## ACTA UNIVERSITATIS LODZIENSIS FOLIA CHIMICA 13, 2004

## JUSTUS LIEBIG LIFE AND WORK

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Fig. 1. Freiherr Justus von Liebig, 1864

Liebig was not only one of the most prominent chemists of the 19<sup>th</sup> century, he had also done important work in agriculture and in nutrition. He even wrote articles about philosophical problems, he improved a special method of fresco painting, and with his *Chemical Letters* he produced one of the best books on chemistry for the laymen. A similar work on modern chemistry is still lacking.

Liebig was born on the 12<sup>th</sup> of May 1803, in Darmstadt, a town some 20 kilometres to the south of Frankfurt.

At this time Darmstadt was the capital of Hessen-Darmstadt, one of the small German states. Duke Ludwig I of Hessen-Darmstadt was interested in the advancement of the sciences. He even had a university at Giessen, founded in 1607. This university is today called Justus Liebig-University after its most prominent scientific scholar.

Liebig's father had a drysalt and hardware shop and he owned a small laboratory where he produced drugs and materials, e.g. pigments for colours.

Through the father's laboratory Justus became interested in chemical processes already in his youth and he wanted to become a chemist.

He read all the books on chemistry he could get hold of. The court library where he borrowed most of these books was unfortunately not very up to date. He could not learn modern chemistry in this way. But it might be that his later interest in history of chemistry came from these readings.

But this life didn't start very promisingly. At the age of 14 he left school without any qualification. It must be said that in this time this was not unusual.

In Heppenheim, a small town to the south of Darmstadt, he started a apprenticeship to an apothecary, but after 6 months he had to quit. It is most probable that his father was not able or willing to pay for his son. He himself wrote later that he had to leave after 10 month because he had conducted dangerous experiments.

For the next two years he stayed at home. On the market place he observed a man producing caps of silver fulminate. He investigated this reaction and published the results in his first article in 1822 with the help of Professor Karl Wilhelm Gottlob Kastner (1783-1853)<sup>1</sup>, an acquaintance of his father. Kastner even invited him to study chemistry at the University of Bonn. At this time it was possible to study without any formal school education. In 1820 he began to study chemistry in Bonn. When Kastner went to Erlangen in 1821, he took Liebig with him.

As a member of a student society he ran into political trouble and - not to be arrested - had to flee home to Darmstadt. The Duke of Hessen-Darmstadt, Ludwig I. - again with the help of Kastner - sent him to Paris, at this time the most important university for chemistry.

There he met not only the important French chemists like Joseph Louis Gay Lussac (1778-1850), and Louis Jacques Thenard (1777-1857) but also Alexander von Humboldt, who was very impressed by this young scientist and supported him.

In the meantime Kastner managed to arrange that Liebig could get his doctorate at the University of Erlangen in absentia. His thesis was entitled *About* 

<sup>&</sup>lt;sup>1</sup> It seems that no picture of Kastner exists.

the relation of mineral chemistry to the chemistry of plants (Über das Verhältnis der Mineralchemie zur Pflanzenchemie) and touched on a problem he was later on very much engaged with. Now he was able to start an academic career. When he came back to Darmstadt on the advice of Kastner and Humboldt, Ludwig I. nominated him for the position of Professor of Pharmacy and Chemistry at his university in Giessen.

Here he ran into a lot of problems, as he was appointed by the duke without the university being consulted. Only when he gained the interest of the students did the attitude of the university change. In 1833 his private institute was integrated into the university as the chemical institute.

In 1826 he married Henriette Moldenhauer and with her he had 5 children: Hermann, Georg, Agnes, Johanna and Marie.

In 1831 he - or probably his glass blower - invented the Kaliapparat with five glass bulbs. With this invention, elementary analysis was dramatically improved. The Kaliapparat became the emblem of Liebig's students, which they wore as a badge.

