BONDING AND VALENCE

Fig. 1.

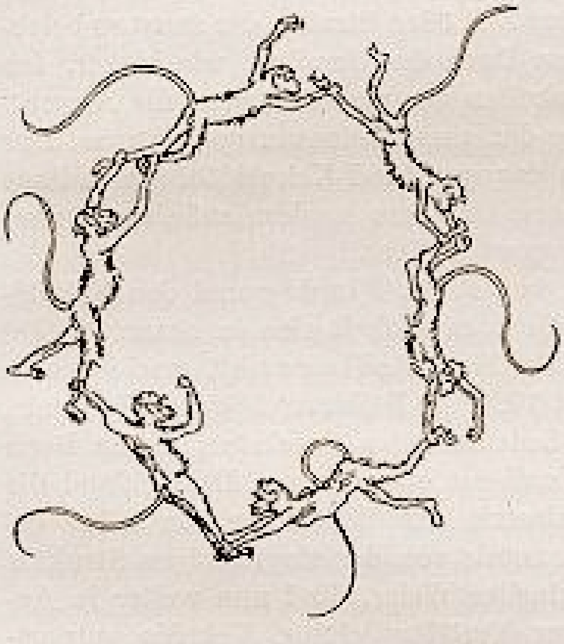


Fig. 2.

Early Ideas

- concept of a ***bond*** can only arise in an atomic metaphysics - what holds atoms together?
- mechanical links, eg, hooks & eyes, or entanglement of differently-shaped atoms was the only hypothesis until the mid 17th century
- Newton’s ideas of short-range forces looked promising for several decades but was eventually discarded
- Dalton proposed ideas only for inter-atomic repulsions (envelopes of repulsive caloric around atoms), and used prevailing notions of affinity for attractive forces
- the idea of elements as chemical atoms led to two competing proposals for the aggregation of atoms:

    i) radical theory, and ii) type theory

The Theory of Radicals

- up to about 1800, chemical ideas were based mainly on inorganic and mineralogical compounds, whose structures could be adequately explained in terms of ordered packing of spherical atoms or ions
- interest in organic compounds grew rapidly in the 19th century as many were isolated and found to be mainly composed of a few simple elements, especially, C, H, and O; novel ideas were needed to explain why similar atoms could produce such a wide variety of compounds
- in late 1790s the word **radical** began to be used for stable groupings of 'compound atoms', eg, in 1815 Gay-Lussac proposed that the <u>cyanogen radical</u> [CN] was a "compound, simple substance"
- soon other radicals were proposed, such as methyl, ethyl, amyl, benzoyl and cacodyl [$As(CH_3)_2$]
- such radicals were believed to behave similarly to simple atoms during compound formation and reaction, and the main difference between lifeless inorganic compounds and organic compounds (produced it was believed only by living things) was that organic compounds could contain stable poly-atomic radicals

- in the late 1820s, Justus Liebig defined a radical as:

1. The unchanging constituent of a series of compounds
2. Capable of replacement by simpler substances
3. When a radical is combined with one element, that element can be substituted by a second element

eg,


Justus Liebig

methyl•bromide + chlorine → methyl•chloride + bromine

- note that Liebig's definition avoids the use of the word 'atom'; a radical was a "package" of elements of constant composition, whether atoms or not
- as the above example shows, there was no fundamental reason why radicals could not be isolated in pure form, and there were several "successful" attempts to do so

- Herman Kolbe in 1849 reported the isolation of the radical "valyl" [C_4H_9], be electrolysis of a valyl salt, ie,

- in 1850, Edward Frankland reported the isolation of "ethyl" by the reaction of ethyl iodide with zinc, ie,

(note that the empirical formula of C_4H_{10} is C_2H_5)

- such [erroneous] isolation of organic radicals confirmed belief in stable organic polyatomic groupings of fixed, <u>but unknown</u>, architecture

- in the 1850s the tendency of certain radicals to have the same atomic formula, eg AB_3 or AB_5, was noted, and Frankland, for example, attributed the common formulas to the " combining power of the attracting element", see text p.B6

- this is the beginning of the idea of ***valency***
- adherents of radical theory were content to

Edward Frankland

specify the elemental composition of each organic radical: - the number and identity of the constituent atoms were enough to characterize each radical; the internal structure of a radical could not be established

