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Liebig and Wöhler and the concept of isomerism

(1) Introduction

These two great scientists, Justus von Liebig and Friedrich Wöhler, have many resemblances: both were German, lived in the same period, were in their youth disciples of two brilliant chemists and had important works in organic chemistry. *Nevertheless, the most important connection point in their lives was another one.*

Liebig in 1822 was in Paris working with Gay-Lussac, whilst Wöhler was in Stockholm with Berzelius. Liebig learned there how to analyse organic material and so he determined the composition of an explosive, silver fulminate. At that time Wöhler analysed silver cyanate. The problem arose when the results of both analyses were identical, although corresponding to compounds with different properties.

(2) The story within the history

The main chapters of this story are as follows:

Chapter I

Starting point: The twenties of the nineteenth century, when a second generation of important chemists begin to emerge as disciples of the great masters of chemistry of those days. That is the case of Liebig and Wöhler.

Justus von Liebig (1803-1873) was born in Darmstadt, a city in the state of Hessen-Darmstadt (Germany), in a middle-lower class family, being his father a dealer in drugs, dyes and chemicals. Maybe this fact led him to a chemical career. In 1817 he was withdrawn from the *Gymnasium* (grammar school) due to increasing poverty of his parents, affected by the general economic depression after the Napoleonic wars. Then he was apprenticed to a pharmacist ... but only during six months. Probably his family could not afford it or perhaps the detonation of an explosive (silver fulminate) he had prepared at home was the real cause.¹

After that, Liebig attended Bonn and Erlangen Universities, as assistant of the Prof. **Karl W. Kastner** (1783-1857), with whom his father had a relationship. Thus, he studied chemistry, as well as French, Latin, mathematics and botany, being so brilliant that in 1822 he got from Erlangen faculty an honorary degree *in absentia* (however, curiously, he never presented a thesis for his doctorate). It was also in this year when Liebig obtained from de Grand-Duke of Hessen-Darmstadt a travel grant to study in Paris.

Now a new chapter of our story comes.

Chapter II

Paris had in that time an intense scientific activity, being leader of European science. So it was with chemistry: many important chemists — such as **Proust, Dulong, Chevreul, Gay-Lussac** or **Thenard** — carried out in this city an intense research activity.

Liebig learned from Thenard and Gay-Lussac how to analyse organic materials, and was admitted to the laboratory of the last one. So he could continue his studies in fulminates, the explosive of his childhood, applying those new techniques to the analysis of *silver fulminate*, as he named this material,

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¹ See W.H. Brock, *The Fontana History of Chemistry* (1992), pp.199–200.

considering that it was a silver salt of an unknown acid (fulminic acid). He finished the analyses (HOCN) and published them together with Gay-Lussac in 1824.

In this period, other young German chemist, **Friedrich Wöhler** (1800-82), was in Stockholm, trying to learn analytical techniques in home laboratory of Berzelius. He worked in the analysis of cyanates, one of his first researches that some years later, in 1828, would led him to his famous synthesis of urea. He analysed a silver compound, *silver cyanate*, concluding that it was a silver salt of another unknown acid (cyanic acid) And, on his turn, he got in those analyses the same results (HOCN) than those of Liebig. Then, one of these two analyses must be erroneous! And one of these two chemists must be a bad analyst!

Who of both young men was right? Liebig, pushed by his aggressive character, accused Wöhler of erroneous results. Liebig repeated carefully the analysis if silver cyanate, verifying they were correct (1826). Then he openly admitted that he was mistaken in his first judgement And curiously this was the starting point of a deep friendship between the two scientists, which after worked jointly in many researches.

Chapter III

Both chemists were right! In consequence, immediately a *dilemma* emerged: *Two compounds with many different properties had the same composition*. But, according to Proust's law, this was not possible: in those days the law of definite proportions was completely accepted, so it was assumed that the properties of a substance were correlated with its composition.