From 1831 Liebig belonged to the publishing team of the Magazine of Pharmacy (Magazin für Pharmazie). From 1840 on it was published under the name of Annals of Chemistry and Pharmacy (Annalen der Chemie und Pharmazie). In this function he also acted as a competent judge of the articles although his criticism was – according to Partington – sometimes beyond all reason.

In 1839 he was able to build his new laboratory. With this design he created the prototype for all laboratories in universities and industry. The old laboratory still looked like that of an alchemist.

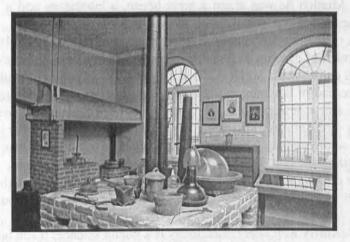


Fig. 2. The old laboratory in the Liebig Museum Giessen

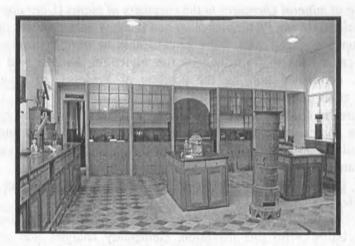


Fig. 3. The new laboratory in the Liebig Museum Giessen

In 1845 he was ennobled and from this time on he was Justus Freiherr von Liebig. He himself had urged the duke to take this step, arguing that he should have the same title as the famous French chemists.

Until 1852 Liebig was a professor in Giessen. During this time 700 students studied in Giessen, among them nearly 200 from foreign countries. An impressive number, as at this time the town had 5500 inhabitants and around 300 students in all faculties.

Then the King of Bavaria invited him to come to Munich. There he was also appointed President of the Bavarian Academy of Science.

In Munich he was given a great house, a laboratory and a lecture hall with 300 seats.

At one of his first public lectures, there was an incident. He performed the experiment of burning carbon disulphide in laughing gas (nitrous oxide). The public was enthusiastic, so he decided to repeat the experiment. But he made a mistake: instead of laughing gas he took a vessel with oxygen, the result was an explosion, and a few persons, even some of the Royal Family were injured, fortunately not seriously. In the journal *Allgemeine Augsburger Zeitung* he reported – anonymously – about this incident and wrote that he was not blamed for his mistake and that the King even asked him about his wounds.

He died on the 18th of March 1873 in Munich and is buried there.

Let us now have a look at Liebig's most important contributions to the sciences.

Chemistry as it is regarded today is a young science. It can be said that it started with the work of Antoine-Laurent Lavoisier (1743-1794). His theory of

burning, which states that oxygen is taken up in this process, can be regarded as the starting point of modern chemistry.

In his *Chemical Letters* Liebig describes the strange celebration in which Madame Lavoisier in the costume of a priestess throws the books of the phlogistonic system into the fire whilst a requiem is played. Lavoisier did this to promote his system. We, in our time, cannot find this celebration very amusing.

The new theory of burning was not readily accepted in Germany. The old theory – the phlogistonic theory - was formulated by the German alchemists Johann Joachim Becher (1635-1682) and Georg Ernst Stahl (1660-1734). This theory explains burning as a loss of a substance named phlogiston. It seems that national interests may have played a role in the lack of acceptance of the new theory.

Christoph Girtanner, in a book on antiphlogistonic chemistry, wrote that he promoted this new system, which was opposed by all great chemists, only because it was true, and that he would defend it only as long as he was convinced that it was true.

The long tradition of alchemy had come to an end, and the modern chemistry began. In contrast to his contemporaries, Liebig regarded alchemy as an important epoch in the history of science, as can be read in his *Chemical Letters*. There he states that alchemy was, with regard to the knowledge of nature, ahead of all other sciences. It was only because they were unaware of the history of chemistry that most chemists, overestimating their own knowledge, looked back with disgust on the period of alchemy as if the very learned men like Francis Bacon, Spinoza, Leibniz were interested in absolutely senseless ideas.

