A Short History of Chemistry

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What are the major discoveries in Chemistry, who are the mayor players? When it comes to (classical) music, ten composers cover most of it that deserves to be part of the indispensable culture, when it comes to painting let us say a hundred might be necessary, and as to literature, maybe a thousand. What about mathematics, physics and chemistry? Here the situation may be thought of as more complicated as many minor workers, if not individually at least collectively, have contributed significantly to the discipline, and this might be particularly the case with chemistry, which more than mathematics and physics depends on tedious work carried out by armies of anonymous toilers in laboratories. But Chemistry is not just routine work but as any science depends on daring hypotheses and flights of fancy to be confronted with an unforgiving empirical reality. Who are the Gausses and Eulers of Chemistry, to say nothing of a Newton. Is there in analogy with Bell's 'Men of Mathematics' a corresponding compilation of chemical heroes? In one sense there is, names such as Scheele, Priestley. Pasteure, may be more well-known to the general public than Gauss, Euler or Lagrange. On the other hand a mathematician taking part of the cavalcade is invariably a bit disappointed, none of the names mentioned and lauded, seem to have the same luster as the kings of mathematics, instead diligence and conscientious steadfast work seems to carry the day. In one way it is unfair, in spite of mathematics supposedly being the least accessible of all the sciences, literally it is the opposite, being entirely cerebral. The accomplishments of a mathematicians are thus far easier to convey faithfully than that of an empirical chemist doing his work in the laboratory, because in retrospect it all seems so easy, but in practice it is a matter of a tacit skill that makes it possible, and which is very hard to verbally describe.

Now chemistry has roots going back to pre-history. It concerns basically metallurgy and herbs, the former for practical work, the latter for health. As to the former there was definite, if slow, progress, as to the latter mostly a stumbling in the dark. Then there was a long period of alchemy. It is not considered as science by us in retrospect, as it did not produce any results, nor any development, but the real reason for the latter was that it was not accompanied by any building of theory, only wishful parodies of the same, and thus not subject to inquiry and subsequent modification. Thus the failure of alchemy gives the lie to the optimistic belief that unprejudiced observation can give us knowledge. But alchemy nevertheless did leave traces and had an influence on subsequent developments as has been pointed out[1], after all the modern laboratory along with its equipment is a more or less direct outcome, as well as the usual routines of mixing and heating and collecting outcomes in vessels and retorts of funny shapes. While the alchemists were driven by a narrow obsession, their successors more by general curiosity. Thus there was a relentless mixing of different entities, it would be premature to refer to them as chemical compounds,

[1] As by e.g. Stephen Toulmin in the 'Architecture of Matter' reviewed earlier

and subsequent heating to observe the results of the reactions, some of which rather violent (the allure of many a school-boy). There are a couple of implicit assumptions guiding the work, and which no doubt have a long pedigree. First there seems to have arisen a certain primitive algebra in which the original constituencies are on the left, and the resulting on the right (maybe in an Arab world it would have been reversed). So if $(A+D)+B = C+D$ and $A + B = F$ then $C = F$. One conclusion of this primitive algebra is the idea that matter may decompose into constituencies, the heart of chemistry. The idea as such is of course old, already the Greek spoke about the primitives of Earth, Water, Fire and Air (with Ether thrown in as a 'joker'), but this was only on a metaphysical level, they had no idea how to make the synthesis in general, not even how to start. But as Popper notes, metaphysics is indispensable to science. The next step was quantification, that the mass before the reaction should be equal to the mass after. Both those assumptions referring to a closed system, a crucial notion in any systematical experimental setting. Now closed systems are easily imagined, but harder to realize in real life, and part of the skill of a successful experimenter is to realize them, meaning to keep materials free from unintended impurities and keep track and contain everything which ensues.

As to early successes we may point out Boyle, a gentleman scientist mainly know for Boyle's law[2], stating that under constant temperature of a gas, its volume and pressure are inversely proportional. This is a beautiful quantitative law, which may be thought of as more physical than chemical, but chemistry depends crucially on physics and the general gas laws would turn out to play a crucial role in future chemistry. Its significance was that it held for all gases, and also that it could be explained by the atomic theory, another metaphysical legacy of the Old Greek. In fact the atomic theory would more or less be accepted as default by the 17th century. Newton was a proponent of it, claiming that the forces between atoms, whether attractive or repulsive, would provide an analogy with the celestial setting and maybe explain the properties of matter. Now with the atomic theory of Chemistry old Pythagoras was dusted off again, as the integers would play an important role, and hence rational proportions, as opposed to the continua of space and time, which are not made up of small entities.

