- Roger Boscovitch (1711-1787), a Polish priest and natural philosopher, extended Newton’s ideas to their logical extreme. He suggested that:

i) fundamental particles were only <u>mathematical points in space</u>, which
ii) served as point centres of a complex, alternately attractive and repulsive, <u>force field</u>, eg,

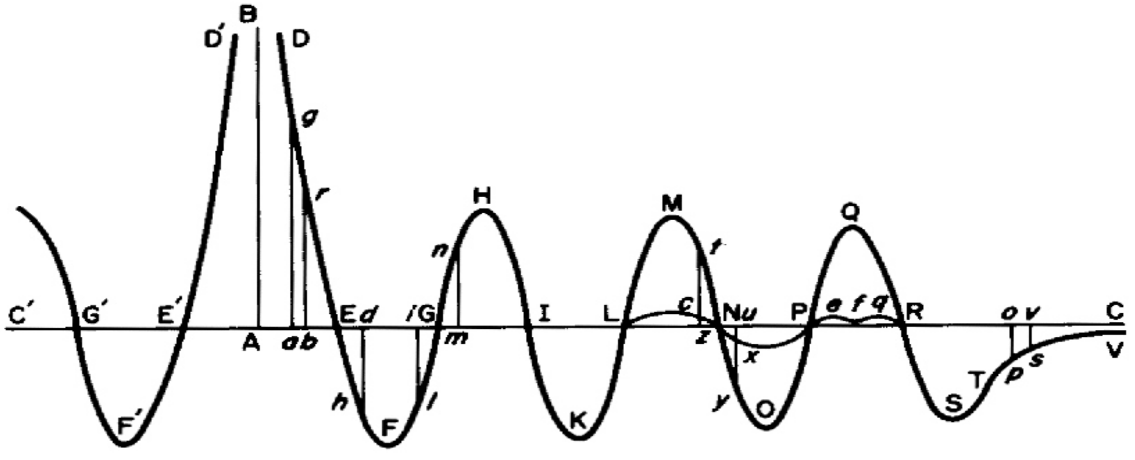


Fig. 8–1.

- Boscovitch’s metaphysical ideas had little impact on chemists who saw no way to measure or verify the forces, nor any way to use them in a useful way

- altho Newton had made the idea of fundamental chemical particles worth consideration, and had even interpreted gas behaviour as due to interparticle repulsions, his ideas were largely swept away by the novel ideas of Lavoisier, who insisted that the chemical elements were to be operationally defined

- of atoms and elements Lavoisier said (Traite, p.xxx)

> "…if, by the term elements we mean to express those simple and indivisible atoms of which matter is composed, it is extremely probable that we know nothing about them; but if we apply the term elements, or principles of bodies, to express our idea of the last point which analysis is capable of reaching, we must admit as elements all the substances into which we are capable, by any means, to reduce bodies by decomposition"

Elements as Atoms

- **John Dalton** (1766-1844) was a Quaker (a non-conformist religious minority in England. Only those who were members of the Church of England - Anglicans - could attend universities or, hold political positions), who became an elementary (Quaker) school teacher at the age of 14. How did he re-introduce atomism into chemistry?

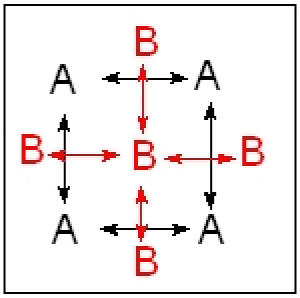
- Quaker schools emphasized practical education, including science topics, and soon Dalton became an instructor at a Quaker college in the booming industrial city of Manchester

- his chief scientific interest was ***meteorology*** (he kept daily records of temperature, pressure and rainfall every day of his life; these reliable records are still consulted by climatologists interested in last climates)