Type Theory

- a competing theory of organic compounds was initiated by J.B.A. Dumas (1800-1884), who believed the most significant feature of organic compounds was the ***arrangement of atoms*** in the molecular framework
- he came to this conclusion after studying the very similar properties of acetic acid and chlorinated acetic acid

- he proposed that acetic acid was a member of a **chemical type**, all members of which had the same internal (unknown) architecture, but differed by substitution of the constituent atoms
- thus, Cl could be substituted for H in the acetic acid type without much affect on its properties

J.B.A. Dumas

- in type theory, the atomic framework of the type was the critical feature, not the specific atoms; in radical theory, the specific atoms were the critical feature, not the internal structure

- in 1850, Hofman and Williamson proposed two other organic types

the ***ammonia type***: comprised of NH_3, NH_2R, NHR_2 and NR_3
the ***water type***: composed of H_2O, HOR and ROR

- all members of these types were assumed to have the same basic architecture, altho the specific geometry was unknown

- a strong advocate of type theory was the Frenchman Charles Gerhardt, who used type theory to explain chemical reactions, eg, the formation of nitrobenzene from benzene and nitric acid

benzene + nitric acid → nitrobenzene + water
[C_6H_6 HNO_3 $C_6H_5NO_2$ H_2O]

- note the similarity to traditional double displacement reactions

- but Gerhardt argued that the <u>types themselves were not to be given a real existence</u> -they were only useful entities for understanding the changes that occurred during reaction (he was what philosophers call a "logical positivist" - someone who explains science only in terms of observable facts and without resort to metaphysical entities; most French chemists of his time were opposed to atomic speculation)

- in 1850 the Englishman Alexander Williamson interpreted ether formation in type terms, ie,

ethanol → ethoxide + methyl iodide → methyl ethyl ether

- in 1851, Williamson gave an atomistic explanation of types (he was not opposed to thinking of atoms as real) in which a central atom played a key role in "holding the components together" (see text p.B7); he viewed alcohols, ethers and acids as members of the 'water type'

Merger of Radical and Type Theories: the Chemical Bond

- a major chemical theorist was **August Kekulé** (1829-1896)
- building on Williamson's ideas, in 1857 he gave the name ***basicity*** to the combining power of the central atom in a radical or a type, and proposed
- elements could have a basicity of 1, 2 or 3, eg,

basicity = 1 (AB)   H–H, H–Cl
= 2 (AB_2)   O–H_2, S–H_2
= 3 (AB_3)   N–H_3, P–Cl_3


August Kekulé

- also, Kekulé suggested the units connected to the central atom could be further substituted to give "multiple types" such as

H_2SO_3

- Kekulé reinterpreted radicals as components of multiple types, and <u>merged radical theory with type theory</u>

- in 1858, Kekulé introduced a new type, the "***marsh gas type***", in which a central C atom had a basicity of 4 (see text p.B8)

basicity = 4 (AB_4)   C–H_4, C–H_3CN

- even more importantly, in 1858 Kekulé recognized that the carbon type could be substituted by other carbon types to form an extended linkage of carbon types - one of the earliest suggestions of extended C–C connections
- using Kekulé's bracket form of representation, ethane and ethanol were shown as:

- in these extended types, Kekulé concluded "it must be assumed that...the carbon atoms themselves are joined together" (text p.B9), altho he believed there was no way of determining their actual structures

- independently of Kekulé, the Scot Archibald Couper published a paper in 1858 in which he suggested that organic compounds are based on carbon atoms, which

1. combine in fixed "degrees of affinity" with other elements, and
2. combine with other carbon atoms

- Couper drew diagrams for ethanol and oxalic acid as below:

- note that Couper used lines for affinity links, and superscripts for number of interatomic links

- perhaps because Kekulé aggressively promoted his own ideas, Couper's contribution was largely ignored by the chemical community

- in1866 Edward Frankland used the word ***bond*** for the attractive force which held atoms together in types

- around 1870 chemists faced a dilemma
i) altho compound formulas suggested a need for atom-to-atom connections and molecular structure
ii) there was no idea how atoms (as solid spheres) could bond to each other in the necessary ways

