Nuclear Binding Energy, Fission and Fusion: Obviating a 'Thermodynamic Ponzi Scheme'. A Historical Perspective

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ABSTRACT

It is argued that the scale of atomic masses rests far too heavily on two possibly dubious pieces of evidence. These are the nineteenth-century determination of the atomic weight of hydrogen, and early mass spectrographic work on the determination of atomic masses. The determination of the atomic weight of hydrogen is possibly prone to overestimation because of adventitious enrichment in deuterium during the experimental procedure. The mass spectrographic work is likely to be susceptible to both systemic and theoretical errors deriving from the assumptions employed; it is also possibly enmeshed in the confusion between the (then prevailing) chemical and physical scales of atomic weight. All these ambiguities may well have led to a dubious confirmation of the atomic mass of hydrogen. The idea of the 'mass defect', deriving from this work, formed a corner-stone of the subsequently developed theory of the structure of the atomic nucleus. A particular problem with the mass-defect idea is that, by mass-energy equivalence, heavier atoms would be less stable than lighter ones. (Thus, the mass defect may well be an artefact deriving from the inherent inaccuracies of early mass-spectrographic studies.) All this has apparently led to a dubious theory of nuclear structure. Thus, the balance between the electrostatic and strong forces should favour the latter with increasing atomic mass – contrary to current theory, which apparently neglects to take account of the predominance of nearest-neighbour interactions between nucleons. Consequently, the origins of nuclear energy, whether by fission or fusion, seem unclear. Taken as a whole, these arguments indicate a fundamental reappraisal of current theoretical ideas: It would appear that mass-energy equivalence may be involved more fundamentally and insidiously in the generation of nuclear energy; it is also possible that the radionuclides arise by the malformation of nuclei during their creation, a consequence of their mass and size.

INTRODUCTION

The Atomic Idea

Dalton's resurrection of the atomic hypothesis (1803), the philosophic roots of which lay in classical Greece, symbolised the spirit of the Enlightenment. Dalton's ideas were thus a key element in a general efflorescence of intellectual culture, which indeed laid the foundations of modern experimental and theoretical science.[1]

One of the key concepts that flowed from the atomic hypothesis was that of atomic weight. In formulating the relative scale of atomic weights, Dalton was influenced to varying extents by related – and often contemporaneous – developments in physico-chemical science. In particular, the ideal gas law (Eqn. 1, the symbols have the usual meaning) and Avogadro's hypothesis were the critical enabling concepts that led to the modern idea of atomic weight. The roots of Eqn. 1, in fact, lie in the kinetic theory of gases, and n may be considered as representing the number of gas particles (atoms or diatomic molecules).

$$PV = nRT \tag{1}$$

Thus, equal volumes of any two gases at the same pressure and temperature would contain the same numbers of particles. (Avogadro's Hypothesis; note that the gas constant R cancels out in the ratio of volumes.) The ratio of the weights of two gases under these conditions would provide the relative weight of a single particle. If one of the gases is taken as an arbitrary standard, a scale of atomic weights can be set up. (The number of atoms in the gas molecule can be estimated from the valence of the element: *vide infra.* This is only a broad outline of the approach, the practical details being available in standard texts on physical chemistry.)

Originally, Dalton chose hydrogen as the standard gas, as it is the lightest element and simplified calculation of the atomic weights of other elements. Thus, with the atomic weight of hydrogen assigned as 1, a scale of atomic weights was set up. Later (1860's) it was found more convenient to employ oxygen as a standard, particularly as it formed compounds more readily (than hydrogen) with almost all elements. This enabled the determination of the atomic weights of the solid elements, along with knowledge of the valence of the element (indicated by the Law of Equivalents, 1792). The original atomic weight of oxygen (16 on the hydrogen scale), however, was retained for convenience. The oxygen standard then held sway for the next hundred years.

The early decades of the 20th century saw momentous developments in the theory of atomic structure, largely aided by brilliant experimental work. Earlier work on the nature of electrical discharges in gases was extended to a study of external electrical and magnetic fields in cathode ray tubes. Photographic capture of the resultant subatomic particles at the receiving end in the tubes, allowed their trajectories and (ultimately) mass/charge (m/e) values to be determined. These developments heralded the arrival of the first mass spectrographs in the 1920's. Clearly, no praise is too high for the inventive genius of the brilliant pioneers of this era.

The determination of atomic masses with the mass spectrograph was now possible, and led to the discovery of isotopes. The discovery of the neutron (1932) provided the necessary insight into the structure of the atomic nucleus, and explained the existence of isotopes. Thus, a picture of the atom – generally accepted to this day – emerged, in which a central nucleus consisting of protons and neutrons was bounded by orbiting electrons. Whilst the number of negatively charged electrons perforce equalled the number of positively charged protons, the number of charge-neutral neutrons varied, not just from element to element, but also within an element.

Thus, an element was characterised by a fixed number of protons (and electrons), which was signified by its atomic number; the number of neutrons, then, characterised an isotope of the element. Hydrogen, exceptionally, possessed no neutron, being composed of a proton and an electron. (Deuterium and tritium, isotopes of hydrogen with 1 and 2 neutrons respectively, were discovered later.) All other elements possessed both protons and neutrons in the nucleus, with the ratio of these two ‘nucleons’ increasing with atomic weight in favour of neutrons.

An important development was the realisation that the atomic weight of an element was not a whole number, which is a consequence of the existence of isotopes. Thus, the atomic weight was an average of the ‘atomic weights’ of all the isotopes of the element, weighted for their relative occurrence (‘natural abundance’). (This was a blow to the 1815 ‘Prout’s Law’ which required integral atomic weights, apparently relative to the archetypal hydrogen atom. Note that the atomic weight need not even be a constant, because of variations in the natural abundances of the isotopes with location, terrestrial or not!) The ‘atomic weight’ of an isotope (relative to oxygen as 16) was now designated as its ‘atomic mass’; closely related to this was the ‘mass number’, equal to the total nucleon count.

It is opportune to take stock of four key conceptual signposts: Atomic number (number of protons in the nucleus); atomic mass (mass of an isotope relative to the oxygen standard); atomic weight (average of all the isotopic atomic masses of an element, weighted for natural abundance); and mass number (total number of protons and neutrons in the nucleus). The mass number (upper left-hand) and the atomic number (lower left-hand) are added to the chemical symbol of an element as designations. (The latter is generally not shown, as it is a constant for an element and hence superfluous in terms of identification.)

Current usage employs several closely related definitions, *viz.* relative atomic mass (synonymous with atomic weight), relative isotopic mass, etc. These are now related to ^{12}C as the standard. However, the above definitions are not only simpler but also accord with the historical evolution of the relevant ideas (as is being sketched out herein), so have been retained herein.