But at the time of Liebig modern chemistry was only in its beginnings. One reason was that in 1850 only 52 of the 92 naturally-existing elements were known, and that it was not clear, which substances were really elements. As a result more than 170 spurious elements were reported in the 19<sup>th</sup> century. Analyzing substances in order to find out if they can be reduced to an elementary state was therfore of the greatest interest.

Not very much was known about chemical compounds too, due to the lack of good analytic methods. It can be said that the developing of analytical methods was of the highest importance at this time.

The study of chemistry can be regarded as consisting of analytical, preparative, and theoretical chemistry. Liebig had contributed to all these branches.

Liebig started in Giessen as a pharmaceutical chemist. This is not surprising since chemistry was part of medicine at this time.

In 1831 he was able to produce chloroform  $(CHCl_3)$ , used as an anaesthetic for quite a long time. In his analysis he could not find the hydrogen atom, so the chemical formula  $(CCl_3)$  which he published was wrong. With the preparation of chloral hydrate he produced the first synthetic sleeping drug, which was used for the first time by Oscar Liebreich in 1869, only a few years after Liebig had produced it.

Liebig and his students worked in the new field of organic chemistry. At this time scientists assumed that organic substances could only be synthesised in the living organism. They could be analysed by men but not produced from elements. Analysis of organic substances was therefore one of the most prominent research programs of the time.

Again Lavoisier was the first to analyse organic compounds by burning and measuring the volumes of water vapour and carbon dioxide. However, with this method he had little success. The French chemists improved the method. Louis-Jacques Thenard (1777-1857) used potassium chlorate in 1810, and Joseph-Louis Gay-Lussac (1778-1850) employed copper oxide in 1815 as an oxidizing agent. But still the elementary analysis of organic compounds was a complicated, time consuming and tricky art. After burning the compound, the volume of the water vapour was measured to determine the amount of hydrogen, then the carbon dioxide gave the amount of carbon in the compound. The amount of oxygen could be found only by calculation from this data. In this way it took 13 years for Michel Eugène Chevreul (1786-1889) to analyse the fats he had separated.

With Liebig's improvements it no longer took months but only days to perform an analysis, and moreover, it could now be done by laboratory assistants.

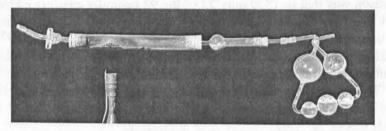


Fig. 4: Elementary analysis. Original apparatus and analysis of sugar. On the left copper oxide, next to it the sugar.

The main improvement was the Kaliapparat with its five glass bulbs. With this device a complete absorption of the carbon dioxide was possible, and the increase in weight could be easily measured, as the Kaliapparat could be hung on the balance. Otherwise the movement of the liquid would influence the weighting.

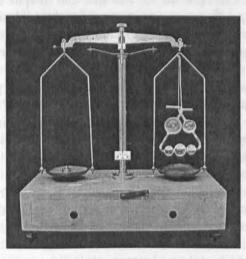


Fig. 5. The Kaliapparat hanging at the balance

The great chemist Jöns-Jakob Freiherr von Berzelius (1779-1848) criticised Liebig for not honouring other scientists sufficiently in his works. This was the beginning of an open conflict between these two great chemists.

With Liebig's improvements the elementary analysis of organic compounds was the standard method until the beginning of the 20<sup>th</sup> century, when the Nobel Prize winner of the year 1913, Fritz Pregl (1869-1930) developed the quantitative microanalysis.

Let us look at the analysis of sugar. We take 0.9 g of sugar and will get ca. 0.54 g of water and 4.14 g of potassiumcarbonate.

The content of hydrogen in the probe of sugar can be calculated:

$$H = \frac{2 \cdot 0.54}{18} = 0.06g$$

as well as that of carbon:

$$C = \frac{12 \cdot 4.14}{138} = 0.36g$$

The content of oxigene is calculated from the differences: 0.9 - 0.06 - 0.36 = 0.48 g

Dividing by 3, we get the relation C (12):O (16):H (1) = 1:1:2

That means the formula of sugar can be either  $CH_2O$  or  $C_6H_{12}O_6$  or in general  $C_nH_{2n}O_n$ .