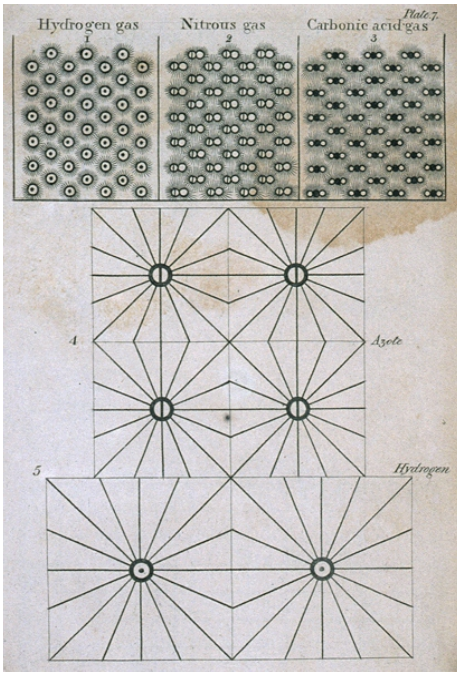
- in a book published in 1793, entitled Meteorology, Dalton gave a novel explanation of why the atmosphere was homogeneous, despite the fact that it contained several gases of different densities (eg, oxygen, nitrogen, carbon dioxide and water)

- building on the ideas of Boyle (variation of gas volume with pressure) and Newton (gases were composed of repelling particles),

☆ Dalton suggested that, in a mixture of two gases, A and B, particles of A repelled only other A particles, and B repelled only B, etc. A particles had no effect on B particles, ie,



- this hypothesis was supported by Dalton’s exptl observation that the solubility of gas A in water (when mixed with B) depended only on the pressure of A, and was totally unaffected by the pressure of B [now known as Henry’s law]



- the repulsion between like atoms was caused by a blanket of heat fluid, known as ***caloric***, which surrounded each material particle, which Dalton referred to as atoms

- this explanation of gas behaviour and the atmosphere’s homogeneity was Dalton’s earliest scientific success, and he remained committed to its correctness for the rest of his life

- this idea suggests that all gases should have the same aqueous solubilities at a given pressure, but Dalton found that gases had different solubilities at atmospheric pressure

☆ Dalton then hypothesized that a gas’s solubility depended on its size (central atom + heat envelope), but this didn’t fit solubility data either, so he devised another hypothesis, which he introduced in lectures in 1803, ie,

☆☆ the solubility of a gas in water depended on the ***weight of its constituent atom***

- Dalton used the word atom for the smallest chemical particle of a specific gas, eg, the atom of water, or oxygen

- beginning about 1803, JD began calculating the relative wts of atoms from combining weights data, based on arbitrarily assigning hydrogen = 1[see back of course text; also Prob set #1]

- in Dalton's hands, the theory of chemical elements as the last point of analysis was united with the smallest particle, ie, ***the chemical elements became chemical atoms with unique atomic wts***

- thus from a start investigating atmospheric homogeneity and gas solubility data, Dalton about 1803 devised a new atomic theory which included the following:

1. Chemical elements represented different atoms, and the atoms (somehow) supplied the chemical and physical properties
2. All atoms of the same element are identical
3. Atoms are indestructible
4. Atoms of different elements have different weights

- of the above atomic ideas only ______ was a novel idea, and it is the key to Dalton's fame

- as Dalton collected and refined his list of relative atomic wts, he became aware of the great explanatory power of his theory, eg,

1) ***combination in definite proportions***

  - if elements combined atom-to-atom when forming compounds, then compound formation in fixed weight ratios must be the result, ie,

oxygen + hydrogen ➜ water

☆ data from such binary combination rxs enabled Dalton to calculate the relative wts of the chemical atoms

2) ***combination in integral multiple proportions***

- when 2 elements combine with each other to form two or more binary cmpds, then the two wts of B that combine with a fixed wt of A must be an integral ratio, ie,

a) nitrogen + oxygen ➜ nitrous gas

b) nitrogen + more oxygen ➜ nitric oxide

- for a given wt of nitrogen, the wt of oxygen in nitric oxide must be ***exactly 2x*** that in nitrous gas
- such integral combining proportions were a necessary consequence of atomic theory, ie, the theory had predictive power
- Dalton's first list of atomic wts was compiled in 1803 and had, for example,

H = 1, N = 5, C = 5, O = 7, P = 9

- one problem arose when two elements combined in two or more ways, eg

carbon + oxygen ➜ carbonic oxide
carbon + more oxygen ➜ carbonic acid

- because Dalton believed like atoms repelled each other, he proposed that compounds would always form with a minimum of inter-atom repulsions, ie,

level of complexity	atomic formula
1st	AB
2nd	A_2B
3rd	AB_2
4th	A_3B
5th	AB_3

- thus JD concluded carbonic oxide = CO
and, carbonic acid = CO_2

- because of his beliefs, JD concluded water must have the formula HO, ie, water was a two-atom compound