The study of gases was fundamental to the development of chemistry, as in this case some fundamental principles are more easily laid bare. Among the early experimentalists Cavendish stand out. He was a master of the exact quantitative measurements, which would be so important for the subject. As many scientists during the age he did not confine himself to one discipline but ranged freely, known also for the first determination of the gravitational constant, which made the weighing of the Earth, as well as the Sun, possible. He was followed by the discoverers of Oxygen, Priestley and Scheele in the 1770's. Scheele was the first, as inspection of his note books reveal, but Priestley was the first to publish. Scheele also have a long list of mostly organic compounds discovered. Throughout the second part of 17th century and most of the 18th, the theory of phlogiston held sway over the minds of chemists. Cavendish believed in it, Priestley and Scheele as well. It was introduced by the German Becher and would in retrospect be viewed as a virtual element, especially as closer inspection revealed that it would have negative weight. It

[2] Actually the law seems to be due to Hooke, maligned and belittled by Newton, and hence never given his proper due.

was intimately connected with combustion, and the theory was only discarded when the brilliant French chemist Lavoisier finally clarified the chemical process of combustion and its relation to oxygen, thus effecting the first modern breakthrough in chemistry.

The early 19th century was devoted to the task of establishing the atomic view of matter and the concomitant Pythagorean principle of rational relations with small denominators. The first name to mention is Proust who spoke about *pondere et mesura* referring to balances and identifying different oxides of metals, depending in retrospect on the number of oxygen atoms attaching to the metal atom. His views were challenged by his older colleague Berthollet who denied those specific combinations and instead claimed that there was a continuous scale. Proust countered with the distinction between a compound and a mixture (*mélanges*) and of course posterity is on the side of Proust, but that does not prevent Berthollet from having many good ideas. There would then be a slew of different chemists establishing fixed proportions, but the definite breakthrough of the atomic point of view had to wait for Dalton. With that theory the basis for the fixed proportions was given and by that also the means and motivations to find out the explicit numbers. Chemistry as we know it, would be impossible without the theory of atoms, which, however, remained controversial throughout the 19th century, and still at the end of that century the physicist-philosopher Mach argued against their physical reality and for their status as just a convenient fiction. Einsteins clarification of Brownian Motion was partly motivated to prove Mach wrong. To return to Dalton and his times, the basic postulates were that atoms of the same elements all had the same weight, and different weights meant different elements, so in principle a chemical element was characterized by the weight of its atoms. Furthermore in compounds atoms combined in fixed numerical relations. Those were postulates that was never stated by the Greeks. From now on the atomic theory ceased to be a metaphysical speculation but a falsifiable scientific theory with specific quantitative implications to be tested. Thus Dalton managed to compute those weights for the common elements, in terms of the lightest known - the hydrogen atoms. He also invented symbols for them, circles marked in different ways which allowed the representations of compounds as combinations, a forerunner to the more modern terminology. Needless to point out Dalton made many mistakes, e.g. in modern terminology he suggested the chemical composition of water to be HO.

The next breakthrough in chemistry was effected by its connection with electricity, more precisely electrolysis in which compounds could be dissolved into their components, which would wander to different poles depending on their charges. Herein the embryo to the modern theory of chemical bindings being electrical ones is to be found, The pioneers[3] were Davy in England and Berzelius in Sweden, their theories were similar, but where they differed, Berzelius was right. The latter was probably the most distinguished chemist of the first half of the 19th century, who in addition to introducing our modern terminology also computed atomic weights more or less in agreement with modern findings, and great advance from the rather primitive efforts of Dalton. As to gases Boyle's law holding under constant temperature had been extended in another direction by Guy-Lussac by

[3] To those should be added Cavendish, but his contributions to the electrical theory of chemistry only came to light long after his death, as he published only a fraction of what he discovered, being independently wealthy to a spectacular degree, thus there were no compelling reasons to obtain funds.

showing that the product of pressure and volume for a fixed (ideal) gas is proportional to the temperature. Furthermore Guy-Lussac had claimed that equal volumes contain equal number of molecules. This led to paradoxes, if one volume contained n oxygen particles and another equal volume contained n nitrogen particles, they would combine to n particles of nitric-oxide but occupying twice the volume (as volumes like masses should add). This paradox was solved by Avogadro, although his solution was ignored for some time, by noting that molecules of oxygen and nitrogen consist of two atoms. In short $O_2 + N_2 \rightarrow 2NO$. Avogadro's number make sense because of the claim that gases of equal volumes and pressure contain the same number of molecules. To determine it is quite another thing.

