is calculated to have fallen to 10^{15} K and this enabled the electromagnetic and weak nuclear forces to separate. By $6 \times 10^{-6} \text{ s}$ ($1.4 \times 10^{12} \text{ K}$) protons and neutrons had been formed from quarks, and this was followed by stabilization of electrons. One second after the big bang, after a period of extensive particle-antiparticle annihilation to form electromagnetic photons, the universe was populated by particles which sound familiar to chemists — protons, neutrons and electrons.

Shortly thereafter, the strong nuclear force ensured that large numbers of protons and neutrons rapidly combined to form deuterium nuclei ($p + n$), then helium ($2p + 2n$). *The process of element building had begun.* During this small niche of cosmic history, from about 10–500 s after the big bang, the entire universe is thought to have behaved as a colossal homogeneous fusion reactor converting hydrogen into helium. Previously no helium nuclei could exist — the temperature was so high that the sea

of radiation would have immediately decomposed them back to protons and neutrons. Subsequently, the continuing expansion of the universe was such that the particle density was too low for these strong (but short-range) interactions to occur. Thus, within the time slot of about eight minutes, it has been calculated that about one-quarter of the mass of the universe was converted to helium nuclei and about three-quarters remained as hydrogen. Simultaneously, a minute $10^{-3}\%$ was converted to deuterons and about $10^{-6}\%$ to lithium nuclei. These remarkable predictions of the big bang cosmological theory are borne out by experimental observations. Wherever one looks in the universe — the oldest stars in our own galaxy, or the “more recent” stars in remote galaxies — the universal abundance of helium is about 25%. Even more remarkably, the expected concentration of deuterium has been detected in interstellar clouds. Yet, as we shall shortly see, stars can only destroy deuterium as soon as it is formed; they cannot create any appreciable equilibrium concentration of deuterium nuclei because of the high temperature of the stellar environment. The sole source of deuterium in the universe seems to be the big bang. At present no other cosmological theory can explain this observed ratio of H:He:D.

Two other features of the universe find ready interpretation in terms of the big bang theory. First, as observed originally by E. Hubble in 1929, the light received on earth from distant galaxies is shifted increasingly towards the red end of the spectrum as the distance of the source increases. This implies that the universe is continually expanding and, on certain assumptions, extrapolation backwards in time indicates that the big bang occurred some 15 billion years ago. Estimates from several other independent lines of evidence give reassuringly similar values for the age of the universe. Secondly, the theory convincingly explains (indeed predicted) the existence of an all-pervading isotropic cosmic black-body radiation. This radiation (which corresponds to a temperature of $2.735 \pm 0.06 \text{ K}$ according to the most recent measurements) was discovered in

1965 by A. A. Penzias and R. W. Wilson⁽²⁾ and is seen as the dying remnants of the big bang. No other cosmological theory yet proposed is able to interpret all these diverse observations.

1.3 Abundances of the Elements in the Universe

Information on the abundances of at least some of the elements in the sun, stars, gaseous nebulae and the interstellar regions has been obtained from detailed spectroscopic analysis using various regions of the electromagnetic spectrum. This data can be supplemented by direct analysis of samples from the earth, from meteorites, and increasingly from comets, the moon, and the surfaces of other planets and satellites in the solar system. The results indicate extensive differentiation in the solar system and in some stars, but the overall picture is one of astonishing uniformity of composition. Hydrogen is by far the most abundant element in the universe, accounting for some 88.6% of all atoms (or nuclei). Helium is about eightfold less abundant (11.3%), but these two elements together account for over 99.9% of the atoms and nearly 99% of the mass of the universe. Clearly nucleosynthesis of the heavier elements from hydrogen and helium has not yet proceeded very far.

Various estimates of the universal abundances of the elements have been made and, although these sometimes differ in detail for particular elements, they rarely do so by more than a factor of 3 ($10^{0.5}$) on a scale that spans more than 12 orders of magnitude. Representative values are plotted in Fig. 1.1, which shows a number of features that must be explained by any satisfactory theory of the origin of the elements. For example:

- (i) Abundances decrease approximately exponentially with increase in atomic mass number A until $A \sim 100$ (i.e. $Z \sim 42$); thereafter the decrease is more gradual and is sometimes masked by local fluctuations.
- (ii) There is a pronounced peak between $Z = 23-28$ including V, Cr, Mn, Fe, Co and Ni, and rising to a maximum at Fe which is $\sim 10^3$ more abundant than expected from the general trend.
- (iii) Deuterium (D), Li, Be and B are rare compared with the neighbouring H, He, C and N.
- (iv) Among the lighter nuclei (up to Sc, $Z = 21$), those having an atomic mass number A divisible by 4 are more abundant than their neighbours, e.g. ^{16}O , ^{20}Ne , ^{24}Mg , ^{28}Si , ^{32}S , ^{36}Ar and ^{40}Ca (rule of G. Oddo, 1914).
- (v) Atoms with A even are more abundant than those with A odd. (This is seen in Fig. 1.1 as an upward displacement of the curve for Z even, the exception at beryllium being due to the non-existence of ^8Be , the isotope ^9Be being the stable species.)

Two further features become apparent when abundances are plotted against A rather than Z :

- (vi) Atoms of heavy elements tend to be neutron rich; heavy proton-rich nuclides are rare.
- (vii) Double-peaked abundance maxima occur at $A = 80, 90$; $A = 130, 138$; and $A = 196, 208$ (see Fig. 1.5 on p. 11).

It is also necessary to explain the existence of naturally occurring radioactive elements whose half-lives (or those of their precursors) are substantially less than the presumed age of the universe.

As a result of extensive studies over the past four decades it is now possible to give a detailed and convincing explanation of the experimental abundance data summarized above. The historical sequence of events which led to our present

²R. W. WILSON, The cosmic microwave background radiation, pp. 113–33 in *Les Prix Nobel 1978*, Almqvist & Wiksell International, Stockholm 1979. A. A. PENZIAS, The origin of the elements, pp. 93–106 in *Les Prix Nobel 1978* (also in *Science* **105**, 549–54 (1979)).