Representations of Atomic Connectivity

- several methods were used for molecular diagrams that revealed the correct “basicity” of the constituent species and gave the correct empirical formula, but without any concept of the nature of a bond
- as above, Couper used lines to represent units of basicity

- Loschmidt (1861) used touching and overlapping (for multiple bonds) circles, eg,

allyl alcohol
[CH_2=$CHCH_2OH$]

- Kekulé initially used ‘sausage’ formulas

acetic acid
[CH_3COOH]

- Frankland also showed bonds as lines, in what he termed <u>graphical formulae</u>

Fe_2Cl_6

- recognize that these different representations were designed to maintain an atom's 'basicity' and make sense of a molecular formula, but were not meant to reveal molecular structure, and did not ***explicitly*** require the reality of atoms

Molecular Structure

- the Russian Aleksandr Butlerov in the 1860s argued in several papers that <u>every chemical compound had a unique and definite structure</u>, and by about 1870 chemists generally came to accept that molecules must have a specific geometry; how this was determined will be covered in **Stereochemistry**

- even though chemists accepted that most chemical compounds formed according to the 'basicities' of the constituent atoms, there were several troublesome compounds that appeared to have atoms of variable 'basicities', or valences

Variable Valency

- Kekulé argued that the "atomicity" [= valence] of an element was a fixed property of that element
- he believed apparent variations could be explained by multiple bonds, eg for N = 5

NH_4Cl NH_3

- this was not a good, or general, solution and chemists began to accept that most elements could have ***variable valences*** and, in general, elements in groups V-VII of the periodic table could have valences of 'n' and '8 - n', eg,

group V = V and III eg, N = 5 and 3
VI = VI and II eg, S = 6 and 2

Unsaturation

- an even more challenging problem than variable valences was unused valences, as in a compound such as C_3H_6; how could unused valences be included in a structure?

Possibilities =

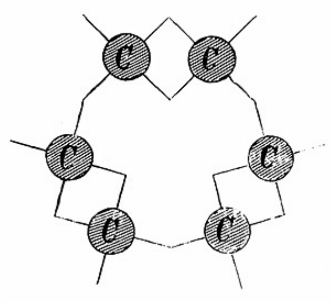
- the structure with unused valences on adjacent carbon atoms was judged to be the most likely, but it was difficult to explain why such compounds could exist in a stable form

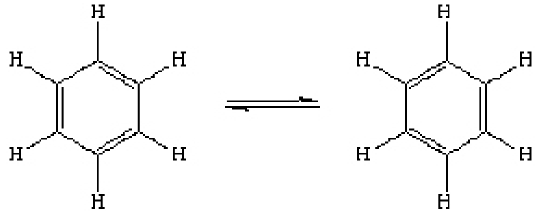
- in 1885 Baeyer, who had studied 3- and 4-membered carbon rings and explained their reactivity as a consequence of “ring strain”, suggested unused valences on adjacent C atoms could be interpreted as a two-membered ring with a large strain energy, ie,

- but the most common, and perplexing, example of unused valences was in benzene. It was difficult to think of a structure for a compound that consisted of 6 C and H atoms, had 8 unused valences, but was very stable and existed in only one form

- while dozing one evening in front of a fireplace, Kekulé dreamed of a snake coiling around to bite its own tail and awoke to think that a chain of carbon atoms could do the same thing - thus was born the idea of 6 C atoms in a ring, each with one unused valence and his first diagram for benzene (1865) had adjacent carbon atoms sharing two valences (see below)

- within a year Kekulé realized that the “double bonds” between adjacent C atoms could not be localized in one place since all C atoms had to be structurally equivalent, and in 1866 he published his two interconverting structures for benzene