Chapter IV

Which was the reason why compounds with identical composition would have different properties? Some years before Gay-Lussac had attributed the difference in properties to different arrangement of the elements. The same opinion also had other chemists.² But really no explanation for this fact could be found. And it is at this point when one of the greatest chemists of that century entered: it was **Jöns Jacob Berzelius** (1779-1849), the Swedish chemist with whom Wöhler had been working.



He admitted that the composition of cyanates and fulminates was the same, although having different properties. And in the following years he collected more examples of that fact, such as:³

- In 1825 Faraday have studied the oily material obtained as by-product in the preparation of illuminating gas by heating whale oil. From that material Faraday isolated two products: one of them was liquid, benzene (C₆H₆) and the other, the more volatile portion, was a gas. The composition of this gas was the same as that of the very well known olefiant gas (although containing twice the number of atoms), but the densities were different (the double in the first case). Nowadays we know that those gases are, respectively, *isobutylene* (C₄H₈) and *ethylene* (C₂H₄).
- In 1822 Berzelius knew the existence of two different *oxides of tin* with the same composition. And also two forms of *phosphoric acid* whose composition was identical (1825).
- In 1828 Wöhler obtained *urea*, which had the same composition than ammonium cyanate, but different properties (CH₄N₂O).
- It was observed that *sulphur crystals* could have different forms (monoclinic or rhombic), according to the way of preparation (Mitscherlich, 1823).⁴
- It was known that *diamond* and *graphite* were carbon.
- *Aragonite crystals* and *calcite crystals* were both calcium carbonate. And *iron pyrites* and *marcasite* were iron disulphide.
- It was discovered (about 1826) that *tartaric* and *racemic acids* had identical composition but some different properties.

² See A.J. Rocke, *Chemical Atomism in the Nineteenth Century* (1984), pp. 168–169.

³ See J.I. Ihde, *The Development of Modern Chemistry* (1984), pp. 170–173.

⁴ See T.H. Levere, *Affinity and Matter* (1971), pp. 153–154.

With all this data in mind, Berzelius devised a system that could cover all these cases. However, the case of cyanic and fulminic acids was the one that led him to the recognition of **isomers**. And so, the end of our story comes now, with this the conclusion:

(3) Emergence of isomerism

In 1831-32 Berzelius proposed the concept of *isomerism* and the concept of *isomer* (from Greek, compounds with equal parts). That is to say: compounds with the same composition but different properties. He distinguished several variations:

Polymerism: when the relative numbers of atoms in two compounds are the same but the absolute numbers are different (e.g. olefiant gas and isobutylene).

Metamerism: when the isomers have different constituent parts.

Isomerism: when the compounds have the same composition and molecular weight, but different properties.

Berzelius proposed the term of *allotrope* some years later (1841) for the different forms of an element (e.g. diamond and graphite). And the term *polymorphism* was used for the case of compounds that occurred in more than one crystalline form.⁵ However, nowadays this term metamer has lost its usefulness and the one of isomer is only one employed.⁶ For him the reason of isomery was due to the fact that the atoms that integrate the substances could unite in different ways. This idea, which can be understood by means of the atomic theory, represents the beginning of the *structural chemistry*, opening the way to the establishment of structural formulas.

The concept of isomer is very useful in chemistry, mainly in organic chemistry. From that it can easily be understood why there can be so many organic compounds just by combining very few atoms (C, H, O, N) but in many different ways.⁷ Thus organic chemistry became clearer because it was possible to do a classification of its compounds and understand their structure. On the one hand, organic chemistry was not a so “dark forest with few or no pathways” anymore, according to the words of Wöhler himself. On the other hand, that concept supposes a basic idea: the importance of the constitution of molecules, because it is the last cause of chemical properties of compounds. And the research of Liebig and Wöhler about silver cyanate and silver fulminate was the starting point for Berzelius’ idea.

Thus apparently incorrect results contributed to build a new doctrine in chemistry and, in turn, a small conflict led to long research collaboration.