The near concordance between the atomic mass of an isotope and its mass number is particularly noteworthy. This essentially arises because the atomic masses of both the proton and the neutron are close to 1, and also because the electrons possess negligible mass. (Thus, the atomic mass is practically identical to the nuclear mass.)

However, although it is entirely to be expected that the atomic weight would not be a whole number (barring coincidence), the origin of the non-integral masses of the proton and the neutron are apparently complex and debatable. In fact, they gave rise to the idea of the 'mass defect', of fundamental importance in the current theory of the atomic nucleus, and key to the current theory of nuclear energy, as discussed below.

DISCUSSION

Atomic Weights and Masses

Clearly, the discovery of isotopes and the determination of their atomic masses would have been practically impossible without the mass spectrograph. However, intriguing questions remain about the manner in which the atomic masses were assigned their particular numerical values, the sequence of events being particularly interesting and remarkable.

The initial assignments (~ 1925) were apparently made with the availability of the first mass spectrographs of enhanced sensitivity (1 in 10^4). Thus, hydrogen was assigned an atomic mass of 1.00778: curiously, practically identical to the then known classical atomic weight value (1.008). This, in fact, was viewed as corroborating the mass spectrographic value.

Furthermore, the mass spectrographs of the period, despite their sensitivity, apparently failed to detect deuterium (^2H), the heavier isotope of hydrogen. The existence of deuterium, however, was suspected (based on the non-integral atomic weight of hydrogen), and was proven ultimately (1932).

In fact, not only was this a few years after the above assignment of the atomic mass (1.00778), but also before the isotopes of oxygen itself were discovered (1929). This is particularly noteworthy because the classical chemical scale of atomic weights took the atomic weight of naturally occurring oxygen as 16 (a whole number), *i.e.* without taking cognisance of the existence of ^{18}O. The new physical scale based on mass-spectrographic determination, apparently also took ^{16}O as the standard (again, apparently, ^{18}O was not detected).

Thus, the chemical scale, although applying only to atomic weights, was prone to the variation in the natural abundance of the oxygen isotopes; this, of course, would be in addition to the variation in the isotopic natural abundances of the element in question. The physical scale, essentially applying to the individual isotopes of an element, was free of these inaccuracies. However, the averaged atomic weights obtained from the physical scale would not accurately match the values of the chemical scale (for the aforementioned variation in defining the oxygen standard).

All this, of course, is hindsight! At the time of the above assignments, the chemical and physical scales, apparently, would have been considered equal as far as the oxygen standard was concerned. Was this, then, the reason for ‘assigning’ the atomic mass of ^{1}H a value practically identical to its chemical atomic weight?

In fact, there are, in principle, two ways in which the atomic mass can be assigned in a mass spectrograph. In one, essentially, the m/e ratio of each isotope can be calculated, and converted to the mass by assuming the charge. Alternatively, an assignment can be made on the basis of ‘prior knowledge’ against a standard, *e.g.*, in the above case, assigning a value for ^{1}H (1.00778) against ^{16}O (16). The latter method would align the then evolving physical scale with the established chemical scale.

Interestingly, a trend in the listing of atomic weights offers an important clue in this regard. The aforementioned assignment of the atomic mass of hydrogen as 1.00778 implies that all atomic masses less than that of ^{16}O ('upstream') would be overestimated, whereas all those greater than that of ^{16}O ('downstream') would be underestimated, relative to the respective mass numbers. This is because the initial assignment for ^{1}H, an apparent overestimation, establishes a linear scale in terms of distance from ^{16}O.

This distance (or length) was the basis for defining the length representing unit atomic mass. Thus, the initial assignment implied that unit length > unit atomic mass. In other words, the length between ^{1}H and ^{16}O did not represent the mass number difference (15) but the atomic mass difference (16 – 1.00778 = 14.99222): Unit length now represented (14.99222/15) = 0.9994813 mass unit. Note that this 'accumulates', so the 'offset' depends on the particular atom.

Based on this representation of atomic mass in terms of unit length, elements 'downstream' from ^{16}O would suffer an underestimation of their atomic masses relative to their respective mass numbers. This is indeed what is generally observed, as may be gleaned from readily available listings, exemplifying data being shown in Table 1.

Table 1

Atom	**Mass**
^{4}He	4.0026
^{9}Be	9.0122
^{14}N	14.003
^{16}O	15.995
^{19}F	18.998
^{23}Na	22.991
^{31}P	30.975
^{45}Sc	44.956
^{75}As	74.922
^{93}Nb	92.906
^{159}Tb	158.925

A possible explanation for this trend is that it is an artefact arising from the initial 'assignment' of the atomic mass of ^{1}H, as argued at length above. Alternatively, of course, it could represent a genuine trend deriving from inherent structural features of the atomic nucleus, particularly the manner in which the constituent nucleons are packed together (*vide infra*).

Artefact or not? A decision on this intriguing question must await the discussion below on the presumed significance of the difference between atomic mass and mass number.

The Mass Defect Idea

An early explanation for the above trend was based on the proposal of the 'packing fraction', which was an attempt to reconcile the observed departures from the whole number rule (*cf.* Prout's Law above). In fact, this had resurfaced with the discovery of isotopes in a new manifestation, which was perhaps more reasonable than the previous form. Thus, the expectation now was that the atomic masses would be whole numbers. (Intriguingly, the packing fraction concept was proposed before the neutron was discovered, so this period presumably represented, conceptually, a middle ground *vis-a-vis* Prout's Law, involving the proton as the unit of nuclear structure.)

The packing fraction (P_F) was defined in terms of a fractional departure of the observed atomic mass (M_A^o) from the mass number (M_N; Eqn. 2, which is a later version incorporating the neutron). Thus, the packing fraction for various atoms was calculated, as shown in Table 2. (Hence P_F restates the trends in Table 1 above in quantitative terms.)

Table 2

Atom	**Packing fraction (P_F)**
^{1}H	77.8
^{4}He	5.4
^{10}Be	13.5
^{12}C	3.7
^{14}N	5.7
^{16}O	0.0
^{19}F	0.0
^{31}P	-5.6
^{75}As	-8.8
^{81}Br	-8.6
^{98}Mo	-5.5

$$P_F = (M_A^o - M_N) \times 10^4/M_N \qquad (2)$$

It was proposed that these trends reflected the relative stability of the atomic nucleus in various elements. The loss of mass as reflected in the P_F value was believed to represent the nuclear binding energy in terms of the mass-energy equivalence formula (Eqn. 3, m being mass and c the velocity of light).

$$E = mc^2 \qquad (3)$$

However, the $P_F = 0$ by definition for the nucleus taken as standard (as for ^{16}O above). Thus, the P_F would represent only a relative binding energy (per nucleon), and would not be valid in any absolute sense.