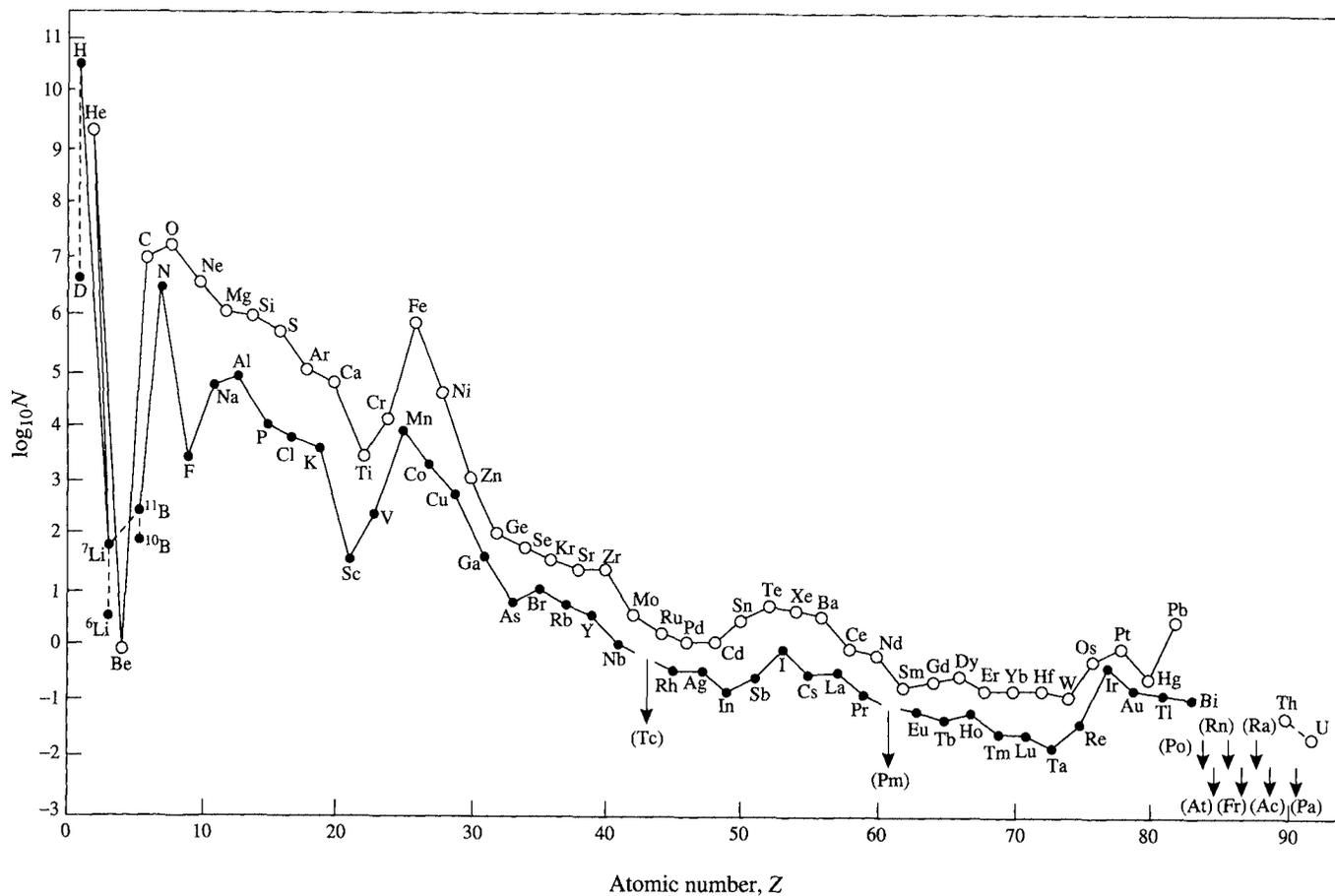


Figure 1.1 Cosmic abundances of the elements as a function of atomic number Z . Abundances are expressed as numbers of atoms per 10^6 atoms of Si and are plotted on a logarithmic scale. (From A. G. W. Cameron, *Space Sci. Rev.* **15**, 121–46 (1973), with some updating.)

understanding is briefly summarized in the Panel. As the genesis of the elements is closely linked with theories of stellar evolution, a short description of the various types of star is given in the next section and this is then followed by a fuller discussion of the various processes by which the chemical elements are synthesized.

1.4 Stellar Evolution and the Spectral Classes of Stars^(3,4)

In broad outline stars are thought to evolve by the following sequence of events. First, there is self-gravitational accretion from the cooled primordial

³ I. S. SHKLOVSKII, *Stars: Their Birth, Life and Death* (translated by R. B. Rodman), W. H. Freeman, San Francisco, 1978, 442 pp. M. HARWIT, *Astrophysical Concepts* (2nd edn) Springer Verlag, New York, 1988, 626 pp.

⁴ D. H. CLARK and F. R. STEPHENSON, *The Historical Supernovae*, Pergamon Press, Oxford, 1977, 233 pp.

hydrogen and helium. For a star the size and mean density of the sun (mass = 1.991×10^{30} kg = $1 M_{\odot}$) this might take ~ 20 y. This gravitational contraction releases heat energy, some of which is lost by radiation; however, the continued contraction results in a steady rise in temperature until at $\sim 10^7$ K the core can sustain nuclear reactions. These reactions release enough additional energy to compensate for radiational losses and a temporary equilibrium or steady state is established.

When $\sim 10\%$ of the hydrogen in the core has been consumed gravitational contraction again occurs until at a temperature of $\sim 2 \times 10^8$ K helium burning (fusion) can occur. This is followed by a similar depletion, contraction and temperature rise until nuclear reactions involving

L. A. MARSCHALL, *The Supernova Story*, Plenum Press, New York, 1989, 276 pp. P. MURDIN, *End in Fire: The Supernova in the Large Magellanic Cloud*, Cambridge University Press, 1990, 253 pp.

Genesis of the Elements — Historical Landmarks

1890s	First systematic studies on the terrestrial abundances of the elements	F. W. Clarke; H. S. Washington and others
1905	Special relativity theory: $E = mc^2$	A. Einstein
1911	Nuclear model of the atom	E. Rutherford
1913	First observation of isotopes in a stable element (Ne)	J. J. Thompson
1919	First artificial transmutation of an element ${}^{14}_7\text{N}(\alpha, p){}^{17}_8\text{O}$	E. Rutherford
1925–8	First abundance data on stars (spectroscopy)	Cecilia H. Payne; H. N. Russell
1929	First proposal of stellar nucleosynthesis by proton fusion to helium and heavier nuclides	R. D'E. Atkinson and F. G. Houtermans
1937	The "missing element" $Z = 43$ (technetium) synthesized by ${}^{99}_{42}\text{Mo}(d, n){}^{99}_{43}\text{Tc}$	C. Perrier and E. G. Segré
1938	Catalytic CNO process independently proposed to assist nuclear synthesis in stars	H. A. Bethe; C. F. von Weizsäcker
1938	Uranium fission discovered experimentally	O. Hahn and F. Strassmann
1940	First transuranium element ${}^{239}_{93}\text{Np}$ synthesized	E. M. McMillan and P. Abelson
1947	The last "missing element" $Z = 61$ (Pm) discovered among uranium fission products	J. A. Marinsky, L. E. Glendenin and C. D. Coryell
1948	Hot big-bang theory of expanding universe includes an (incorrect) theory of nucleogenesis	R. A. Alpher, H. A. Bethe and G. Gamow
1952–4	Helium burning as additional process for nucleogenesis	E. E. Salpeter; F. Hoyle
1954	Slow neutron absorption added to stellar reactions	A. G. W. Cameron
1955–7	Comprehensive theory of stellar synthesis of all elements in observed cosmic abundances	E. M. Burbidge, G. R. Burbidge, W. A. Fowler and F. Hoyle
1965	2.7 K radiation detected	A. P. Penzias and R. W. Wilson

still heavier nuclei ($Z = 8-22$) can occur at $\sim 10^9$ K. The time scale of these processes depends sensitively on the mass of the star, taking perhaps 10^{12} y for a star of mass $0.2 M_{\odot}$, 10^{10} y for a star of 1 solar mass, 10^7 y for mass $10 M_{\odot}$, and only 8×10^4 y for a star of $50 M_{\odot}$; i.e. the more massive the star, the more rapidly it consumes its nuclear fuel. Further catastrophic changes may then occur which result in much of the stellar material being ejected into space, where it becomes incorporated together with further hydrogen and helium in the next generation of stars. It should be noted, however, that, as iron is at the maximum of the nuclear binding energy curve, only those elements up to iron ($Z = 26$) can be produced by exothermic processes of the type just considered, which occur automatically if the temperature rises sufficiently. Beyond iron, an input of energy is required to promote further element building.

The evidence on which this theory of stellar evolution is based comes not only from known nuclear reactions and the relativistic equivalence of mass and energy, but also from the spectroscopic analysis of the light reaching us from the stars. This leads to the spectral classification of stars, which is the cornerstone of modern experimental astrophysics. The spectroscopic analysis of starlight reveals much information about the

chemical composition of stars — the identity of the elements present and their relative concentrations. In addition, the “red shift” or Doppler effect can be used to gauge the relative motions of the stars and their distance from the earth. More subtly, the surface temperature of stars can be determined from the spectral characteristics of their “blackbody” radiation, the higher the temperature the shorter the wavelength of maximum emission. Thus cooler stars appear red, and successively hotter stars appear progressively yellow, white, and blue. Differences in colour are also associated with differences in chemical composition as indicated in Table 1.1.

If the spectral classes (or temperatures) of stars are plotted against their absolute magnitudes (or luminosities) the resulting diagram shows several preferred regions into which most of the stars fall. Such diagrams were first made, independently, by E. Hertzsprung and H. N. Russell about 1913 and are now called HR diagrams (Fig. 1.2). More than 90% of all stars fall on a broad band called the main sequence, which covers the full range of spectral classes and magnitudes from the large, hot, massive O stars at the top to the small, dense, reddish M stars at the bottom. However, it should be emphasized that the terms “large” and “small” are purely relative since all stars within the main sequence are classified as dwarfs.