- Dalton published details of his atomic theory for the first time in 1808 in his New System of Chemical Philosophy; only after its publication did others give the theory serious consideration

Reception of Dalton's Atomic Theory

- two British chemists soon published experimental results which gave support to Dalton's theory

- the Scot, Thomas Thomson, a well-known chemical analyst, reported two strontium salts of oxalic acid in late 1808, ie,

oxalic acid + strontia → salts

- Thomson claimed his data proved Dalton's theory to be correct

- the englishman, William Hyde Wollaston, one of England's most famous scientists, also published a paper in 1808 which contained several examples of multiple combining proportions, eg, oxalic acid + potash ➜ salts

- Wollaston also stated that Dalton’s theory gave a satisfactory explanation for the integral proportions

- because Thomson and Wollaston were highly-respected chemists (and Dalton was not in 1808), their publications in the best scientific journal <u>Philosophical Transactions of the Royal Society</u> brought Dalton’s atomic theory to everyone’s attention

Thomas Thomson

William Hyde Wollaston

<u>Further developments</u>

- also in 1808, the French chemist, Joseph-Louis Gay Lussac, published his results on the combining volumes of gases, ie,

- he concluded that, when gases combine to form binary products, their volume ratios are always whole numbers, such as 1:1, 2:1, 3:1, etc, and he suggested that this was further evidence in support of Dalton's theory

- in 1811, an Italian lawyer and chemist, **Amadeo Avogadro**, published a paper in which he argued that Gay-Lussac's results could only be understood by an atomic theory if:

1) all gases, at the same temp and pressure, contain the same number of particles, and

2) the fundamental particles of gases could be subdivided into 2, 4 or more sub particles


Amadeo Avogadro

- consider the experimental results for the formation of water

oxygen + hydrogen ➜ water

volumes:

particles:

- assuming 'x' particles in each unit volume, the 2 volumes of water must have 2x total particles and, since each water particle contains an oxygen atom, the x oxygen particles in oxygen gas must be capable of being split into '2y' "***demi-atoms***"

- Avogadro then applied the same reasoning to hydrogen gas - if hydrogen gas also consisted of demi-atoms, then 2 volumes of hydrogen could contain 2 x 2x = 4x hydrogen demi-atoms, and the product water would contain 2x demi-atoms of H and 1y demi-atoms of oxygen and ***water would have the formula*** H_2O

- Avogadro thus came up with the formulas O_2, H_2O and H_2 for oxygen, water and hydrogen gases, and was able to predict the observed order of measured gas densities $O_2 > H_2O > H_2$

whereas Dalton's ideas predicted HO > O > H, contrary to observation
[we now know densities do vary with MM, ie, $PM = \delta RT$]

- by collecting values of gas densities, and combining them with his idea that many elemental gases were composed of "demi-atoms" [in our terminology, descended from Avogadro's ideas, many gases are diatomic molecules], Avogadro came up with different values of atomic weights, eg, O = 15, N = 14 (double Dalton's values)
[recognise that atomic wts derived from combination with hydrogen double if elemental hydrogen is viewed as H_2 instead of H_1]

- interestingly, Dalton rejected Avogadro's ideas outright, because:
1) he believed the concept of an "atom" became meaningless if it could be subdivided into "demi-atoms", and
2) interparticle repulsions made the proposed A_2 particle for gaseous elements too unstable (compared to the single atom A)

- because Avogadro's reasoning was seen as the only way to reconcile Gay-Lussac's results with atomic theory, Dalton consequently refused to accept the whole number ratios of Gay-Lussac's results

- Avogadro's hypothesis [which we now accept as correct] was generally rejected by the chemistry community for the following reasons:
1) Avogadro was an obscure chemist who did not do his own expts
2) his proposal required that indivisible "atoms" be divisible into demi-atoms
3) attempts to obtain a consistent set of atomic wts were

unsuccessful, so the value of his hypothesis declined

- at the time of his death (1856), Avogadro's ideas had been almost totally forgotten

More Problems with Chemical Atoms

- **Jons Berzelius** (1779-1848) became Europe's leading analytical chemist in the early 19th century and obtained good compositional data for many chemical compounds