Later treatments apparently preferred the 'mass defect' criterion (M_D), defined (per nucleon) as in Eqn. 4. In this, M_A is the atomic mass calculated from the known masses of the constituent nucleons, M_A^o is the observed atomic mass and M_N is the mass number.

$$M_D = (M_A - M_A^o)/M_N \qquad (4)$$

This differs from the packing fraction in that the departure is essentially defined relative to the calculated mass M_A, rather than M_N itself. It is noteworthy that M_A is derived from the observed mass of ^1H (1.00778) and the related neutron mass (*vide infra* for a detailed critique).

It is also noteworthy that the P_F scale is essentially 'anchored' at ^{16}O, so the differences between the expected and observed mass values are proportional to 'distance from anchor'. On the 'upstream' side the scale terminates with a maximum difference at ^1H. On the 'downstream' side the differences take on negative values, but their absolute magnitudes increase with 'distance from anchor'. (The P_F scale, apparently, is based on an idealised building block with a mass of exactly 1.0 relative to ^{16}O, a notion that is a relic of Prout's Law.)

Table 3

Item No.	Atom (Isotope)	Atomic Weight (Year)		
		1900	**1925**	**1961**
1	^{9}Be	9.1	9.02	9.0122
2	^{19}F	19.05	19.00	18.9984
3	^{23}Na	23.00 (1909)	22.997	22.9898
4	^{27}Al	27.1	26.97	26.9815
5	^{31}P	31.0	31.027	31.9738
6	^{45}Sc	45.1	45.10 (1921)	44.956
7	^{55}Mn	55	54.93 (1909)	54.9380
8	^{59}Co	59.0	58.94	58.9332
9	^{75}As	75.0	74.96 (1910)	74.9216
10	^{89}Y	89.0	88.9	88.905
11	^{93}Nb	93.7	93.3 (1931)	92.906
12	^{103}Rh	103.0	102.91	102.905
13	^{133}Cs	132.9	132.91 (1934)	132.904
14	^{141}Pr	143.6 (1897)	140.92	140.907
14	^{159}Tb	159.2 (1907)	158.88 (1953)	158.924
15	^{165}Ho	163.5 (1913)	164.94 (1941)	164.930
16	^{169}Tm	171 (1903)	169.4	168.934
17	^{197}Au	197.2 (1900)	197.0 (1953)	196.967

The M_D scale, however, is essentially ‘anchored’ to the observed masses of the nucleons (which go into calculating M_A). These, along with the M_A^o values, are ‘taken’ from the P_F scale, *i.e.* are related to ^{16}O. Since these (M_A^o) are continuously decreasing relative to the corresponding M_A values, M_D increases with nuclear mass. This is because $M_A > M_N$, and the difference (M_A - M_N) increases with M_N; $M_A^o > M_N$ ('upstream') and $M_A^o < M_N$ ('downstream') relative to ^{16}O, but the difference (M_A^o - M_N) steadily decreases with M_N.

However, there are serious ambiguities plaguing the mass defect (M_D) scale, the prime among them being that M_A may not be calculated for ^{16}O, which by definition is 16.00. Thus, the initial assignment of the mass of ^1H (1.00778) is itself based on ^{16}O = 16.00, <u>so this fixes both the masses</u>! This means that the scale of M_A values relates to the mass of ^1H (1.00778), whereas the scale of M_A^o values relates to the mass of ^{16}O (16.00). Thus, the mass defect (Eqn. 4), comprising both M_A and M_A^o values, is unviable in itself.

Atomic Weights and Atomic Masses

Interestingly, the classical atomic weight of hydrogen dates back to 1894 (around the time the ^{16}O scale was adopted). It may appear that the later mass spectrographic determinations confirmed the non-integral value, and thus indicated that the idea of the mass defect had a sound chemical basis. The arguments are complicated as the original non-integral atomic weights were later deemed non-integral because of the existence of isotopes. In the case of hydrogen, deuterium had not been detected by the early mass spectrographs, so the non-integral atomic weight of hydrogen led to the idea of the mass defect.

However, it is noteworthy that a large number of classical atomic weights – of elements which possessed only a single stable isotope – not only possessed non-integral values but also often exceeded the corresponding mass numbers. Table 3 lists the atomic weights of the common elements which possess a single isotope that occurs in 100% natural abundance.[2] Thus, these fractional values would represent either genuine departures from the whole number rule or experimental error.

This is interesting in light of the later finding that atoms 'downstream' from ^{16}O possessed atomic masses below their expected integral values (purportedly by the mass defect). This raises the question whether the classical atomic weight of hydrogen, which was in excess of 1, reflected experimental error! If so, the later mass spectrographic 'corroboration' is bound to be dubious.[3]

In other words, the classical atomic weights generally indicate no mass defect, as almost all values – not just for hydrogen – were generally overestimations relative to the mass spectrographic ones.

The change in the atomic weight as a function of the year of determination (Table 3), to reiterate, indicates that almost all the classical values (~ 1900) overestimated the atomic mass regardless of the mass number. Interestingly, the 1925 values – around the time of the first mass spectrographic reports – show a downward trend. This is further exacerbated in the 1961 values (now relative to ^{12}C).[4]

It is also noteworthy that, prior to the discovery of isotopes, deviations from Prout's Law had been accepted – perhaps grudgingly – although they remained mystifying, all the same. Ironically, however, Prout's Law apparently acquired renewed significance with increasing knowledge of atomic structure, as it was now incumbent on the investigator to explain why Prout's Law was not obeyed in the case of atomic masses, if the proton and the neutron were the basic building blocks! (Thus, if ^{16}O possessed an integral mass equal to 16, then its building blocks too should possess integral fractions of this.)

The mass defect idea perhaps evolved in response to this need. However, the question of the origin of these minuscule variations, whether in the classical values (in Table 3) or the mass spectrographic determinations, remains: are the determinations accurate enough to rule out the possibility of experimental errors? (Thus, was Prout's Law perhaps abandoned in haste? It is particularly noteworthy that assigning the atomic mass of ^{1}H as 1.00778 and that of ^{16}O as 16, ineluctably leads to the mass defect idea.)

Nuclear Binding Energy

The currently accepted explanation for the above trends in the P_F and the M_D values is that they represent nuclear binding energy, *via* the mass-energy equivalence relation proposed by Einstein (Eqn. 3).

Thus, the difference in mass corresponds to the energy that was ‘lost’ when the nucleus first formed from the composite free nucleons. This, then, represents the binding energy of the nucleus. This explanation was proposed along with the P_F, and so dates back to the early years of the mass spectrograph. These ideas were apparently bolstered by parallel developments in radioactivity and nuclear fission, and thus struck deep roots in the conceptual firmament of modern physics and chemistry. (They also – ostensibly, as it now appears – represented an early success of Eqn. 3.)