Table 1.1 Spectral classes of stars

Class ^(a)	Colour	Surface (T/K)	Spectral characterization	Examples
O	Blue	>25 000	Lines of ionized He and other elements; H lines weak	10 Lacertae
B	Blue-white	11 000–25 000	H and He prominent	Rigel, Spica
A	White	7 500–11 000	H lines very strong	Sirius, Vega
F	Yellow-white	6 000–7 000	H weaker; lines of ionized metals becoming prominent	Canopus, Procyon
G	Yellow	5 000–6 000	Lines of ionized and neutral metals prominent (especially Ca)	Sun, Capella
K	Orange	3 500–5 000	Lines of neutral metals and band spectra of simple radicals (e.g. CN, OH, CH)	Arcturus, Aldebaran
M	Red	2 000–3 500	Band spectra of many simple compounds prominent (e.g. TiO)	Betelgeuse, Antares

^(a)Further division of each class into 10 subclasses is possible, e.g. . . . F8, F9, G0, G1, G2, . . . The sun is G2 with a surface temperature of 5780 K. This curious alphabetical sequence of classes arose historically and can perhaps best be remembered by the mnemonic “Oh Be A Fine Girl (Guy), Kiss Me”.

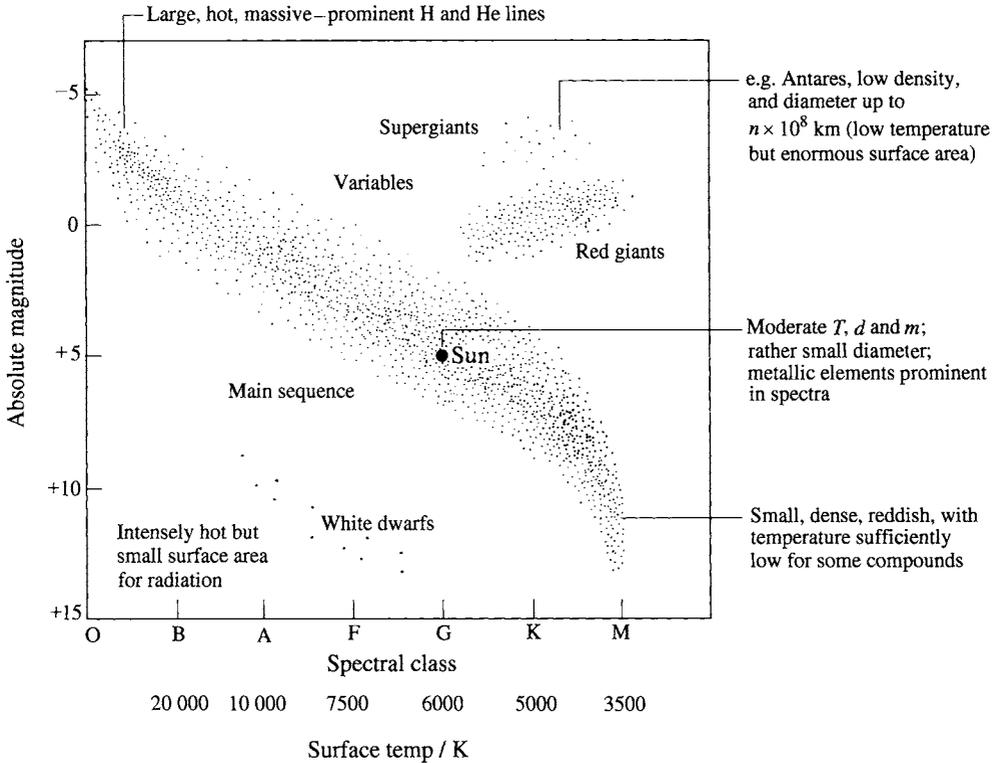


Figure 1.2 The Hertzsprung-Russell diagram for stars with known luminosities and spectra.

The next most numerous group of stars lie above and to the right of the main sequence and are called red giants. For example, Capella and the sun are both G-type stars yet Capella is 100 times more luminous than the sun; since they both have the same temperature it is concluded that Capella must have a radiating surface 100 times larger than the sun and thus has about 10 times its radius. Lying above the red giants are the supergiants such as Antares (Fig. 1.3), which has a surface temperature only half that of the sun but is 10,000 times more luminous: it is concluded that its radius is 100 times that of the sun. By contrast, the lower left-hand corner of the HR diagram is populated with relatively hot stars of low luminosity which implies that they are very small. These are the white dwarfs such as Sirius B which is only about the size of the earth though its mass is that of the sun: the implied density

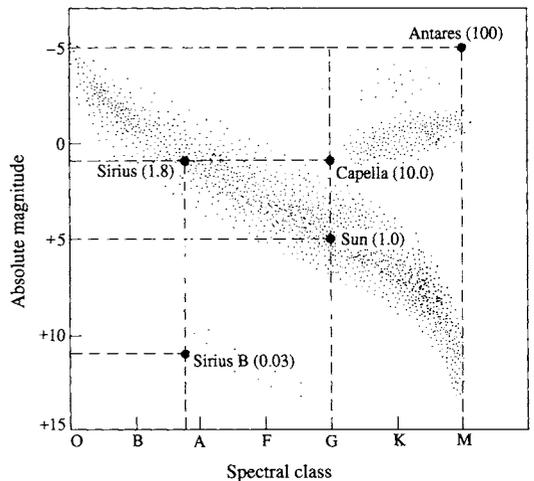


Figure 1.3 The comparison of various stars on the HR diagram. The number in parentheses indicates the approximate diameter of the star (sun = 1.0).

of $\sim 5 \times 10^4 \text{ g cm}^{-3}$ indicates the extraordinarily compact nature of these bodies.

It is now possible to connect this description of stellar types with the discussion of the thermonuclear processes and the synthesis of the elements to be given in the next section. When a protostar begins to form by gravitational contraction from interstellar hydrogen and helium, its temperature rises until the temperature in its core can sustain proton burning (p. 9). A star of approximately the mass of the sun joins the main sequence at this point and spends perhaps 90% of its life there, losing little mass but generating colossal amounts of energy. Subsequent exhaustion of the hydrogen in the core (but not in the outer layers of the star) leads to further contraction to form a helium-burning core which forces much of the remaining hydrogen into a vast tenuous outer envelope — the star has become a red giant since its enormous radiating surface area can no longer be maintained at such a high temperature as previously despite the higher core temperature. Typical red giants have surface temperatures in the range 3500–5500 K; their luminosities are about 10^2 – 10^4 times that of the sun and diameters about 10–100 times that of the sun. Carbon burning (p. 10) can follow in older red giants followed by the α -process (p. 11) during its final demise to white dwarf status.

Many stars are in fact partners in a binary system of two stars revolving around each other. If, as frequently occurs, the two stars have different masses, the more massive one will evolve faster and reach the white-dwarf stage before its partner. Then, as the second star expands to become a red giant its extended atmosphere encompasses the neighbouring white dwarf and induces instabilities which result in an outburst of energy and transfer of matter to the more massive partner. During this process the luminosity of the white dwarf increases perhaps ten-thousandfold and the event is witnessed as a nova (since the preceding binary was previously invisible to the naked eye).

As we shall see in the description of the e-process and the γ -process (p. 12), even more spectacular instabilities can develop in larger

main sequence stars. If the initial mass is greater than about 3.5 solar masses, current theories suggest that gravitational collapse may be so catastrophic that the system implodes beyond nuclear densities to become a black hole. For main sequence stars in the mass range 1.4–3.5 M_{\odot} , implosion probably halts at nuclear densities to give a rapidly rotating neutron star (density $\sim 10^{14} \text{ g cm}^{-3}$) which may be observable as a pulsar emitting electromagnetic radiation over a wide range of frequencies in pulses at intervals of a fraction of a second. During this process of star implosion the sudden arrest of the collapsing core at nuclear densities yields an enormous temperature ($\sim 10^{12} \text{ K}$) and high pressure which produces an outward-moving shock wave. This strikes the star's outer envelope with resulting rapid compression, a dramatic rise in temperature, the onset of many new nuclear reactions, and explosive ejection of a significant fraction of the star's mass. The overall result is a supernova up to 10^8 times as bright as the original star. At this point a single supernova is comparable in brightness to the whole of the rest of the galaxy in which it is formed, after which the brightness decays exponentially, often with a half-life of about two months. Supernovae, novae, and unstable variables from dying red giants are thus all candidates for the synthesis of heavier elements and their ejection into interstellar regions for subsequent processing in later generations of condensing main sequence stars such as the sun. It should be stressed, however, that these various theories of the origin of the chemical elements are all very recent and the detailed processes are by no means all fully understood. Since this is at present a very active area of research, some of the conclusions given in this chapter are correspondingly tentative, and will undoubtedly be modified and refined in the light of future experimental and theoretical studies. With this caveat we now turn to a more detailed description of the individual nuclear processes thought to be involved in the synthesis of the elements.