- he was a strong supporter of Dalton's atomic theory; after Humphry Davy electrolytically decompose soda (to sodium and oxygen) in 1807, Berzelius proposed that atoms were held together by ***electrical charges, positive and negative***
- he argued that, in soda, the sodium atom had a +ve charge and the oxygen atom a -ve one; other stable binary compounds formed from the union of +ve and -ve atoms

- Berzelius also believed elements of the form A_2 could not be stable so he too rejected Avogadro's hypothesis

- Berzelius believed Dalton's iconic symbols for the elements were too ambiguous so he suggested the (latin) ***alphabetic abbreviations***, eg, Na, O, Pb that we still use today


Jons Berzelius

- many chemists, following Dalton's lead, consistently gave integral values for atomic weights, and in 1815 the English physician William Prout published his idea that:
1) all atomic weights were whole numbers, because
2) all elements were made up of hydrogen atoms

- ***Prout's hypothesis***, as it became generally known, was debated for the next century as it fell in and out of favour depending on accepted values for atomic wts
[how different is Prout's idea from our modern one that all atoms are made up of protons, ie, hydrogen nuclei??]

- Berzelius denounced Prout's suggestion because he found that his best expts yielded non-integral values for some elements, eg, in 1818 Berzelius published the following at wts

Mg 50.66 [24.31]   Cu 126.62 [63.55]
[Berzelius' values were off by a factor of 2 because of the H = 1 or 2 problem]

- the debate prompted several chemists to seek novel ways to determine accurate atomic wts:

1) Berzelius: calculated relative at wts by the usual method of measuring combining wts of binary compounds

2) Dulong and Petit: in 1819 published their observation that, for metals,

	Specific heat	x	atomic weight	≈ 6.1
eg, Cu	0.0949		63.3	6.01

this method was largely neglected because it had no theoretical basis and did not apply to non-metals

3) J.B.Dumas in 1826 revived an idea first suggested by Avogadro, ie, the ratio of the vapour densities of gases should be the same as their atomic wt ratios (on assumption that equal volumes contain same # of particles)

- Dumas developed good methods of measuring gas densities and obtained good values for gases whose gaseous forms were the same as their elemental forms, eg, oxygen, nitrogen, hydrogen, mercury, etc, but wildly different results for elements such as phosphorus (P_4 in gas phase) and sulfur (S_6, S_8, etc)

4) Mitscherlich in 1827 discovered that one element could be substituted for another is some crystalline substances, a phenomenon he termed ***isomorphism***

- he proposed that atoms of one element replaced all atoms of a second element in the crystalline structure, so the weight ratios between the two elements must equal their atomic wt ratios
eg, potassium sulfate [K_2SO_4] and potassium selenate [K_2SeO_4]

% composition [K_2SO_4]		% composition [K_2SeO_4]
K	44.83	35.29
O	36.78	28.96
S	18.39	35.75

and ratio Se:S =

- altho each of the above methods gave good values for some elements, their lack of generality and conflicting results led many to believe that chemical atoms of fixed relative wts did not exist, and belief in Daltonian atomism weakened after about 1830

Alternatives to Atomism

1) unconvinced of chemists' ability to conclusively demonstrate the reality of elemental atoms, Wollaston suggested in 1814 that chemists should use the term ***equivalents*** for the relative combining wts of elementary substances; such a change in nomenclature, he believed, could free chemists from concerns about the reality of chemical atoms

- Wollaston compiled a large table of equivalent wts, and promoted the use of a slide rule-like device which allowed the quick calculation of combining wts in reactions
- many chemists started to use the term equivalents in place of atomic wts after about 1820

2) Humphry Davy (1778-1829) refused to believe that the true number of chemical elements could be so high (~50 in 1810), and that methods would ultimately be found to reduce many elements to a smaller number (as he had done by decomposing soda to sodium and oxygen)

3) Michael Faraday (1791-1867) disapproved of material atoms altogether and favoured instead the suggestion of Boscovich that atoms were only the point centres of force fields (much like th magnetic fields he proposed around magnets)

- all the troubles with atomic weights and renewed skepticism about the reality of chemical atoms resulted in diminished support for atomic theory from about 1830 on

Return of the Chemical Atom

- in 1858, an Italian chemist, **Stanislao Cannizzaro** (1826-1910), published a paper which resurrected Avogadro's ideas and applied them to the determination of atomic weights