A key problem with invoking the mass-energy equivalence idea in this manner is that it also implies that the heavier nuclei are relatively less stable. (Greater mass is associated with higher energy content by Eqn. 3.) The energy corresponding to the mass defect is but a fraction of the total nuclear mass, as revealed by Eqns. 2 and 4 (M_N being nearly identical with the atomic mass). Thus, the increase in M_D with nuclear mass – supposedly representing enhanced nuclear binding – would be subsumed in the increase in energy due to the corresponding increase in atomic mass.

Yet, it is believed that the M_D estimates the nuclear binding energy *via* Eqn. 3, as depicted in the familiar binding energy diagram (Fig. 2). This is believed to indicate that the nuclear binding energy increases steeply for the lighter atoms up to ^{16}O; it then increases less steeply – curving gently, in fact – to reach a maximum at ^{56}Fe; the line thence descends slowly towards the uranium isotopes.

This behaviour is explained by current theory on the basis of a balance between two forces acting in opposition within the confines of the atomic nucleus. One of these is the electrostatic force (E_F), derived from the repulsion between the positively charged protons; the other is believed to be the strong nuclear force (N_F), which binds all nucleons together. Also, the E_F is a longer range force, whereas the stronger N_F wanes relatively rapidly with distance.

Thus, in the lighter nuclei, the N_F is believed to predominate, so binding energy steadily increases (up to ^{56}Fe). Beyond this, however, and because of the increase in nuclear size, the N_F weakens and yields (to an extent) to its repulsive counterpart, the E_F; thus, in the heavier elements (beyond around ^{56}Fe), the overall binding energy begins to decrease with atomic mass. (However, *vide infra* for a critique.)

An Alternative Possibility

However, an alternative explanation for the profile in Fig. 2 is also possible. In this, the mass defect relationship (Eqn. 4) is treated as a purely mathematical function, without any assumptions about nuclear stability and binding energy.

For this, it would be useful to recast Eqn. 4 into Eqn. 5; in this, the ratio (M_A/M_N) defines the average nucleon mass (M_{av}), and the ratio (M_A^o/M_N) is represented by the variable x.

$$M_D = (M_A/M_N) - (M_A^o/M_N) = (M_{av} - x) \qquad (5)$$

$$M_{av} = (M_A/M_N) = (M_nN_n + M_pN_p)/(N_n + N_p) \qquad (6)$$

These definitions arise as M_A is the calculated mass based on the masses of the proton and the neutron, and M_A^o is the observed atomic mass which is related to the mass number (M_N) by a factor which is characteristic for each nucleus (*cf.* Table 1).

Also, M_{av} can be expanded as in Eqn. 6; in this, $M_A = (M_nN_n + M_pN_p)$ and $M_N = (N_n + N_p)$, M_n and M_p being the masses of the neutron and the proton respectively, and N_n and N_p the numbers of neutron and proton respectively. Eqn. 6 can be recast into Eqn. 7, by dividing both numerator and denominator by M_nN_n, and representing (M_p/M_n) by y and (N_p/N_n) by z. Eqn. 7 leads to Eqn. 8, which relates M_D to M_N, x, y and z.

Table 4

Atom	**z (N_p/N_n)**	**M_{av}**	**x (M_A^o/M_N)**	**M_D (M_{av}-x)**
^{4}He	1.00	1.007970	1.00065	0.00732
^{9}Be	0.80	1.008047	1.00136	0.00669
^{14}N	1.00	1.007970	1.00021	0.00776
^{16}O	1.00	1.007970	0.99969	0.00828
^{19}F	0.90	1.008007	0.99989	0.00812
^{23}Na	0.92	1.008000	0.99961	0.00839
^{31}P	0.93	1.008000	0.99919	0.00881
^{45}Sc	0.88	1.008015	0.99902	0.00900
^{56}Fe	0.87	1.008015	0.99884	0.00918
^{75}As	0.79	1.008052	0.99896	0.00909
^{93}Nb	0.79	1.008052	0.99898	0.00907
^{112}Cd	0.75	1.008070	0.99913	0.00894
^{159}Tb	0.69	1.008098	0.99953	0.00857
^{235}U	0.64	1.008123	1.00019	0.00794

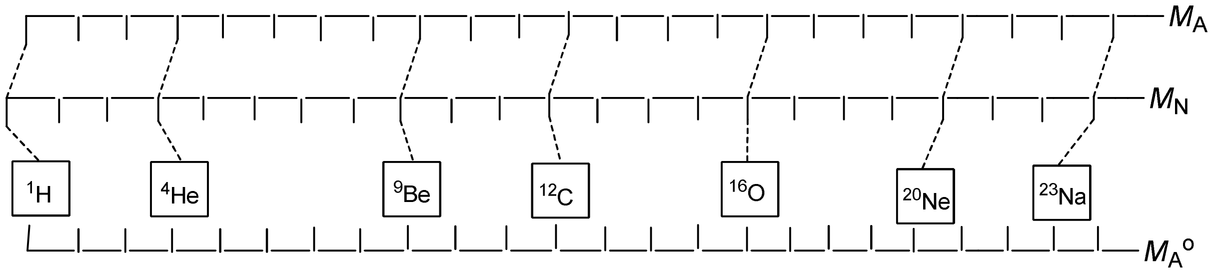

Fig. 1. Depiction of the scale of decreasing offsets. The two top linear scales represent the calculated mass (M_A) and the mass number (M_N) of each of the major isotopes of the various elements up to ^{23}Na. The bottom scale represents the corresponding observed masses ($M_A{}^o$). Whilst the M_A values are offset relative to the M_N in a nearly consistent manner for all the atoms, the $M_A{}^o$ values are offset in a more complicated manner.

Thus, the $M_A{}^o$ values are offset relative to the M_N values, except at ^{16}O, at which point the two scales coincide. The offset is maximum at ^{1}H, and decreases steadily thereafter (being 0 at ^{16}O); beyond this the offsets acquire negative values, their absolute magnitudes increasing steadily till ^{56}Fe (not shown), at which point they begin to increase again (*cf.* Tables 1-3). The angle of the dashed connector relative to the vertical is a measure of the offset, which represents (M_N – $M_A{}^o$), a measure of the packing fraction (P_F, Eqn. 2). Also, $M_A{}^o/M_N = x$ (Eqn. 5, typical values in Table 4).

The (marginal) lack of consistency in the case of the offsets of M_A derives from differential proton to neutron ratios (z) in different atoms, and the fact that neutrons are marginally heavier than protons. The combined offsets represent (M_A – $M_A{}^o$), a measure of the mass defect (M_D, Eqn. 4). Also, (M_A/M_N) = M_{av} (average atomic mass, Eqn. 6, typical values in Table 4).