1.5 Synthesis of the Elements⁽⁵⁻⁹⁾

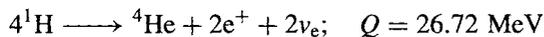
The following types of nuclear reactions have been proposed to account for the various types of stars and the observed abundances of the elements:

- (i) Exothermic processes in stellar interiors: these include (successively) hydrogen burning, helium burning, carbon burning, the α -process, and the equilibrium or e-process.
- (ii) Neutron capture processes: these include the s-process (slow neutron capture) and the r-process (rapid neutron capture).
- (iii) Miscellaneous processes: these include the p-process (proton capture) and spallation within the stars, and the x-process which involves spallation (p. 14) by galactic cosmic rays in interstellar regions.

1.5.1 Hydrogen burning

When the temperature of a contracting mass of hydrogen and helium atoms reaches about 10^7 K, a sequence of thermonuclear reactions is possible of which the most important are as shown in Table 1.2.

The overall reaction thus converts 4 protons into 1 helium nucleus plus 2 positrons and 2 neutrinos:



⁵ D. N. SCHRAMM and R. WAGONER, Element production in the early universe, *A. Rev. Nucl. Sci.* **27**, 37-74 (1977).

⁶ E. M. BURBIDGE, G. R. BURBIDGE, W. A. FOWLER and F. HOYLE, Synthesis of the elements in stars, *Rev. Mod. Phys.* **29**, 547-650 (1957). This is the definitive review on which all later work has been based.

⁷ L. H. ALLER, *The Abundance of the Elements*, Interscience, New York, 1961, 283 pp.

^{7a} L. H. AHRENS (ed.), *Origin and Distribution of the Elements*, Pergamon Press, Oxford, 1979, 920 pp.

⁸ R. J. TAYLOR, *The Origin of Chemical Elements*, Wykeham Publications, London, 1972, 169 pp.

⁹ W. A. FOWLER, The quest for the origin of the elements (Nobel Lecture), *Angew. Chem. Int. Edn. Engl.* **23**, 645-71 (1984).

Table 1.2 Thermonuclear consumption of protons

Reaction	Energy evolved, Q	Reaction time ^(a)
$^1\text{H} + ^1\text{H} \rightarrow ^2\text{H} + e^+ + \nu_e$	1.44 MeV	1.4×10^{10} y
$^2\text{H} + ^1\text{H} \rightarrow ^3\text{He} + \gamma$	5.49 MeV	0.6 s
$^3\text{He} + ^3\text{He} \rightarrow ^4\text{He} + 2^1\text{H}$	12.86 MeV	10^6 y

(a) The reaction time quoted is the time required for half the constituents involved to undergo reaction — this is sensitively dependent on both temperature and density; the figures given are appropriate for the centre of the sun, i.e. 1.3×10^7 K and 200 g cm^{-3} .

1 MeV per atom $\equiv 96.485 \times 10^6 \text{ kJ mol}^{-1}$.

Making allowance for the energy carried away by the 2 neutrinos ($2 \times 0.25 \text{ MeV}$) this leaves a total of 26.22 MeV for radiation, i.e. 4.20 pJ per atom of helium or $2.53 \times 10^9 \text{ kJ mol}^{-1}$. This vast release of energy arises mainly from the difference between the rest mass of the helium-4 nucleus and the 4 protons from which it was formed (0.028 atomic mass units). There are several other peripheral reactions between the protons, deuterons and ^3He nuclei, but these need not detain us. It should be noted, however, that only 0.7% of the mass is lost during this transformation, so that the star remains approximately constant in mass. For example, in the sun during each second, some 600×10^6 tonnes ($600 \times 10^9 \text{ kg}$) of hydrogen are processed into 595.5×10^6 tonnes of helium, the remaining 4.5×10^6 tonnes of matter being transformed into energy. This energy is released deep in the sun's interior as high-energy γ -rays which interact with stellar material and are gradually transformed into photons with longer wavelengths; these work their way to the surface taking perhaps 10^6 y to emerge.

In fact, the sun is not a first-generation main-sequence star since spectroscopic evidence shows the presence of many heavier elements thought to be formed in other types of stars and subsequently distributed throughout the galaxy for eventual accretion into later generations of main-sequence stars. In the presence of heavier elements, particularly carbon and nitrogen, a catalytic sequence of nuclear reactions aids the fusion of protons to helium (H. A. Bethe

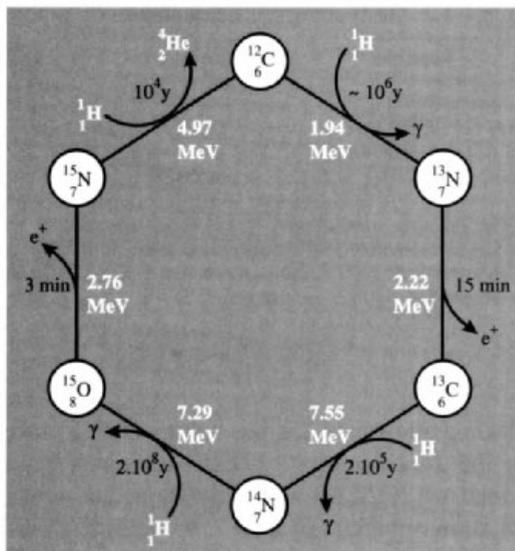


Figure 1.4 Catalytic C–N–O cycle for conversion of ^1H to ^4He . The times quoted are the calculated half-lives for the individual steps at 1.5×10^7 K.

and C. F. von Weizsäcker, 1938) (Fig. 1.4). The overall reaction is precisely as before with the evolution of 26.72 MeV, but the 2 neutrinos now carry away 0.7 and 1.0 MeV respectively, leaving 25.0 MeV (4.01 pJ) per cycle for radiation. The coulombic energy barriers in the C–N–O cycle are some 6–7 times greater than for the direct proton–proton reaction and hence the catalytic cycle does not predominate until about 1.6×10^7 K. In the sun, for example, it is estimated that about 10% of the energy comes from this process and most of the rest comes from the straightforward proton–proton reaction.

When approximately 10% of the hydrogen in a main-sequence star like the sun has been consumed in making helium, the outward thermal pressure of radiation is insufficient to counteract the gravitational attraction and a further stage of contraction ensues. During this process the helium concentrates in a dense central core ($\rho \sim 10^5$ g cm $^{-3}$) and the temperature rises to perhaps 2×10^8 K. This is sufficient to overcome the coulombic potential energy barriers surrounding the helium nuclei, and helium burning (fusion)

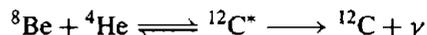
can occur. The hydrogen forms a vast tenuous envelope around this core with the result that the star evolves rapidly from the main sequence to become a red giant (p. 7). It is salutary to note that hydrogen burning in main-sequence stars has so far contributed an amount of helium to the universe which is only about 20% of that which was formed in the few minutes directly following the big bang (p. 2).