There is a classical division in chemistry between organic and inorganic chemistry and a fundamental discovery was that there was no essential difference between them, they were all built up by atoms, but in the organic case the compounds were much more complicated. Berzelius was a pioneer, as in so many others things having to do with chemistry. Another one was Chevreul, who was blessed with a long, vigorous life up to the age of (almost) 103 (1786-1889), and who clarified the chemical composition of many organic elements, in particular that of soap. A long list of contributors can be given stating with Gay-Lussac, Thenard, Dumas, Liebig, Wöhler, Bunsen. For the first time really, the scientific revolution reached into the quotidian life of people in general, and chemistry actually started to go beyond the old dream of transformation, as was the ambition of the alchemists, to that of creation. Thus for the first time really, you could do inventions in chemistry, to make up new compounds with new tailor-made properties, and thus change the world for better of for worse, something which has dominated science since then. Liebig, later ennobled to von Liebig, is a point. To him chemistry was applied chemistry, and he in particular concentrated on agricultural improvements. Wöhler was a colleague with whom he often collaborated and instigated the theory of radicals, in particular singling out Benzoyl and Ethyl, with Bunsen continuing the work. The theory is a first step in understanding the hierarchical composition of compounds, that combinations of atoms may form stable structures, which in their ways acts as irreducible components. Incidentally Wöhlers was the first to show that organic molecules (in his case urea) could be created from inorganic ones, thus that there is no vital force, the living being made out of the dead. Wöhler also identified a number of basic elements, a classical line of investigation among fundamental chemists.

In order to do inventions in chemistry, you need to know how chemical reactions works, to be able to predict what will happen when two compounds interact. What happens is not clearcut but will have to be inferred. Modern students are just told about it and hence do not appreciate how much goes into figuring it out. One first step was taken by Dumas with his theory of substitution. He posited three laws.

i) Any substance containing hydrogen when submitted to the dehydrogenating action of chlorine, bromine, iodine or oxygen etc, for each atom of hydrogen it loses it gains an atom of chlorine, bromine, iodine or half an atom of oxygen etc.

ii) The same rules holds good if hydrogen is replaced by oxygen

iii) If the hydrogenized body contains water, it loses the first hydrogen without replacement and then reduces to the first law.

As an example of the first he suggested the action of chlorine on acetic acid. In formulas

$$C_4H_4O_2 + 6Cl \rightarrow C_4HCl_3O_2 + 3HCl$$

and as to the third he considered chlorine acting on alcohol $C_8H_{12}O_2 = (C_8H_8{+}2H_2O)$ giving rise to

$$(C_8H_8 + 2H_2O) + Cl_4 \rightarrow C_8H_8O_2 + H_4Cl_4$$

and then to

$$C_8H_8O_2 + Cl_{12} \rightarrow C_8H_2Cl_6O_2 + H_6Cl_6$$

The important thing was that by this substitutions the chemical properties of the compounds were not changed, and Dumas proposed the notion of chemical types differing by such substitutions but otherwise the same. The proposals by Dumas were attacked by Berzelius, the former had support from Liebig who was becoming the great authority in Chemistry replacing Berzelius. To give an example. Malaguti has proposed

$$(C_8H_8 + 2H_2O) + Cl_8 \rightarrow (C_8G_4Cl_4 + H_2O] + H_4Cl_4$$

according to Dumas rule. Berzelius preferred instead (as he wrote things) to write the resulting compound as $(C^4H^6O{+}C^4Cl^4)$ which had a total different structure. There were also other strange formulas for which he was entirely guided by mere instinct, claiming that he could recognize a wrong formula, even if he did not knew the right one, in the same way as the ear apprehends a wrong note or one recognizes a bad form in social life by feeling rather than by reason. An assistant of Dumas made an experiment to show that Berzelius was wrong, which made the latter make some modifications, converging to an acceptance of Dumas substitution, yet with some ideas which contained an important germ of truth. As we see knowing the atomic components do not determine the structure, and such was to a large extent based on intuition i.e. guesswork. Only the patient accumulation of a large number of formulas would make the pieces of the puzzle congeal. Another attack on the authority of Berzelius was done by Graham studying various phosphoric acids, which was further developed by Liebig.