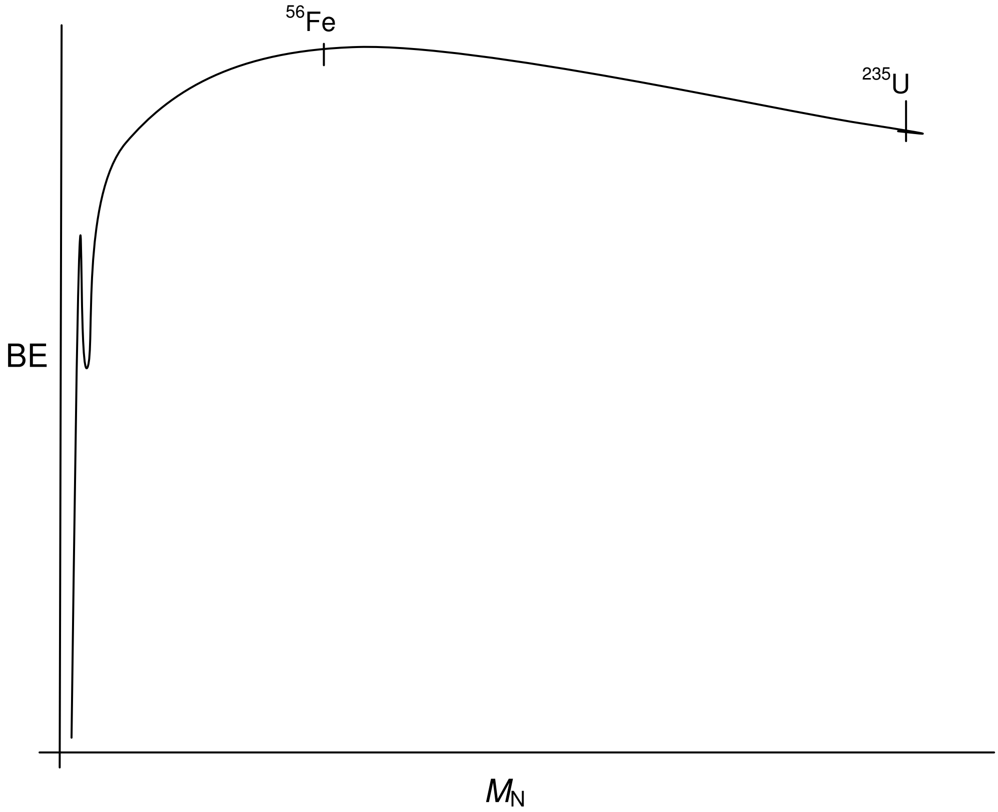

Fig. 2. Familiar plot (general shape) of the average binding energy per nucleon (designated BE on the *y* axis) *vs.* the mass number (M_N on the *x* axis). The profile indicates that the nuclear binding energy per nucleon increases sharply among the lighter elements up to ^{56}Fe and gradually decreases thereafter. This is believed to reflect the mass defect inherent in the respective nuclei, so the heavier nuclei are generally more stable than the lighter ones. However, this does not hold beyond ^{56}Fe; thus, the lower binding energy of (say) ^{235}U is believed to be the basis of nuclear fission

$$M_{\text{av}} = (M_n)[1 + (M_p/M_n)(N_p/N_n)]/[1 + (N_p/N_n)] = (M_n)(1 + yz)/(1 + z) \quad (7)$$

$$M_D = [M_n(1 + yz)/(1 + z)] - x \quad (8)$$

Note that y (M_p/M_n) is a constant (= 0.9986235). However, both x and z (N_p/N_n) vary, z rather more than x (*cf.* Table 4), and these determine the variations in M_D. The x can be obtained from the data in Table 1, by dividing the observed atomic mass by the corresponding mass number; the resulting values are listed in Table 4 (along with z, M_{av} and M_D). In Eqn. 8, the factor $(1 + yz)/(1 + z)$ would be marginally less than 1, as $y = 0.999821$.

In Eqn. 5, M_{av} is calculated from the known masses of the proton and the neutron. On the other hand, x is essentially a function of the offsets of M_A^{o} relative to M_N that – in principle – decrease steadily (*cf.* Fig. 1). However, it is observed that x reaches a minimum at ^{56}Fe, and thence increases again. This, of course, relates to the characteristic decrease in the binding energy profile in Fig. 2 (beyond ^{56}Fe).

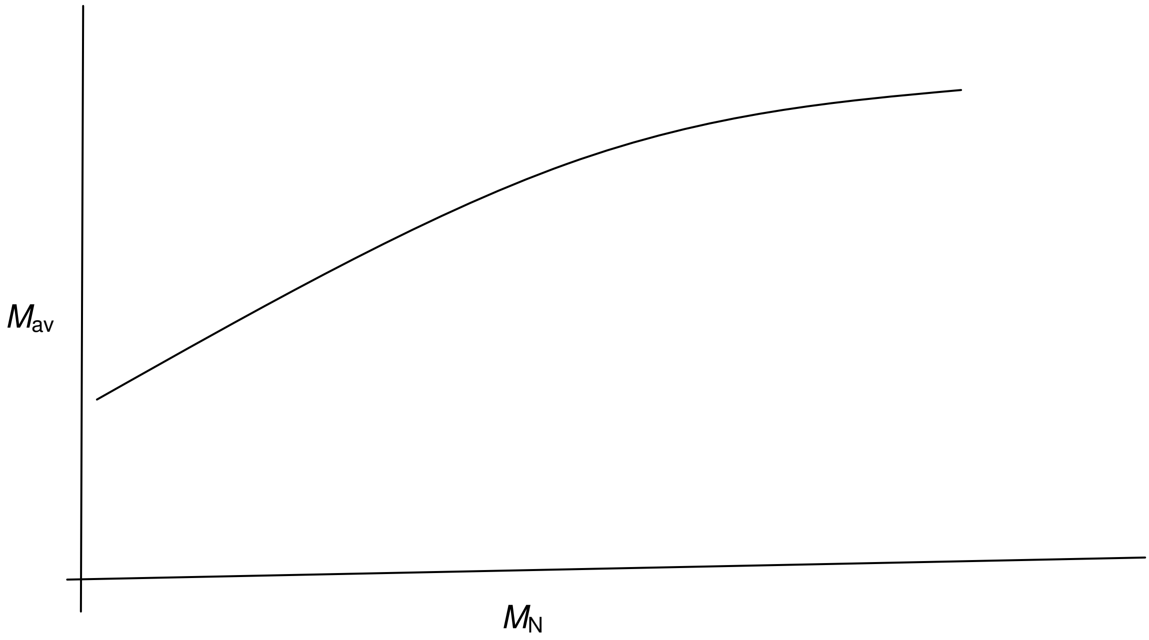

Fig. 3. Plot (general shape) of the average nucleon mass (M_{av}, *cf.* Eqn. 7) *vs.* the mass number (M_N)