1.5.2 Helium burning and carbon burning

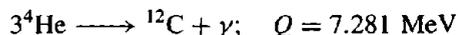
The main nuclear reactions occurring in helium burning are:



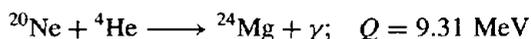
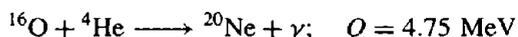
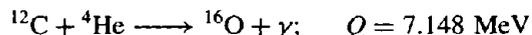
and



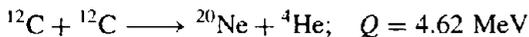
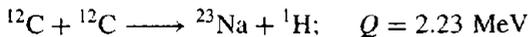
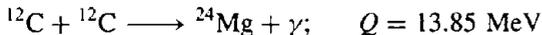
The nucleus ^8Be is unstable to α -particle emission ($t_{1/2} \sim 2 \times 10^{-16}$ s) being 0.094 MeV less stable than its constituent helium nuclei; under the conditions obtaining in the core of a red giant the calculated equilibrium ratio of ^8Be to ^4He is $\sim 10^{-9}$. Though small, this enables the otherwise improbable 3-body collision to occur. It is noteworthy that, from consideration of stellar nucleogenesis, F. Hoyle predicted in 1954 that the nucleus of ^{12}C would have a radioactive excited state $^{12}\text{C}^*$ 7.70 MeV above its ground state, some three years before this activity was observed experimentally at 7.653 MeV. Experiments also indicate that the energy difference $Q(^{12}\text{C}^* - 3^4\text{He})$ is 0.373 MeV, thus leading to the overall reaction energy



Further helium-burning reactions can now follow during which even heavier nuclei are synthesized:



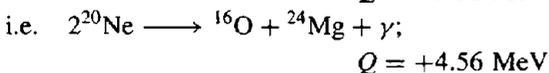
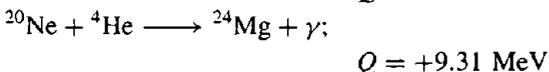
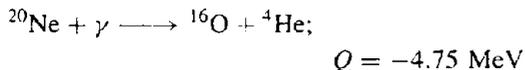
These reactions result in the exhaustion of helium previously produced in the hydrogen-burning process and an inner core of carbon, oxygen and neon develops which eventually undergoes gravitational contraction and heating as before. At a temperature of $\sim 5 \times 10^8$ K carbon burning becomes possible in addition to other processes which must be considered. Thus, ageing red giant stars are now thought to be capable of generating a carbon-rich nuclear reactor core at densities of the order of 10^4 g cm^{-3} . Typical initial reactions would be:



The time scale of such reactions is calculated to be $\sim 10^5$ y at 6×10^8 K and ~ 1 y at 8.5×10^8 K. It will be noticed that hydrogen and helium nuclei are regenerated in these processes and numerous subsequent reactions become possible, generating numerous nuclides in this mass range.

1.5.3 The α -process

The evolution of a star after it leaves the red-giant phase depends to some extent on its mass. If it is not more than about $1.4 M_{\odot}$ it may contract appreciably again and then enter an oscillatory phase of its life before becoming a white dwarf (p. 7). When core contraction following helium and carbon depletion raises the temperature above $\sim 10^9$ K the γ -rays in the stellar assembly become sufficiently energetic to promote the (endothermic) reaction $^{20}\text{Ne}(\gamma, \alpha)^{16}\text{O}$. The α -particle released can penetrate the coulomb barrier of other neon nuclei to form ^{24}Mg in a strongly exothermic reaction:



Some of the released α -particles can also scour out ^{12}C to give more ^{16}O and the ^{24}Mg formed can react further by $^{24}\text{Mg}(\alpha, \gamma)^{28}\text{Si}$. Likewise for ^{32}S , ^{36}Ar and ^{40}Ca . It is this process that is considered to be responsible for building up the decreasing proportion of these so-called α -particle nuclei (Figs. 1.1 and 1.5). The relevant numerical data (including for comparison those for ^{20}Ne which is produced in helium and carbon burning) are as follows:

Nuclide	^{20}Ne	^{24}Mg	^{28}Si	^{32}S	^{36}Ar	^{40}Ca	^{44}Ca	^{48}Ti
Q_r/MeV	(9.31)	10.00	6.94	6.66	7.04	5.28		9.32
Relative abundance (as observed)	(8.4)	0.78	1.00	0.39	0.14	0.052	0.0011	0.0019

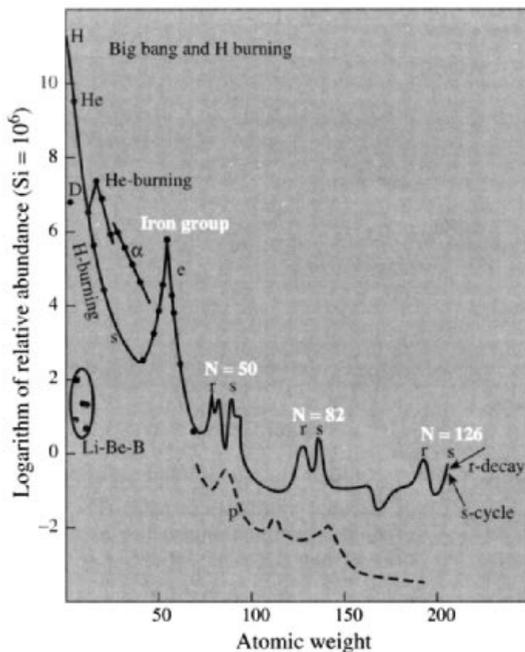


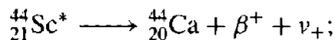
Figure 1.5 Schematic representation of the main features of the curve of cosmic abundances shown in Fig. 1.1, labelled according to the various stellar reactions considered to be responsible for the synthesis of the elements. (After E. M. Burbidge *et al.*⁽⁶⁾.)

In a sense the α -process resembles helium burning but is distinguished from it by the quite

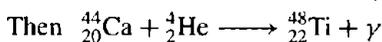
different source of the α -particles consumed. The straightforward α -process stops at ^{40}Ca since $^{44}\text{Ti}^*$ is unstable to electron-capture decay. Hence (and including atomic numbers Z as subscripts for clarity):



$$t_{1/2} \sim 49 \text{ y}$$



$$t_{1/2} \text{ 3.93 h}$$



The total time spent by a star in this α -phase may be $\sim 10^2 - 10^4 \text{ y}$ (Fig. 1.6).

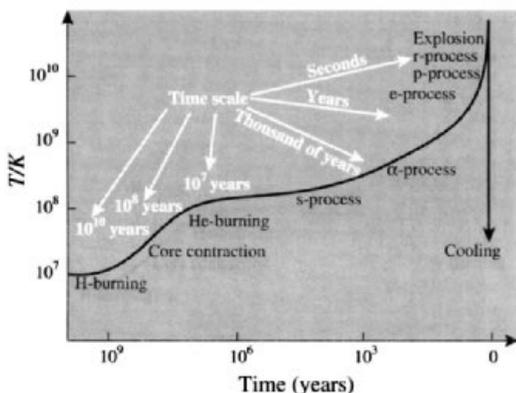


Figure 1.6 The time-scales of the various processes of element synthesis in stars. The curve gives the central temperature as a function of time for a star of about one solar mass. The curve is schematic.⁽⁶⁾

1.5.4 The e-process (equilibrium process)

More massive stars in the upper part of the main-sequence diagram (i.e. stars with masses in the range $1.4 - 3.5 M_{\odot}$) have a somewhat different history to that considered in the preceding sections. We have seen (p. 6) that such stars consume their hydrogen much more rapidly than do smaller stars and hence spend less

time in the main sequence. Helium reactions begin in their interiors long before the hydrogen is exhausted, and in the middle part of their life they may expand only slightly. Eventually they become unstable and explode violently, emitting enormous amounts of material into interstellar space. Such explosions are seen on earth as supernovae, perhaps 10 000 times more luminous than ordinary novae. In the seconds (or minutes) preceding this catastrophic outburst, at temperatures above $\sim 3 \times 10^9 \text{ K}$, many types of nuclear reactions can occur in great profusion, e.g. (γ, α) , (γ, p) , (γ, n) , (α, n) , (p, γ) , (n, γ) , (p, n) , etc. (Fig. 1.6). This enables numerous interconversions to occur with the rapid establishment of a statistical equilibrium between the various nuclei and the free protons and neutrons. This is believed to explain the cosmic abundances of elements from ^{22}Ti to ^{29}Cu . Specifically, since $^{56}_{26}\text{Fe}$ is at the peak of the nuclear binding-energy curve, this element is considerably more abundant than those further removed from the most stable state.