At the time Liebig did his elementary analysis it was not possible to know which of the options was the right one. There were other methods needed, not yet developed. Liebig wrote for example that in spite of the differences of acid of sauerkraut, milk sugar, and cotton fibre the analysis showed that these substances had the same composition. I must add that Liebig's results were not always without any doubt. He never performed a calculation of error with on his results.

The advancement in elementary analysis was not possible without the development of balances of a higher accuracy. In the 19<sup>th</sup> century the balance makers learned to build balances with an accuracy unattainable before. Liebig found even in Giessen a fine mechanic who was able to build such balances. But weighting was still a time-consuming job. Liebig smoked, it is said, a lot of cigars, sitting in front of the balance.

It must be remembered that this analysis gave no information about the structures of molecules. Only at the end of the 19<sup>th</sup> century did chemists begin to understand the importance of structural analysis, and only then were appropriate methods developed.

Some of Liebig's important works are concerned with theoretical chemistry.

In 1824 he finished his work of fulminic acid (HONC) and the fulminates. At the same time another young chemist, Friedrich Wöhler (1800-1882) was working on cyanic acid (HOCN) and the cyanates. From these salts he was later able to synthesise urea.

Gay-Lussac remarked on reading both reports that these two compounds had the same atomic composition. He informed Berzelius, who couldn't believe it, but after finding other examples, he named such compounds isomeric (Gr.: same parts). This was the first indication that compounds are not just an assemblage of atoms and that the ordering of the atoms plays a crucial role. Just as with the letters A, R, and T, the words RAT and ART can be composed, giving a different sense, another ordering of the atoms leads to molecules with different characteristics.

Liebig and Wöhler became good friends and collaborated from this time on.

Already in earlier times acids were known. First acid fruit juices and vinegar, which can easily be produced from wine to give acetic acid were used. In the course of time other acids, especially the mineral acids like hydrochloric acid, sulphuric acid were discovered. The salts of these acids are found in minerals. Therefore they are called mineral acids. Bases were less common, soda - sodium carbonate - was known in old Egypt, and potash - potassium carbonate - was extracted from wood ash.

A first theory of acids and bases formulated by Lavoisier said that oxygen is the effective principle of all acids. Hydrochloric acid does not contain oxygen so the theory did not fit all cases. Chlorine was not accepted for years as an element, as is was still assumed to contain oxygen to fit Lavoisiers' theory.

In 1838, Liebig going back to an idea of Humphrey Davy (1778-1829) from the year 1810, when the latter proposed hydrogen as the effective element of acids, and to the studies of Thomas Graham (1805-1869) on the poly-protonic phosphoric acid, developed a theory of acids and bases.

His definition says that an acid is a compound where hydrogen can be replaced by a metal. A still valid definition.

In the reaction of an acid with a metal the development of hydrogen depends on the strength of the acid. At the same time a strong acid will produce more hydrogen than a weak acid. The weight of hydrogen or the degree of its production is used to differentiate between strong and weak acids. The measure is the pH-value (abbreviated from pondus hydrogenium - weight of hydrogen or potentia hydrogenium - strength of the hydrogen production).

A first effort to bring order into the mass of organic compounds was the theory of radicals. Liebig and Wöhler invented a system of radicals, saying that a group of atoms can behave as a single atom. We would today call such groups "functional groups". In this theory there was an important assumption that the same rules are effective in organic and in inorganic chemistry. Organic chemistry is not a special case anymore. Organic compounds can be synthesised in the laboratory - an important step to modern carbon chemistry.