Kekulé’s 1st structure



Kekulé’s 2nd structure

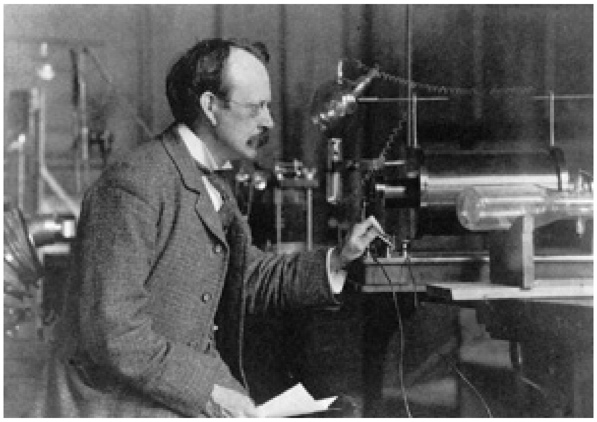
- altho the alternating double bond description could rationalise valency requirements, it did not explain why benzene did not undergo normal C=C reactions, whereas C_8H_8 did
- up to the end of the 19th century theories of valency gave only partial answers to bonding in organic compounds, and were especially incomplete for ‘unsaturated’ compounds

The Electron Pair Bond

- J.J. Thomson’s discovery of the electron in 1897 brought revolutionary change to chemistry, even though chemists originally saw no role for the electron in chemistry

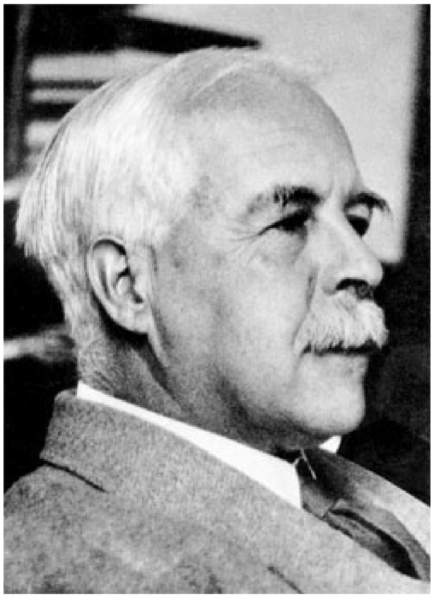
- Thomson proposed the “plum pudding” model of the atom,in which electrons were embedded within the atom’s core

- in the early years of the 20th century, Ernest Rutherford

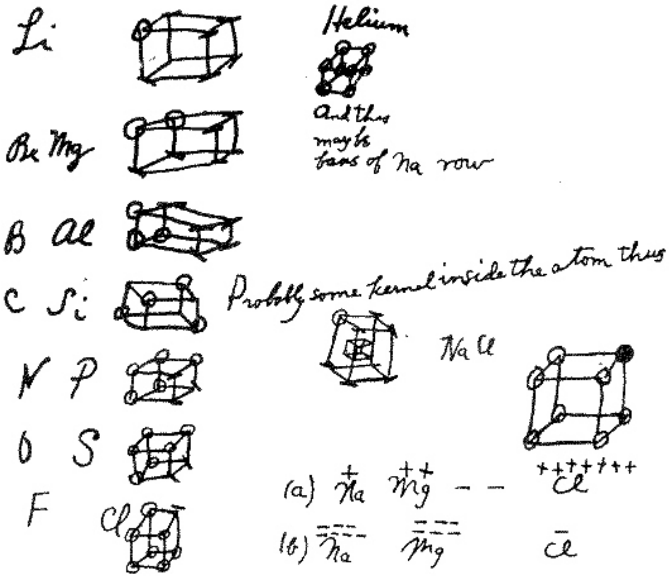

J.J.Thomson, 1856-1940

discovered that atoms consisted of a very small positive nucleus surrounded by orbiting electrons, much like a miniature solar system

- in 1902 an American chemist, **G.N.Lewis,** first envisioned that electrons could be responsible for atom-to-atom bonding if each atom contributed one electron to a mutually-shared pair. He didn't publish his proposal until 1916 when he had become more confident of his idea
- Lewis believed that electrons could occupy the 8 corners of a cube around a central atom, which enabled him to picture the electron structure of the first row of the periodic table