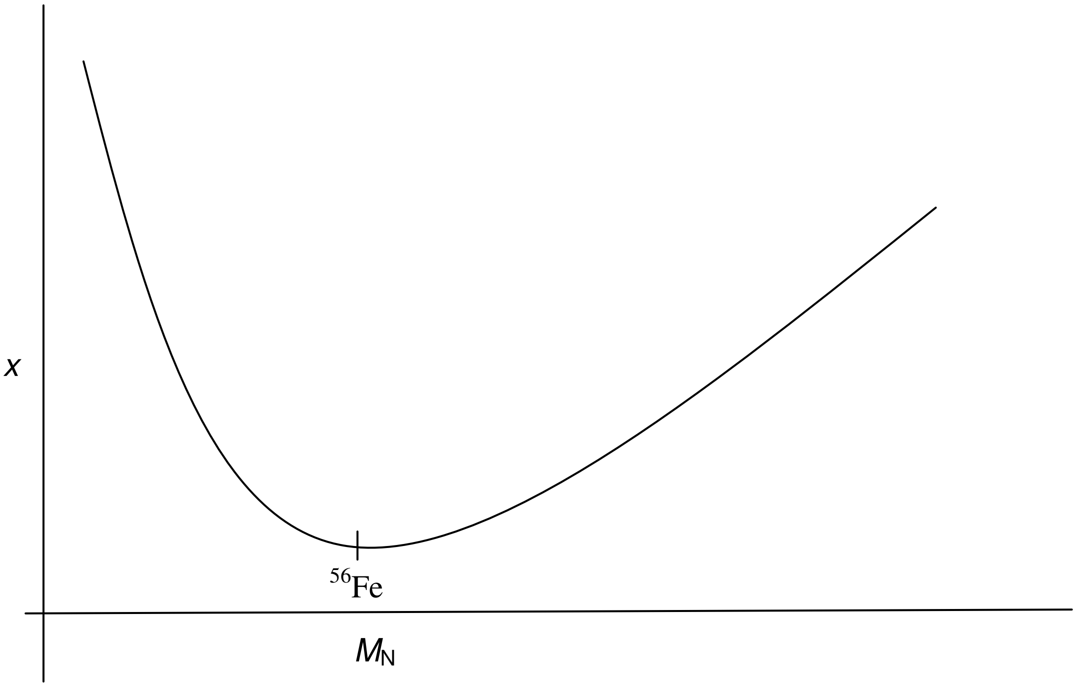

Fig. 4. Plot (general shape) of x (M_A^o/M_N, *cf.* Eqn. 7) *vs.* M_N (M_A^o is the observed atomic mass and M_N the atomic number)

Interestingly, plotting M_{av} *vs.* M_N leads to the curve in Fig. 3; plotting x *vs.* M_N leads to the curve in Fig. 4. Thus, apparently, M_{av} by itself partly captures the overall profile of Fig. 2: in other words, the shape of this profile is, to an extent, due to the relative increase in the neutron content in the heavier nuclei (decrease of z, as reflected in the increase in M_{av}). Thus, this analysis of the data in Table 4 leads to the profile in Fig. 2 only for the case of the lighter elements. The abrupt decrease in M_D beyond ^{56}Fe is not replicated by the above theoretical analysis based on Eqn. 8. These trends, therefore, are likely to be due to other effects as discussed below.

Possible Mass Spectrographic Inaccuracies

Early mass spectral studies, although characterised by great experimental ingenuity, were possibly plagued by errors and inaccuracies. Whilst many of these were unavoidable during the pioneering years, and were indeed appropriately addressed, a few may have escaped due scrutiny. Two in particular are noteworthy, as they may well bear upon the above problems.

Firstly, the theoretical basis of the mass spectrograph, that the extent of deflection of a magnetised particle in an external magnetic field is inversely related to the mass of the particle, may be oversimplified. This is because a heavier particle would offer greater inertial resistance than a lighter one. This would curtail the extent of deviation of the heavier particle.

The inertial resistance – representing a 'stickiness' – is generally to be expected whenever a moving body changes its path. In the general case, this largely arises from interactions (friction, etc.) between the moving body and the surrounding medium. The particles in a mass spectrograph, of course, move in a vacuum. However, the external magnetic field may be considered the 'medium', in the sense that particles of different mass, size and polarisability interact differently with it. This is usually neglected, but may well exist and effect fine changes in trajectory.

The gross deviations are described as in Eqn. 9, wherein H is the strength of the external magnetic field and r is the radius of curvature of the parabolic path adopted by the particle, m, e and v being the mass, charge and velocity associated with the particle.

$$m(v/eH) = r \tag{9}$$

If v, e and H are held constant, a linear relationship exists between m and r. Thus, heavier particles suffer smaller deviations (larger r). By the above arguments, the inertial resistance should marginally increase r further, leading to correspondingly larger observed masses. Perhaps a relation of the form in Eqn. 10 would better explain the observations (p is a constant, $0 \leq p \leq 1$).

$$m(1+p)(v/eH) = r \tag{10}$$

The 'inertial drift' is represented by the term '$mp(v/eH)$' and would gain importance with increasing m. This may well be contributing to the apparently smaller 'mass defects' observed in the case of the heavier atoms beyond ^{56}Fe, as discussed above. (The 'inertial drift' would be weaker in the lighter elements, and thus subsumed in the other changes discussed above.)

It is also noteworthy that the purported 'inertial drift' is apparently associated with relatively large neutron content (*i.e.* lower z values in the heavier elements, *cf.* Table 4). This means a relatively lower charge density in the nucleus, possibly leading to a smaller 'secondary deviation' in the trajectory. 'Secondary deviation' here implies that the 'primary deviation' arises from the magnetic moment of the particle derived from the overall positive charge on the atom (as a result of the loss of an electron during ionisation). Hence, the 'secondary deviation' possibly represents a minor contribution arising from the nuclear charge. Also, the polarisability of the atom's electron cloud may influence the extent of the deflection. (All these secondary effects contribute to 'p' in Eqn. 10.)

Secondly, the assumption that relative deviations can be related to the relative r values (Eqn. 9) can be a serious source of error. Thus, it is believed that the spacing between two lines can be related to the difference between two r values, which then leads to the difference between the two masses (m values). However, this would be only valid if the r values represent radii derived from concentric circles, *i.e.* with a common centre.

This is, of course, impossible in practice, as the ions (in effect) exit from a common source. Thus, the trajectories can only be related to parts of intersecting circles without a common centre. In fact, Eqn. 9 is derived on the basis of the presumed circular motion of each ion, *i.e.* each trajectory being part of an independent circle. The placement of the detecting photographic plate (or a luminescent screen) also assumes importance, as the angle it subtends with the incoming rays also determines the line spacing. This is because the trajectories diverge from a common source point, so the projection of their relative position would depend on the angle of projection. (These arguments are represented in Fig. 5.)