Carl August Steinheil (1801-1870) had the idea that mirrors of silver instead of bronze would improve the quality of his mirror-telescopes and asked Liebig for help. The Englishman Drayton<sup>2</sup> had already tried to produce silver mirrors but had had no success. One of the reason was the reaction of silver with sulphur, resulting in the black silver sulphide, which made the mirror blind. Liebig was able to solve the problem and meet Steinheil's needs by applying electrochemically a layer of copper over the silver deposit.

He then tried to go into the mirror production in Fürth in Bavaria. At this time mirrors were still made with the help of mercury, a poison - a very unhealthy method not only for the workers but also for the buyers, as mercury evaporates from these mirrors for years. A good example of this effect is – by the way - the Mad Hatter in the famous novel by Lewis Caroll, *Alice in the Wonderland*, who has been poisoned with mercury.

There were backlashes for Liebig. The glass used for the mirror production was not of a sufficient quality and the silver mirrors had a different

<sup>&</sup>lt;sup>2</sup> I couldn't find any information about him yet.

reflection colour to that of the mercury-tin amalgam mirrors. This colour was not accepted by the ladies of the time. Liebig wrote that especially in France it was impossible to produce his mirrors, because they reflected a yellowish or greenyellowish colour and, he continued, as the French ladies already had a yellowish complexion, they looked even more unattractive then they already were in his bright mirror. Not very polite.

Only at the end of the century were silver mirrors successful due to safety regulations. Today most mirrors have surfaces of aluminium.

In Munich a new method for fresco painting was invented by a number of artists. This method, called stereochromy, made the paintings not only weatherproof but also fireproof by applying water glass in a special way to the paintings. After improving it he had two landscapes and two allegories painted on the garden front of his laboratory in Munich. Stereochromy was also used for the decorations in theatres.

Unfortunately this paintings disappeared with the demolition of the building and only the drafts of the two allegories can still be seen in the Surmondt-Ludwig Museum in Aachen.



Fig. 6. Allegory of chemistry. Draft by Ludwig Thiersch (1825-1909)



Fig. 7. The goddess Pomona as allegory of agriculture. Draft by Ludwig Thiersch

There are quite a few chemists who say Liebig was not a real chemist but an agriculturist or nutritional scientist. It is true that in both fields he did a lot of important work.

Beginning around 1830 he became more and more interested in these two fields. One of the reasons was certainly the fact that in Central Europe and also in Hessen there had been poor harvests and great famines, even forcing a lot of the population to emigrate to America.

Liebig was of the opinion that the main interest of science should be to improve the life of human beings. For him chemistry was in this respect the most important science. When through science and technology we are able to fulfil all needs of human beings, revolutions will be at an end, he wrote, formulating the hopes of the industrial era. These hopes have still not been fulfilled.

In 1840 his book Organic Chemistry in its Applications to Agriculture and Physiology in short Agriculture appeared simultaneously in German, English, and French. In this book he explains that the fertility of the soil can only be preserved when the minerals used by the plants are given back to the soil. A lot of experiments analysing the plants and the soil were performed to find out the concentrations of minerals in the soil for an optimal growth. Unfortunately, Liebig's experiments with fertilizers were completely unsuccessful. Liebig thought he had to take sparingly soluble minerals to avoid their being washed out by the rain. When he read an article by the viticulturist J. Ph. Bronner (1792-1865), who wrote that he had noticed that soil could absorb the coloured substances of liquid manure and soluble salts, he changed his opinion in the 8<sup>th</sup> edition of his *Agriculture* of 1862. In this case he mentioned the work of Bronner. He wrote that he had not taken into account the wisdom of the Creator and for this he had recived his just deserved punishment.

With the soluble fertilizers he had some successes. He even noticed that the soil could purify water. Therefore for the waterworks in London he proposed that waste should be given back to the soil. This proposal was not picked up by the London authorities.



Fig. 8. The minimum tub

Well known is his minimum tub. Fertilizing follows the minimum principle. The element which is in the lowest concentration determines the growth of plants. The idea which is normally attributed to Liebig had already been formulated in 1828 by Carl Sprengel (1787-1859). Liebig must have known his articles but he gave no credit to him.