1.5.5 The s- and r-processes (slow and rapid neutron absorption)

Slow neutron capture with emission of γ -rays is thought to be responsible for synthesizing most of the isotopes in the mass range $A = 63 - 209$ and also the majority of non- α -process nuclei in the range $A = 23 - 46$. These processes probably occur in pulsating red giants over a time span of $\sim 10^7 \text{ y}$, and production loops for individual isotopes are typically in the range $10^2 - 10^5 \text{ y}$. Several stellar neutron sources have been proposed, but the most likely candidates are the exothermic reactions $^{13}\text{C}(\alpha, n)^{16}\text{O}$ (2.20 MeV) and $^{21}\text{Ne}(\alpha, n)^{24}\text{Mg}$ (2.58 MeV). In both cases the target nuclei ($A = 4n + 1$) would be produced by a (p, γ) reaction on the more stable $4n$ nucleus followed by positron emission.

Because of the long time scale involved in the s-process, unstable nuclides formed by (n, γ) reactions have time to decay subsequently by β^- decay (electron emission). The crucial factor in determining the relative abundance of elements

formed by this process is thus the neutron capture cross-section of the precursor nuclide. In this way the process provides an ingenious explanation of the local peaks in abundance that occur near $A = 90, 138$ and 208 , since these occur near unusually stable nuclei (neutron “magic numbers” $50, 82$ and 126) which have very low capture cross-sections (Fig. 1.5). Their concentration therefore builds up by resisting further reaction. In this way the relatively high abundances of specific isotopes such as $^{89}_{39}\text{Y}$ and $^{90}_{40}\text{Zr}$, $^{138}_{56}\text{Ba}$ and $^{140}_{58}\text{Ce}$, $^{208}_{82}\text{Pb}$ and $^{209}_{83}\text{Bi}$ can be understood.

In contrast to the more leisureed processes considered in preceding paragraphs, conditions can arise (e.g. at $\sim 10^9$ K in supernovae outbursts) where many neutrons are rapidly added successively to a nucleus before subsequent β^- decay becomes possible. The time scale for the *r*-process is envisaged as ~ 0.01 – 10 s, so that, for example, some 200 neutrons might be added to an iron nucleus in 10 – 100 s. Only when β^- instability of the excessively neutron-rich product nuclei becomes extreme and the cross-section for further neutron absorption diminishes near the “magic numbers”, does a cascade of some 8 – 10 β^- emissions bring the product back into the region of stable isotopes. This gives a convincing interpretation of the local abundance peaks near $A = 80, 130$ and 194 , i.e. some 8 – 10 mass units below the nuclides associated with the *s*-process maxima (Fig. 1.5). It has also been suggested that neutron-rich isotopes of several of the lighter elements might also be the products of an *r*-process, e.g. ^{36}S , ^{46}Ca , ^{48}Ca and perhaps ^{47}Ti , ^{49}Ti and ^{50}Ti . These isotopes, though not as abundant as others of these elements, nevertheless do exist as stable species and cannot be so readily synthesized by other potential routes.

The problem of the existence of the heavy elements must also be considered. The short half-lives of all isotopes of technetium and promethium adequately accounts for their absence on earth. However, no element with atomic number greater than 83 Bi has any stable isotope. Many of these (notably ^{84}Po , ^{85}At , ^{86}Rn , ^{87}Fr , ^{88}Ra , ^{89}Ac and ^{91}Pa) can be

understood on the basis of secular equilibria with radioactive precursors, and their relative concentrations are determined by the various half-lives of the isotopes in the radioactive series which produce them. The problem then devolves on explaining the cosmic presence of thorium and uranium, the longest lived of whose isotopes are ^{232}Th ($t_{1/2} 1.4 \times 10^{10}$ y), ^{238}U ($t_{1/2} 4.5 \times 10^9$ y) and ^{235}U ($t_{1/2} 7.0 \times 10^8$ y). The half-life of thorium is commensurate with the age of the universe ($\sim 1.5 \times 10^{10}$ y) and so causes no difficulty. If all the present terrestrial uranium was produced by an *r*-process in a single supernova event then this occurred 6.6×10^9 y ago (p. 1257). If, as seems more probable, many supernovae contributed to this process, then such events, distributed uniformly in time, must have started $\sim 10^{10}$ y ago. In either case the uranium appears to have been formed long before the formation of the solar system (4.6 – 5.0) $\times 10^9$ y ago. More recent considerations of the formation and decay of ^{232}Th , ^{235}U and ^{238}U suggest that our own galaxy is $(1.2$ – $2.0) \times 10^{10}$ y old.

1.5.6 The *p*-process (proton capture)

Proton capture processes by heavy nuclei have already been briefly mentioned in several of the preceding sections. The (p, γ) reaction can also be invoked to explain the presence of a number of proton-rich isotopes of lower abundance than those of nearby normal and neutron-rich isotopes (Fig. 1.5). Such isotopes would also result from expulsion of a neutron by a γ -ray, i.e. (γ, n) . Such processes may again be associated with supernovae activity on a very short time scale. With the exceptions of ^{113}In and ^{115}Sn , all of the 36 isotopes thought to be produced in this way have even atomic mass numbers; the lightest is $^{74}_{34}\text{Se}$ and the heaviest $^{196}_{80}\text{Hg}$.

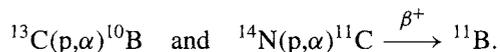
1.5.7 The *x*-process

One of the most obvious features of Figs. 1.1 and 1.5 is the very low cosmic abundance of the stable isotopes of lithium, beryllium and

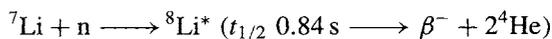
boron.⁽¹⁰⁾ Paradoxically, the problem is not to explain why these abundances are so low but why these elements exist at all since their isotopes are bypassed by the normal chain of thermonuclear reactions described on the preceding pages. Again, deuterium and ^3He , though part of the hydrogen-burning process, are also virtually completely consumed by it, so that their existence in the universe, even at relatively low abundances, is very surprising. Moreover, even if these various isotopes were produced in stars, they would not survive the intense internal heat since their bonding energies imply that deuterium would be destroyed above 0.5×10^6 K, Li above 2×10^6 K, Be above 3.5×10^6 and B above 5×10^6 . Deuterium and ^3He are absent from the spectra of almost all stars and are now generally thought to have been formed by nucleosynthesis during the last few seconds of the original big bang; their main agent of destruction is stellar processing.

It now seems likely that the 5 stable isotopes ^6Li , ^7Li , ^9Be , ^{10}B and ^{11}B are formed predominantly by spallation reactions (i.e. fragmentation) effected by galactic cosmic-ray bombardment (the x-process). Cosmic rays consist of a wide variety of atomic particles moving through the galaxy at relativistic velocities. Nuclei ranging from hydrogen to uranium have been detected in cosmic rays though ^1H and ^4He are by far the most abundant components [^1H : 500; ^4He : 40; all particles with atomic numbers from 3 to 9: 5; all particles with $Z \geq 10$: ~ 1]. However, there is a striking deviation from stellar abundances since Li, Be and B are vastly over abundant as are Sc, Ti, V and Cr (immediately preceding the abundance peak near iron). The simplest interpretation of these facts is that the (heavier) particles comprising cosmic rays, travelling as they do great distances in the galaxy, occasionally collide with atoms of the interstellar gas (predominantly ^1H and ^4He) and thereby fragment. This fragmentation, or spallation as it

is called, produces lighter nuclei from heavier ones. Conversely, high-speed ^4He particles may occasionally collide with interstellar iron-group elements and other heavy nuclei, thus inducing spallation and forming Li, Be and B (and possibly even some ^2H and ^3He), on the one hand, and elements in the range Sc–Cr, on the other. As we have seen, the lighter transition elements are also formed in various stellar processes, but the presence of elements in the mass range 6–12 suggest the need for a low-temperature low-density extra-stellar process. In addition to spallation, interstellar (p, α) reactions in the wake of supernova shock waves may contribute to the synthesis of boron isotopes:



A further intriguing possibility has recently been mooted.⁽¹¹⁾ If the universe were not completely isotropic and uniform in density during the first few minutes after the big bang, then the high-density regions would have a greater concentration of protons than expected and the low-density regions would have more neutrons; this is because the diffusion of protons from high to low density regions would be inhibited by the presence of oppositely charged electrons whereas the electrically neutral neutrons can diffuse more readily. In the neutron-abundant lower-density regions certain neutron-rich species can then be synthesized. For example, in the homogeneous big bang, most of the ^7Li formed is rapidly destroyed by proton bombardment ($^7\text{Li} + p \rightarrow ^2\text{He}$) but in a neutron-rich region the radioactive isotope $^8\text{Li}^*$ can be formed:



If, before it decays, $^8\text{Li}^*$ is struck by a prevalent ^4He nucleus then ^{11}B can be formed ($^8\text{Li}^* + ^4\text{He} \rightarrow ^{11}\text{B} + n$) and this will survive longer than in a proton-rich environment ($^{11}\text{B} + p \rightarrow ^3\text{He}$). Other neutron-rich species could also be synthesized and survive in greater numbers than would

¹⁰ H. REEVES, Origin of the light elements, *A. Rev. Astron. Astrophys.* **12**, 437–69 (1974).