Two brilliant chemists stand out in the first half of the 19th century, Laurent and his disciple Gerhardt, both dying prematurely and shunned by their contemporaries, and their true achievements only recognized posthumously. Gerhardt is notable for his homological series, especially alcohols, showing how they can be built up inductively. He also identified four basic inorganic molecules, (he was a pioneer as to the notion of molecules meaning fixed combinations of atoms), which could be used as building blocks in creating more complex compounds, especially the organic one. Thus he more than anybody else recognized the different level of structures when it comes to compounds, a sentence is not made up of letters, but words and subsidiary sentences, thus a compound should be thought of as made up of 'words' of atoms. This made the structure of compounds more transparent and simplified the combinatorial problem. Gerhardt also recognized that the mass formulas of compounds were too simple, the same atoms could be made into entirely different compounds due to how they were fitted together in space, but he despaired of there being any ways of founding out, X-ray diffraction still being in the future. And even now, the determination of structure is very diffucult. Still there was a lot of confusion about atomic weights, much clarification was achieved by Cannizzaro who was the first to really appreciate Avogadro and consistently apply his principles.

The theory of valences started slowly to emerge, among the pioneers were Kolbe (working in the tradition of Berzelius, even when the latter had been rejected), Frankland, and Blomstrand. It was sometimes thought that the valency was constant, while others recognized that it could vary. In this context the notion of multiple bounds occurred, The first really structural presentation of a compound was given by Kekulé in his elucidation (supposedly inspired by a dream) of benzen as a hexagonal ring of carbon atoms, double bounds alternating with simple. The spatial configuration of some simple compounds were being guessed at, especially carbon compounds tetrahedrally arranged, this allowed mirror images, and other reversions, and was manifested by different optical properties. Pasteure, mainly known as a micro-biologist, was here a pioneer, his work extended by Van' Hoff.

At the end of the century the ability to design complicated molecules arose, which had momentous consequences as to commercialization and effects on quotidian life. Chemistry became an applied science *par excellence*. This was mostly a German tradition, and names like Beyer, Fischer and Meyer should be brought forward.

Physical chemistry, meaning chemistry of general elegant principles, as such we encounter in physics and hence being amenable to mathematical treatment, has a history going back to the 18th century, even the 17th if such things as Boyle's law should qualify as chemistry. Lavoisier was the first who clearly enunciated the invariance of mass in chemical reactions, and together with his compatriot the mathematician and celestial mechanic Laplace, laid the foundation for thermochemistry, by noting that the heat produced by a reaction is equal to the heat absorbed by the reverse. This lead to questions about speed of reactions and equilibria, notably by the Norwegians Guldberg and Waage, who stated the law of mass action. If we have two compounds A, B with a tendency to change to A', B' then the force, or rather as later specified by Van't Hoff, the velocity with which the reaction occurs is proportional to the concentration p, q of the compounds with an affinity constant k as constant of proportionality, Thus $v = kpq$. Similarly for the reverse process $v' = k'p'q'$. Equilibrium is attained when $v = v'$. By determining k and k' equilibria could be predicted. Another feature of physical chemistry pertains to solutions and osmotic pressures, which can be thought of as completely analogous to the gas laws. And finally the behavior of ions in solutions as studied by Arrhenius, later clarified by Nernst, leading to low temperature physics.

Everyone knows about Mendelevs Periodic Table, and his ability to predict chemical properties of missing elements, but the idea of periodicity predates his proposal, which was also presented by the German Julius Meyer at about the same time. The story of Mendelev is a romantic one, born as the 14th child to a poor Siberian schoolteacher, taken by his mother on a long trek to Moscow in the hope that he would enter the university. He was denied entrance but in St-Petersburg he was admitted to a teachers college.

The final chapter deals with the great revolution in natural science of the early 20th century, with the discovery of radioactivity, quantum theory and the inner workings of atoms, allowing an explanation of valency. Nowadays chemical reactions can in principle be determined from first principles, but of course not in practice, thus in effect unifying chemistry with physics.

The book as such is too much of a catalogue, giving a through documentation of important chemists with thumb-nail biographies and short descriptions of their work. However, there is no attempt at providing a narrative, of pointing out what was important and how the subject really has developed. Hence it is rather difficult to retain its contents after one has plowed through it.

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