Liebig, it must be said, was not a friend of mineral fertilization. He was a friend of a recycling agriculture. All the substances in growing plants taken from the field should be given back to the soil. Only if this is, for whatever reasons, not possible, is mineral fertilization necessary and then it must be done in the right way. The Chinese coolie who brings back all waste to the field is his shining example. In his *Chemical Letters* Liebig described this in detail, even mentioning that in China you cannot leave the house without going to the toilet as you would otherwise take good things with you.

He would not have liked overproduction, ecological damage by overfertilization. In his opinion men cannot interfere with nature without being punished by it.

In his book Organic Chemistry in Its Application to Physiology and Pathology in short Animal Chemistry he created the basis for a scientific theory of nutrition – although it contained a lot of errors, partly due to the rudimentary knowledge of his time.

A result was Liebig's meat extract.



um faden Speisen den köstlich mundenden und stärkenden Fleischgeschmack zu verleihen

Fig. 9. Advertising for Liebig's Meat extract

Meat extracts were already known, but again he made an improvement omitting the gelatine. Today it is only regarded as a sort of spice, as it has, in fact, no nutritional value.

In his family there were problems with breast-feeding. He invented the first baby food, and the babies survived. The high rate of infantile mortality at that time was mostly due to deficits in hygiene and in nutrition. With his substitute for mother milk and his food for babies a whole industry started.

For an English girl who was suffering from tuberculosis and could no eat any more, he prepared a special soup and was able to help her. This soup was a cold maceration of chicken meat with distilled water and a little hydrochloric acid.

He also invented an instant coffee. Every guest had to taste it, but only Liebig liked it.

Liebig was also an aggressive scientist. His criticisms were not always reasonable. Sometimes he corrected himself, as in his differences with Louis Pasteur (1822-1895). He didn't like the idea that alcoholic fermentation is performed by living cells. In his opinion it was a purely inorganic process. Together with Wöhler he wrote a satire on Pasteur's living cells, to show how ridiculous this idea was.

It should not be forgotten that he was also a great writer. With his *Chemical Letters* he produced a wonderful book about the chemistry of his time. The book has been translated into many languages - also into Polish - and is still worth reading.

In his later years he became interested in the philosophy of nature. His main interest concentrated on Francis Bacon, Baron Verulam since 1619 (1561-1626). He wrote that the great authority of Bacon was responsible for the lack of interest in theories in England. Liebig was a well-known and accepted person in England. He taught a lot of English students in Giessen. Even Queen Victoria was fond of him. But with his criticism of Bacon the English were not at all content. In an academic address. *Induktion und Deduktion*, he stated that chemistry is a deductive science. This stands in contradiction to Bacon, who regarded all sciences as inductive. Karl E. Popper (1902-1994), the famous philosopher of science, cites this article favourably in his work.

Liebig was, in his time, one of the most prominent and famous scientists. He was a propagandist of science and especially of chemistry and of himself. Even inventions he did not make were named after him, like the Liebig cooler, an invention of Christian Ehrenfried Weigel (1748-1831) made in the year 1771.

His most important contribution was probably the training of his students. He had learned in Paris that students should take part in the research process and he improved this system systematically. This new system of practical education in chemistry was responsible for the rise of the chemical industry in Germany, as he was always looking for application for the results of science in industry.

William H. Brock writes in his biography: "Liebig was a complex human being, full of contradictions and inner conflicts. At one moment, genial, charming, pleasant, and affectionate, in another he was difficult, emotional, easily provoked, and on the lookout for quarrels. Always overworked and overworking, because of his obsessive determination to make chemistry the fundamental science for modern societies, it thrived. Liebig was wilful, but never arrogant."

He will be regarded for all time without any doubt as an example of a great scientist, whose interest was to work for the benefit of mankind.

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