¹¹ K. CROSSWELL, *New Scientist*, 9 Nov. 1991, 42–8.

be possible with higher concentrations of protons, e.g.:



The relative abundances of the various isotopes of the light elements Li, Be and B therefore depend to some extent on which detailed model of the big bang is adopted, and experimentally determined abundances may in time permit conclusions to be drawn as to the relative importance of these processes as compared to x-process spallation reactions.

In overall summary, using a variety of nuclear syntheses it is now possible to account for the presence of the 270 known stable isotopes of the elements up to ${}^{209}\text{Bi}$ and to understand, at least in broad outline, their relative concentrations in the universe. The tremendous number of hypothetically possible internuclear conversions and reactions makes detailed computation extremely difficult. Energy changes are readily calculated from the known relative atomic masses of the various nuclides, but the cross-sections (probabilities) of many of the reactions are unknown and this prevents precise calculation of reaction rates and equilibrium concentrations in the extreme conditions occurring even in stable stars. Conditions and reactions occurring during supernova outbursts are even more difficult to define precisely. However, it is clear that substantial progress has been made in the last few decades in interpreting the bewildering variety of isotopic abundances which comprise the elements used by chemists. The approximate constancy of the isotopic composition of the individual elements is a fortunate result of the quasi-steady-state conditions obtaining in the universe during the time required to form the solar system. It is tempting to speculate whether chemistry could ever have emerged as a quantitative science if the elements had had widely varying isotopic composition, since gravimetric analysis would then have been impossible and the great developments of the nineteenth century could hardly have occurred. Equally, it should no longer cause surprise that the atomic weights of the

elements are not necessarily always “constants of nature”, and variations are to be expected, particularly among the lighter elements, which can have appreciable effects on physicochemical measurements and quantitative analysis.

1.6 Atomic Weights⁽¹²⁾

The concept of “atomic weight” or “mean relative atomic mass” is fundamental to the development of chemistry. Dalton originally supposed that all atoms of a given element had the same unalterable weight but, after the discovery of isotopes earlier this century, this property was transferred to them. Today the possibility of variable isotopic composition of an element (whether natural or artificially induced) precludes the possibility of defining *the* atomic weight of most elements, and the tendency nowadays is to define *an* atomic weight of an element as “the ratio of the average mass per atom of an element to one-twelfth of the mass of an atom of ${}^{12}\text{C}$ ”. It is important to stress that atomic weights (mean relative atomic masses) of the elements are dimensionless numbers (ratios) and therefore have no units.

Because of their central importance in chemistry, atomic weights have been continually refined and improved since the first tabulations by Dalton (1803–5). By 1808 Dalton had included 20 elements in his list and these results were substantially extended and improved by Berzelius during the following decades. An illustration of the dramatic and continuing improvement in accuracy and precision during the past 100 y is given in Table 1.3. In 1874 no atomic weight was quoted to better than one part in 200, but by 1903 33 elements had values quoted to one part in 10^3 and 2 of these (silver and

¹² N. N. GREENWOOD, Atomic weights, Ch. 8 in Part I, Vol. 1, Section C, of Kolthoff and Elving's *Treatise on Analytical Chemistry*, pp. 453–78, Interscience, New York, 1978. This gives a fuller account of the history and techniques of atomic weight determinations and their significance, and incorporates a full bibliographical list of Reports on Atomic Weights.

iodine) were quoted to 1 in 10^4 . Today the majority of values are known to 1 in 10^4 and 26 elements have an accuracy exceeding 1 in 10^6 . This improvement was first due to improved chemical methods, particularly between 1900 and 1935 when increasing use of fused silica ware and electric furnaces reduced the possibility of contamination. More recently the use of mass spectrometry has effected a further improvement in precision. Mass spectrometric data were first used in a confirmatory role in the 1935 table of atomic weights, and by 1938 mass spectrometric values were preferred to chemical determinations for hydrogen and osmium and to gas-density values for helium. In 1959 the atomic weight values of over 50 elements were still based on classical chemical methods, but by 1973 this number had dwindled to 9 (Ti, Ge, Se, Mo, Sn, Sb, Te, Hg and Tl) or to 10 if the coulometric determination for Zn is counted as chemical. The values for a further 8 elements were based on a judicious blend of chemical and mass-spectrometric data, but the values quoted for

all other elements were based entirely on mass-spectrometric data.

Accurate atomic weight values do not automatically follow from precise measurements of relative atomic masses, however, since the relative abundance of the various isotopes must also be determined. That this can be a limiting factor is readily seen from Table 1.3: the value for praseodymium (which has only 1 stable naturally occurring isotope) has two more significant figures than the value for the neighbouring element cerium which has 4 such isotopes. In the twelve years since the first edition of this book was published the atomic weight values of no fewer than 55 elements have been improved, sometimes spectacularly, e.g. Ni from 58.69(1) to 58.6934(2).

1.6.1 Uncertainty in atomic weights

Numerical values for the atomic weights of the elements are now reviewed every 2 y by the Commission on Atomic Weights and Isotopic

Table 1.3 Evolution of atomic weight values for selected elements^(a); (the dates selected were chosen for the reasons given below)

Element	1873-5	1903	1925	1959	1961	1997	
H	1	1.008	1.008	1.0080	1.00797	1.00794(7)	gmr
C	12	12.00	12.000	12.011 15	12.011 15	12.0107(8)	g r
O	16	16.00	16.000	16	15.9994	15.9994(3)	g r
P	31	31.0	31.027	30.975	30.9738	30.973 761(2)	
Ti	50	48.1	48.1	47.90	47.90	47.867(1)	
Zn	65	65.4	65.38	65.38	65.37	65.39(2)	
Se	79	79.2	79.2	78.96	78.96	78.96(3)	
Ag	108	107.93	107.880	107.880	107.870	107.8682(2)	g
I	127	126.85	126.932	126.91	126.9044	126.90447(3)	
Ce	92	140.0	140.25	140.13	140.12	140.116(1)	g
Pr	—	140.5	140.92	140.92	140.907	140.907 65(2)	
Re	—	—	188.7 ^(b)	186.22	186.22	186.207(1)	
Hg	200	200.0	200.61	200.61	200.59	200.59(2)	

^(a)The annotations g, m and r appended to some values in the final column have the same meanings as those in the definitive table (facing inside front cover). The numbers in parentheses are the uncertainties in the last digit of the quoted value.

^(b)The value for rhenium was first listed in 1929.

Note on dates:

1874 Foundation of the American Chemical Society (64 elements listed).

1903 First international table of atomic weights (78 elements listed).

1925 Major review of table (83 elements listed).

1959 Last table to be based on oxygen = 16 (83 elements listed).

1961 Complete reassessment of data and revision to $^{12}\text{C} = 12$ (83 elements).

1997 Latest available IUPAC values (84 + 28 elements listed).

Abundances of IUPAC (the International Union of Pure and Applied Chemistry). Their most recent recommendations⁽¹³⁾ are tabulated on the inside front fly sheet. From this it is clear that there is still a wide variation in the reliability of the data. The most accurately quoted value is that for fluorine which is known to better than 1 part in 38 million; the least accurate is for boron (1 part in 1500, i.e. 7 parts in 10^4). Apart from boron all values are reliable to better than 5 parts in 10^4 and the majority are reliable to better than 1 part in 10^4 . For some elements (such as boron) the rather large uncertainty arises not because of experimental error, since the use of mass-spectrometric measurements has yielded results of very high precision, but because the natural variation in the relative abundance of the 2 isotopes ^{10}B and ^{11}B results in a range of values of at least ± 0.003 about the quoted value of 10.811. By contrast, there is no known variation in isotopic abundances for elements such as selenium and osmium, but calibrated mass-spectrometric data are not available, and the existence of 6 and 7 stable isotopes respectively for these elements makes high precision difficult to obtain: they are thus prime candidates for improvement.