- while giving an undergrad lecture, Cannizzaro realized that the last point of division of a chemical element may not be in its pure elemental form, but instead when present in a molecule


Stanislao Cannizzaro

- then, by accepting Avogadro’s claim that elemental, gaseous hydrogen was H_2, Cannizzaro stated that the chemical atom of H, of wt = 1, would combine in compounds
- on this assumption he was able to generate a coherent and consistent table of atomic wts that i) included the common elemental gases as diatomic, ii) gave internally consistent molecular formulas, iii) made sense of Dumas’ gas density values, and iv) finally made sense of monoatomic, diatomic and polyatomic elements

- Cannizzaro’s paper made no impact, so he decided to present his ideas to a large meeting of 140 chemists held in Karlsruhe, Germany in 1860. Few attended his talk, so Cannizzaro handed out copies of his paper to everyone who would take a copy, and many read it on the train ride back to their hometowns
- one prominent chemist, Lothar Meyer, said that upon reading the paper, the scales fell from his eyes, and many others became converts to Cannizzaro’s, and thence Avogadro’s ideas

- within a year or two, atomic wts that were very close to modern values became widely accepted, and atomic theory came back into prominence. Within a few years, Avogadro’s remains were exhumed and reburied under a large memorial monument

- a consistent set of atomic wts resulted also in a consistent set of molecular formulas and soon ideas of molecular structure and geometry began to be discussed.

-1860 marks a major turning point in chemistry

Periodicity of the Elements

- as soon as a relative atomic wts began to be calculated, chemists began to notice interesting relationships

- in 1829 Döbereiner noted that several elements could be grouped into chemically-similar triads, in which the atomic wt of one member was an avg of the other two, eg,

Li
Na
K

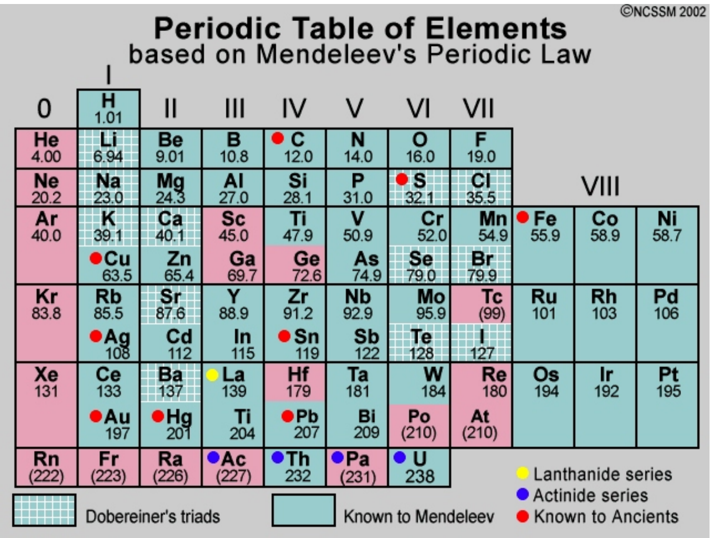
Ca
Sr
Ba

Cl
Br
I

- such relationships were judged to be meaningless coincidences until a consistent set of atomic wts became generally accepted (about 1860)
- in 1862 the French chemist de Chancourtois arranged the elements in a spiral helix by ascending atomic wt; each turn corresponded to an increase of 16 weight units, ie,

- in 1863, the Englishman Newlands published a table of elements with 8 columns containing elements of similar properties
- he believed this was analogous to a musical octave

- in 1869 the Russian **Dimitri Mendeleev** (1834-1907), constructed at able of 8 columns of chemically-similar elements [our groups IA-VIIA, and VIIIB]



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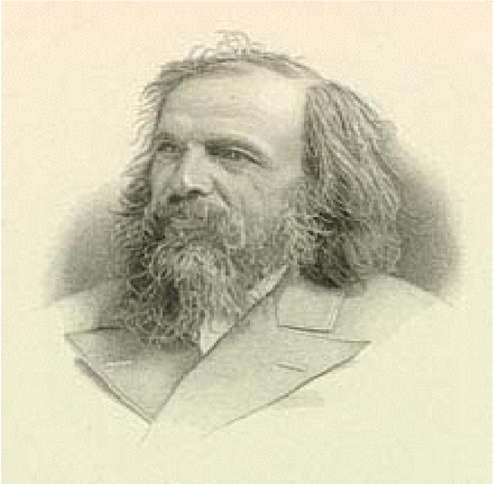
Periodic Table of Elements
based on Mendeleev's Periodic Law