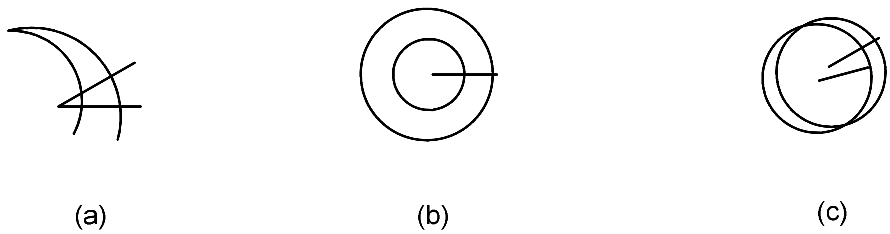

Fig. 5. (a) Two mass spectral ion trajectories emanating from a common source. The two straight lines represent a recording plate or screen at two different angles. Different line spacings are projected onto the plate. (b) Two concentric circles with a common centre. The difference in the radii can be related to the difference in the masses of two ions which adopt the two circular paths. (c) Two intersecting circles as opposed to the case in (b). These have no common centre, hence, in the case of two circulating masses, the difference in masses cannot be simply related to the difference in radii, which is not easily determined. This is similar to the case shown in (a)

Finally, early studies apparently do not pay sufficient heed to the level of accuracy in the various terms involved in the equation describing the deflection. Thus, although the final atomic mass is cited to 6 significant digits, the magnetic field strength and the electric field were not always defined to the same accuracy. By Eqn. 9, m may not be determined to a higher level of accuracy than either H or r.

In fact, the thickness of the observed lines may not allow the level of accuracy claimed in the final masses. Even if these lines are well separated, the accuracies of the separations would be limited by the thickness of the lines themselves! Taking the mid-point of each line only leads to the average value of the spacing between them, and does not eliminate the error *per se.*

These arguments also apply to the widely-used high resolution mass spectrometric determination of atomic masses. Although this apparently leads to the correct results in terms of the elemental composition of the molecular ion, the apparent success may be largely based on empirical correlations. Thus, different molecular ions with ‘identical mass’ (identical M_N values) would differ in terms of their interaction with the external magnetic field, as argued at length above. This would partly reflect the ‘mass defect’ in the exact masses of the constituent atoms.)

Mass Defect and Nuclear Binding Energy: Fact or Fiction?

The above extended arguments have traced the origins of the mass defect idea and its evolution to current status as the basis of nuclear structure and energy. It appears, however, that fundamental questions remain as to the validity of this basis. Perhaps unsurprisingly, then, the current theory of nuclear structure itself raises questions not easily answered, as discussed below.

A particular problem, as noted above, is that the mass-energy equivalence idea enshrined in Eqn. 3 implies that atoms of higher mass possess more energy than those of lower mass. This flies in the face of the current view that – generally – the heavier atoms are more stable, as indicated in Fig. 2. The increase in the purported mass defect would be but a minuscule fraction of the increase in mass – and its equivalent in energy by Eqn. 3 – on going from one element to the next higher in atomic mass.

Furthermore, current theory posits a balance between the strong nuclear force (N_F) and the electrostatic force of repulsion (E_F) between the constituent protons. Both wane with increasing distance, but N_F more rapidly. The result is that N_F predominates at shorter distances, whereas E_F predominates at larger distances. Intriguingly, this is believed to support the mass-defect idea and Fig. 2: as an increase in nuclear mass is accompanied by a corresponding increase in size, so E_F gains, gradually and incrementally, over N_F. Ultimately, the incremental repulsive force (E_F) overtakes the strong force (N_F) at ^{56}Fe, beyond which the nuclear binding energy decreases steadily.

A serious problem with this view is that an increase in nuclear mass (by the addition of a nucleon) results in an increase in both short-range and long-range interactions with other nucleons. The short-range interactions – with 'nearest-neighbour nucleons' – would be far greater than the long-range interactions with remote nucleons. The short-range interactions would be dominated by the strong force (N_F), hence would be strongly attractive in the sum. The long-range interactions would be less attractive than the short-range ones in the medium-sized nuclei, but would be dominated by the repulsive force in the larger nuclei (*i.e.* $E_F > N_F$). <u>However, this would be overwhelmed by the short-range, net-attractive forces between the nearest-neighbour nucleons</u>.

Thus, current theory is likely flawed by the neglect of this dominant short-range interaction, possibly because it relies implicitly on the mass-defect idea. Interestingly, it is currently believed that in nuclear fission the product nuclei are more stable by virtue of the mass defect (as in the case of the fission of ^{235}U, *cf.* Eqn. 11). However, the collapse of the mass defect idea, as discussed at length above, invalidates this argument. Also, although a heavier atom would possess higher energy (by Eqn. 3), overall mass is conserved in the products of the fission process (*e.g.* Eqn. 11). Thus, apparently, this cannot be the source of fission energy.

$$^{235}\mathrm{U} \rightarrow {}^{92}\mathrm{Kr} + {}^{141}\mathrm{Ba} + 2n \qquad (11)$$

It is, of course, possible that the product nuclei in a fission reaction are indeed more stable than the original nucleus, for reasons other than the mass defect. Alternatively, a process as yet unrecognised may be involved. An intriguing possibility would be the conversion of a part of the mass of a neutron into energy, the fission process then providing a pathway for this conversion. (Fission, of course, is accompanied by an increase of entropy, but this would be too minuscule to account for the observed energy released.)

As argued at length above, mass-energy equivalence (Eqn. 3) implies that larger, heavier nuclei should be less stable than smaller, lighter nuclei, in general: Thus, fission should be observed even among the lighter nuclei. However, this by itself would not generate energy as mass would be conserved in the process (implying an equilibrium constant of unity).

It is also particularly noteworthy that, although the binding energy is believed to decrease for nuclei heavier than ^{56}Fe, it is still much higher relative to many of the lighter nuclei! This indicates that the instability of the radionuclides does not derive from the purported mass defect. It would appear that these nuclei are malformed and hence metastable, perhaps because of their size. Possibly, the likelihood of malformation increases with mass and size, because of the need for precise incorporation of the nucleons and consequent structural organisation of the nuclei during their creation. (Analogous chemical phenomena involve the malformation of crystals, super-cooling and glass formation, polymorphism, etc.)

The interpretation of the mass-energy equivalence principle (Eqn. 3) may indeed be subtle. All the same, the above discussion indicates that the origins of fission energy are as yet unclear. Further discussion, however, is clearly beyond the scope of this paper.