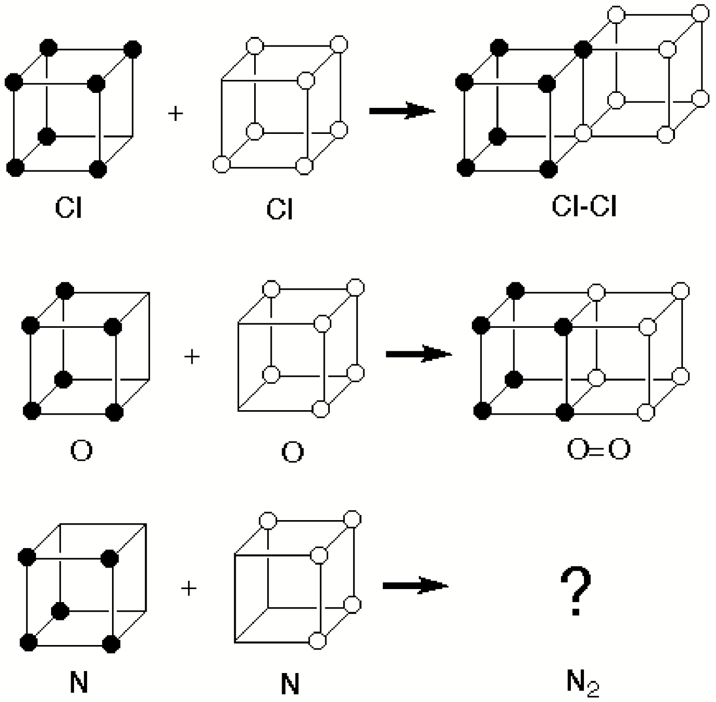
Gilbert Newton Lewis
1875-1946



Page from Gilbert's notebook, 1902

- Lewis then proposed that atoms could bond with each other by contributing one electron each to a shared electron pair
- both bonded atoms retained their cubic electron arrangement

- -Lewis proposed that a single bond involved edge-to-edge sharing, a double bond involved face-to-face sharing but a triple bond could not be incorporated into the model, ie,



-Lewis recognized that his model was incomplete, and that it was most unlikely that electrons could be positioned in a stable cubic arrangement, but it was a model that led him to appreciate that the key to his bonding picture was the two-electron shared bond, and the cubes were unnecessary

- he then moved to his second bonding model, in which two electrons were shared between two bonded atoms, and he began to use ‘electron dot’ diagrams, which could be used to depict single, double and triple bonds, ie

$CH_3CH{=}CHCN$

- Lewis extended his bonding theory further to explain polar bonds (unequal sharing of the electron pair) and inductive effects

- Lewis’ electron-pair theory of bonding was applied to elements beyond the first two rows of the periodic table by another

American chemist, Irving Langmuir
- Langmuir was a very effective speaker who constructed a general bonding interpretation based on the two-electron bond and became the recipient of the Nobel Prize in 1932 (see quotes in text, p.B24-B25); the omission of Lewis is one of the greatest injustices in Nobel Prize history

Troubles with the Electron Pair Bond

- localized electron pair bonds provided adequate explanations for most compounds, but not all
- in 1924, Arndt explained the polar character of γ-pyrones by proposing two interconverting electronic forms, ie,

- in the 1930s, ***Linus Pauling*** introduced the concept of ***resonance***, in which forms such as the two γ-pyrone structures had no independent existence but were merely contributing representations of a single resonance electron-delocalised structure

- in 1924, the physicist Louis de Brogli extended the wave-particle duality of light to all particles, such that


Linus Pauling, 1901-1994

where λ = wavelength, h = Planck's constant, m = mass and v = velocity

- according to de Broglie, all moving particles could be treated as waves, and electrons, being the lightest particles then known, were well suited to wave interpretations

- Schrodinger extended the wave principle to electrons in atoms mathematically and produced wave equations, ψ, whose square, ψ^2, could be interpreted as electron density (electron as wave) or a position probability (electron as particle)

- chemists have since expanded Schrodinger's wave mechanics to bonding (and antibonding) orbitals, in the process delocalising an electron's position over several atoms, in some cases even over an entire molecule

- in wave mechanics, a two-electron bond is depicted as a molecular orbital that encompasses both bonded atoms
- but chemists still use the simpler Lewis electron dot diagrams to illustrate electron positions, eg for NaCl

- the resonance arrow, ↔, has been adopted to represent extremes of electron positions (position probabilities), no one of which has a real existence

- in modern chemistry, the two-electron bond is no longer seen as being fixed between two atoms, but as a distribution of electron density over two or more atoms, and electrons can be described as particles or waves
- maybe the early Greek philosophers had it right two thousand years ago (!)