0	I	II	III	IV	V	VI	VII	VIII		
	H 1.01									
He 4.00	Li 6.94	Be 9.01	B 10.8	● C 12.0	N 14.0	O 16.0	F 19.0			
Ne 20.2	Na 23.0	Mg 24.3	Al 27.0	Si 28.1	P 31.0	● S 32.1	Cl 35.5			
Ar 40.0	K 39.1 ● Cu 63.5	Ca 40.1 Zn 65.4	Sc 45.0 Ga 69.7	Ti 47.9 Ge 72.6	V 50.9 As 74.9	Cr 52.0 Se 79.0	Mn 54.9 Br 79.9	● Fe 55.9	Co 58.9	Ni 58.7
Kr 83.8	Rb 85.5 ● Ag 108	Sr 87.6 Cd 112	Y 88.9 In 115	Zr 91.2 ● Sn 119	Nb 92.9 Sb 122	Mo 95.9 Te 128	Tc (99) I 127	Ru 101	Rh 103	Pd 106
Xe 131	Ce 133 ● Au 197	Ba 137 ● Hg 201	● La 139 Ti 204	Hf 179 ● Pb 207	Ta 181 Bi 209	W 184 Po (210)	Re 180 At (210)	Os 194	Ir 192	Pt 195
Rn (222)	Fr (223)	Ra (226)	● Ac (227)	● Th 232	● Pa (231)	● U 238				

▦ Dobereiner's triads
🟦 Known to Mendeleev
● Lanthanide series
● Actinide series
● Known to Ancients



Dimitri Mendeleev

- Mendeleev’s innovation was to leave gaps in the table where elements of expected properties and atomic weight were unknown. Naturally others began to look for the “missing” elements
- in 1875, the element under Al was discovered and named gallium, Ga, and Mendeleev’s fame began

- there were many false “discoveries” of missing, or new, elements such as “canadium” in 1907 by Thomas French

Nelson B.C. Nov. 12th, 1911

"You will be pleased and may be surprised to learn that I have discovered and isolated a new metal of the platinum group — a noble metal. I have been following it up since May last. It is a beauty — certainly the whitest and most lustrous of all the white metals. [...] In the mean time I have lodged a specimen and a provisional description in the Royal Bank of Canada here in Nelson to safeguard me against any public anticipation, and show it to three friends, the banker, and my two partners, in some of the igneous dykes which produced it, and later on I purpose to send a specimen to the Royal Society in England formally announcing the discovery. [...] I have named it ‘Canadium’ in honour of the country where it had been found. It occurs along with platinum, palladium, and the other platinum metals in metallic grains and scales in igneous dykes in granite country. [...] It will push out palladium for search light mirrors, as it is more brilliant and easier to work, and it will do well for setting of diamonds, &c., in jewellery."

- discovery of the noble gases in the late 19th century led to a reorganization of Mendeleev’s table, but he remains the principal architect of the modern Periodic Table

More Trouble with Atoms

- chemists/physicists who studied the physical properties of gases in the mid 19th century found that all gases obeyed similar laws, such as the “ideal gas law”, which seemed to suggest that there was **not** much difference in the elemental atoms
- in 1860 Bunsen and Kirchhoff constructed a spectroscope and began to study the emission and absorption lines of chemical

elements; it was unclear to them how atoms could interact with light in such a unique way
- in 1864, Thomas Graham suggested that all the chemical atoms were no more than different energetic forms of a single nucleus
- later, Clerk Maxwell (of Maxwell's equations) suggested that atoms must have some form of vibratory component in order to selectively interact with light of certain wavelengths, so the solid, spherical atom of the chemists had to be an oversimplification

- the solution to this dilemma came with the discovery of electrons (ca1895), protons (ca 1919) and neutrons (1932), and other subatomic particles
- the course text gives a summary of the 20th century advances in atomic structure and theory (ppA27-A31); those pages are for your reading enjoyment only

- there are now more subatomic particles known than chemical elements, and the debate continues whether or not "particles" are the smallest unit of material reality, or whether atoms are merely spatial concentrations of energy, but chemists can work merrily away at the atomic level, content to remain "naive realists"