Something more about Liebig’s life

During his stay in Paris he met the famous geographer Alexander von Humboldt, who recommended him for an academic position in the University of Giessen (1824). In 1852 he moved to the University of Munich where he remained until his death (1873). In Giessen he taught chemistry during twenty-eight years and built up a teaching and research school of chemistry. His reputation was so great that he received students of the entire world to learn practical chemistry, mainly analysis of organic compounds as well as qualitative and quantitative analysis. Liebig improved extremely the organic analysis, but he worked also in other fields of chemistry. He is considered the founder of agricultural chemistry because of his experimental studies on artificial manures. On physiological chemistry he devised an effective method of producing extract of meat from carcasses, the manufacture of which began in 1865.

On the other hand, he was a prolific writer and since 1832 he became the editor of a journal of chemistry, *Annalen der Chemie und Pharmacy*.

Due to all his merits, he became baron (Freiherr) in 1845.



⁵ See J.R. Partington, *A History of Chemistry* (1962–1970), vol.IV, pp. 256–259.

⁶ See B. Bensaude and I. Stengers, *Histoire de la Chemie* (1992), pp. 189–190.

⁷ See H. Metzger, *Chemistry* (1991), pp. 115–119.

Something about Wöhler's life

He was also a great chemist, although his life was not as intense and interesting as Liebig's one. He was born in 1822, in a town near Frankfurt, son of a veterinary surgeon. Wöhler began to study medicine, but he always felt a great attraction for experimenting in chemistry. So, although he took a medical degree in 1823, he preferred to be a chemist. And went to study with Gmelin and Berzelius. In 1825 he became a teacher in the Technical School of Berlin, after in Cassel and finally in the University of Göttingen. Brilliant as professor he was also a great researcher too. In organic chemistry, in addition to other remarkable works the ones on quinone and hydroquinone must be remembered. After 1839 he mainly researched in the field of inorganic chemistry, being the most important works his studies on boron, silicon and phosphorus, as well as his discovery of a new method to prepare aluminium.



Liebig-Wöhler friendship

Their temperaments were very different. Liebig, although sincere and of a good heart, had an aggressive temperament, fiery and even violent. This fact led him to enter very often in bitter controversies. Wöhler, on the contrary, was quiet and had a particular sense of humour, avoiding all type of disputes. In spite of that, after their short controversy they kept a long-life friendship, proved by about thousand letters exchanged between them. Besides being so close friends, they carried out work jointly. The most remarkable was their research on oil of bitter almonds (1832), whose result was the discovery of the first radical with three types of elements, the *benzoyl radical*, and this fact represented “the beginning of a new day in vegetable chemistry”, according to the words of Berzelius.⁸

(4) Reflections

Nowadays the number of students in sciences at university level has generally decreased. In consequence, it becomes a necessity to enhance the interest for science. Fairs, Weeks or Centres of Sciences are created mainly with this objective. And the history of science is a good help as well.⁹ Thus, among other aspects, it is a source of examples that focused in the proper direction can contribute to make science learning more attractive.¹⁰

That is the case of the subject treated in this paper. From a didactical perspective, by focusing our story in this direction, some useful ideas for the classroom can emerge, such as:

- Teamwork is important in research;
- Careful work in laboratory is necessary to be sure of results
- Apparently incongruous results should not be forgotten
- Imagination and reliable experimental data contribute to the construction of theories
- Controversies in science can lead to remarkable advances
- Interrelations with other scientists and their works can be established (e.g. Gay-Lussac, von Humboldt, ...)
- Activities regarding this subject can be done to reinforce these ideas (e.g. readings, lectures, experiments, discussions, debates, panels or searching in Internet, among many others).

In sum, the history of science offers many examples like this one, which would show to students a more interesting face of science.

⁸ See J.R. Partington, *A History of Chemistry* (1962–1970), vol. IV, pp. 327–332.

⁹ For more details about the interest of the inclusion of the history of chemistry in institutional programs, see J.T. Stock, “The Teaching of the History of Chemistry” (2004), *J. Chem. Educ.*, vol. 81, pp. 793–794.

¹⁰ See S.Esteban, *Introducción a la Historia de la Química* (2002), pp. 24–25.