CONCLUSIONS

The assignment of the atomic mass of hydrogen, based on early mass-spectrographic work, represented a conceptual watershed in the history of science. In enforcing the abandonment of Prout’s Law – which required integral values for atomic weights, and by later implication, for atomic masses – it imparted a new and revolutionary meaning to the idea of the atom itself. In particular, it seminally influenced the development of the theory of the atomic nucleus by introducing the idea of the ‘mass defect’. This, in conjunction with the mass-energy equivalence principle proposed by Einstein, lead to the current theory of nuclear binding energy, apart from indicating the nature and significance of radioactivity.

However, the accuracy of the mass spectrographic work is apparently not beyond doubt. Also, importantly, the sequence of events leading up to the assignment of the atomic mass of hydrogen is intriguing, as it predated the detection of both ^{2}H and ^{18}O. The assignment to the mass of ^{1}H a value practically identical to the then known atomic weight of hydrogen is also curious and intriguing. It raises the possibility that the assignment may have been influenced by a need to align the evolving physical scale of atomic masses with the established chemical scale of atomic weights. All this indicates that the basis of the mass defect – itself of key importance in the current theory of nuclear structure and energy – is possibly not beyond doubt.

These doubts are apparently reinforced by the possibility that, by mass-energy equivalence, heavier atoms would generally be unstable relative to lighter ones. This would very effectively overcome the purported mass defect criterion of nuclear stability, and clearly invalidate currently held views on the nature and origin of the nuclear binding energy. Thus, it would appear that current theory leans too heavily on early work, which, despite its pioneering brilliance, was possibly not without flaw. (It seems that the high resolution mass spectral technique of determining molecular elemental composition, an important spinoff of the early mass spectral studies, has an empirical basis.)

Furthermore, the nature of the two nuclear forces – the repulsive electrostatic force (E_F) between the protons and the attractive strong force (N_F) between all nucleons – raises several questions. Current theory is apparently flawed in neglecting short-range interactions in the heavier nuclei, possibly in order to conform to the mass defect idea. These arguments raise fundamental questions about the nature and the origin of the energy released in the process of nuclear fission.

NOTES

1. In view of the contentious nature of the arguments presented herein, no references are listed (except for ref. 2), in order to avoid acrimony and misunderstanding with selected authors. The arguments are based on information readily available in a variety of standard sources and text books.

2. Coplen, T. B.; Peiser, H. S. *Pure Appl. Chem.* **1998,** *70 (1)*, 237-257.

3. Admittedly, however, the atomic weight of natural hydrogen, *i.e.* including deuterium, and based on integral atomic masses, is calculated to be 1.00043. This is well below the classical value of 1.008, and could be viewed as supporting the mass defect idea in the heavier atoms. Alternatively, it could also indicate experimental error. (Natural abundance values of 99.985% for ^{1}H, 0.015% for ^{2}H, 99.759 for ^{16}O, 0.204 for ^{18}O and 0.037 for ^{17}O were assumed in the above calculation.)

In fact, a highly likely source of error derives from the greater density of deuterium (D_2) relative to hydrogen (H_2). Classical atomic weights were determined by the vapour density method (particularly for gases), employing large glass globes. It involved the repeated filling and refilling of the globes by the gas in question that was (presumably) prepared, purified and stored prior to the determinations. The repeated operations of sweeping out the gases in the globes would have lead to a gradual enrichment of the stored hydrogen in deuterium. (This is because of the existence of a density gradient, and also assuming the gas was drawn out from the top of the stored container). Thus, the resulting atomic weight would not reflect the normal abundance values of deuterium, but would lead to a positive error. A considerable part of the deviation from Prout's Law in the classical atomic weight of hydrogen may well be due to this, noting that a three-fold enhancement in the deuterium content over the natural value would fully account for the observed deviation (*i.e.* the value of 1.008).

Another likely source of error derives from the purification procedures employed in the preparation of hydrogen. Usually, hydrogen was prepared by the action of dilute sulphuric acid on zinc and purified elaborately by passing through tubes containing: lead nitrate (to remove H_2S), silver sulphate (to remove arsine, stibine, etc.), caustic potash (thrice, to remove acid vapours), concentrated H_2SO_4 and P_2O_5 (for drying). It seems likely that many of these purifying reagents would adsorb hydrogen itself to varying extents. Also, H_2 is generally more reactive than D_2 because of an expected isotope effect, leading to a corresponding enrichment of the sample in favour of deuterium.

4. There have been essentially three changes in the reference standard for atomic weights and masses. The first was from hydrogen (1.0) to oxygen (16.0) which occurred in 1894, *i.e.* prior to the discovery of isotopes, so these refer to classical atomic weights. The second was from the chemical to the physical scale, which occurred with the arrival of the early mass spectrographic results (~1925). These are now relative to ^{16}O, and refer to atomic masses of individual isotopes. The third was from the ^{16}O standard to the ^{12}C standard (1961).

Interestingly, the first of the above changes would, in principle, not alter the values of the atomic weights. This is because – as far as was known – neither hydrogen nor oxygen, apparently, deviated from Prout's Law. Thus, the values listed for these in 1892 were 1.00 and 16.00 respectively. (However, several other elements deviated, often substantially, from Prout's Law.) Intriguingly, the 1894 values for hydrogen and oxygen are listed as 1.008 and 16.000 respectively. The deviation from Prout's Law in the case of hydrogen presumably reflects enhanced confidence in the determinations.

The second of the above changes would, in principle, alter the earlier values of atomic weights. This is because of the realisation of the existence of isotopes of both hydrogen and oxygen (although early mass spectrographic results did not indicate this). As improved mass spectrographic results emerged, it became apparent that the new atomic mass values would be substantially different for two reasons, *viz.* the earlier atomic weights were weighted averages of atomic masses, which themselves apparently flouted Prout's Law (purportedly the mass defect).

The inclusion of the mass of ^{2}H into the weighted-average atomic weight of hydrogen leads to a value of 1.0002. Clearly, the presence of deuterium makes only a marginal contribution to the substantial deviation from Prout's Law seen in the 1894 value of 1.008. The inclusion of ^{18}O into the averaged atomic weight of oxygen, likewise, leads to a value of 16.0045. This would alter the earlier atomic weight values upward by a factor of 1.00028, and would embody the new physical scale.

The third of the above changes eliminated the ambiguity between the earlier chemical scale (relative to natural oxygen, *i.e.* a mixture of isotopes) and the new physical scale (relative to ^{16}O). This required defining a new standard that was both widely prevalent and easily determined. Thus was ^{12}C chosen and assigned a value of 12.0000. This entailed a downward revision of the atomic masses, and consequently the atomic weights too, as the atomic mass of ^{12}C relative to ^{16}O in the earlier physical scale was 12.0036.