Atomic weights are known most accurately for elements which have only 1 stable isotope; the relative atomic mass of this isotope can be determined to at least 1 ppm and there is no possibility of variability in nature. There are 20 such elements: Be, F, Na, Al, P, Sc, Mn, Co, As, Y, Nb, Rh, I, Cs, Pr, Tb, Ho, Tm, Au and Bi. (Note that all of these elements except beryllium have odd atomic numbers — why?)

Elements with 1 predominant isotope can also, potentially, permit very precise atomic weight determinations since variations in isotopic composition or errors in its determination have a correspondingly small effect on the mass-spectrometrically determined value of the atomic weight. Nine elements have 1 isotope that is more than 99% abundant (H, He, N, O, Ar, V, La, Ta

and U) and carbon also approaches this category (^{13}C 1.11% abundant).

Known variations in the isotopic composition of normal terrestrial material prevent a more accurate atomic weight being given for 13 elements and these carry the footnote r in the Table of Atomic Weights. For each of these elements (H, He, Li, B, C, N, O, Si, S, Ar, Cu, Sr and Pb) the accuracy attainable in an atomic weight determination on a given sample is greater than that implied by the recommended value since this must be applicable to any sample and so must embrace all known variations in isotopic composition from commercial terrestrial sources. For example, for hydrogen the present attainable accuracy of calibrated mass-spectrometric atomic weight determinations is about ± 1 in the sixth significant figure, but the recommended value of 1.00794(± 7) is so given because of the natural terrestrial variation in the deuterium content. The most likely value relevant to laboratory chemicals (e.g. H_2O) is 1.00797, but it should be noted that hydrogen gas used in laboratories is often inadvertently depleted during its preparation by electrolysis, and for such samples the atomic weight is close to 1.00790. By contrast, intentional fractionation to yield heavy water (thousands of tonnes annually) or deuterated chemicals implies an atomic weight approaching 2.014, and great care should be taken to avoid contamination of "normal" samples when working with or disposing of such enriched materials.

Fascinating stories of natural variability could be told for each of the 13 elements having the footnote r and, indeed, determinations of such variations in isotopic composition are now an essential tool in unravelling the geochemical history of various ore bodies. For example, the atomic weight of sulfur obtained from virgin Texas sulfur is detectably different from that obtained from sulfate ores, and an overall range approaching ± 0.01 is found for terrestrial samples; this limits the value quoted to 32.066(6) though the accuracy of atomic weight determinations on individual samples is ± 0.00015 . Boron is even more adversely

¹³ IUPAC Inorganic Chemistry Division, Atomic Weights of the Elements 1995, *Pure Appl. Chem.* **68**, 2339–59 (1996).

affected, as previously noted, and the actual atomic weight can vary from 10.809 to 10.812 depending on whether the mineral source is Turkey or the USA.

Even more disconcerting are the substantial deviations in atomic weight that can occur in commercially available material because of inadvertent or undisclosed changes in isotopic composition (footnote m in the Table of Atomic Weights). This situation at present obtains for 8 elements (H, Li, B, Ne, Cl, Kr, Xe and U) and may well also soon affect others (such as C, N and O). The separated or partially enriched isotopes of Li, B and U are now extensively used in nuclear reactor technology and weaponry, and the unwanted residues, depleted in the desired isotopes, are sometimes dumped on the market and sold as "normal" material. Thus lithium salts may unsuspectingly be purchased which have been severely depleted in ${}^6\text{Li}$ (natural abundance 7.5%), and a major commercial supplier has marketed lithium containing as little as 3.75% of this isotope, thereby inducing an atomic weight change of 0.53%. For this reason practically all lithium compounds now obtainable in the USA are suspect and quantitative data obtained on them are potentially unreliable. Again, the practice of "milking" fission-product rare gases from reactor fuels and marketing these materials, produces samples with anomalous isotopic compositions. The effect, particularly on physicochemical computations, can be serious and, whilst not wishing to strike an alarmist note, the possibility of such deviations must continually be borne in mind for elements carrying the footnote m in the Table of Atomic Weights.

The related problem arising from radioactive elements is considered in the next section.

1.6.2 The problem of radioactive elements

Elements with radioactive nuclides amongst their naturally occurring isotopes have a built-in time variation of the relative concentration of their isotopes and hence a continually

varying atomic weight. Whether this variation is chemically significant depends on the half-life of the transition and the relative abundance of the various isotopes. Similarly, the actual concentration of stable isotopes of several elements (e.g. Ar, Ca and Pb) may be influenced by association of those elements with radioactive precursors (i.e. ${}^{40}\text{K}$, ${}^{238}\text{U}$, etc.) which generate potentially variable amounts of the stable isotopes concerned. Again, some elements (such as technetium, promethium and the transuranium elements) are synthesized by nuclear reactions which produce a single isotope of the element. The "atomic weight" therefore depends on which particular isotope is being synthesized, and the concept of a "normal" atomic weight is irrelevant. For example, cyclotron production of technetium yields ${}^{97}\text{Tc}$ ($t_{1/2}$ 2.6×10^6 y) with an atomic weight of 96.9064, whereas fission product technetium is ${}^{99}\text{Tc}$ ($t_{1/2}$ 2.11×10^5 y), atomic weight 98.9063, and the isotope of longest half-life is ${}^{98}\text{Tc}$ ($t_{1/2}$ 4.2×10^6 y), atomic weight 97.9072.

At least 19 elements not usually considered to be radioactive do in fact have naturally occurring unstable isotopes. The minute traces of naturally occurring ${}^3\text{H}$ ($t_{1/2}$ 12.33 y) and ${}^{14}\text{C}$ ($t_{1/2}$ 5730 y) have no influence on the atomic weights of these elements though, of course, they are of crucial importance in other areas of study. The radioactivity of ${}^{40}\text{K}$ ($t_{1/2}$ 1.28×10^9 y) influences the atomic weights of its daughter elements argon (by electron capture) and calcium (by β^- emission) but fortunately does not significantly affect the atomic weight of potassium itself because of the low absolute abundance of this particular isotope (0.0117%). The half-lives of the radioactive isotopes of the 16 other "stable" elements are all greater than 10^{10} y and so normally have little influence on the atomic weight of these elements even when, as in the case of ${}^{115}\text{In}$ ($t_{1/2}$ 4.41×10^{14} y, 95.7% abundant) and ${}^{187}\text{Re}$ ($t_{1/2}$ 4.35×10^{10} y, 62.6% abundant), they are the most abundant isotopes. Note, however, that on a geological time scale it has been possible to build up significant concentrations of ${}^{187}\text{Os}$ in rhenium-containing

ores (by β^- decay of ^{187}Re), thereby generating samples of osmium with an anomalous atomic weight nearer to 187 than to the published value of 190.23(3). Lead was the first element known to be subject to such isotopic disturbances and, indeed, the discovery and interpretation of the significance of isotopes was itself hastened by the reluctant conclusion of T. W. Richards at the turn of the century that a group of lead samples of differing geological origins were identical chemically but differed in atomic weight — the possible variation is now known to span almost the complete range from 204 to 208. Such elements, for which geological specimens are known in which the element has an anomalous isotopic composition, are given the footnote g in the Table of Atomic Weights. In addition to Ar, Ca, Os and Pb just discussed, such variability affects at least 38 other elements, including Sr

(resulting from the β^- decay of ^{87}Rb), Ra, Th and U. A spectacular example, which affects virtually every element in the central third of the periodic table, has recently come to light with the discovery of prehistoric natural nuclear reactors at Oklo in Africa (see p. 1257). Fortunately this mine is a source of uranium ore only and so will not affect commercially available samples of the other elements involved.

In summary, as a consequence of the factors considered in this and the preceding section, the atomic weights of only the 20 mononuclidic elements can be regarded as “constants of nature”. For all other elements variability in atomic weight is potentially possible and in several instances is known to occur to an extent which affects the reliability of quantitative results of even modest precision.