Justus Freiherr von Liebig

Gopalpur Nagendrappa

Liebig is one of the most honoured and influential scientists of the mid-nineteenth century. Liebig's major contributions were in the chemistry of fulminates, organic chemistry, agricultural chemistry and physiology. He invented a better technique for C, H and N analysis, which brought about a sort of revolution in the elucidation of molecular structure. His greatness as a teacher is evident from his innovations in teaching methods. He laid the foundation for the modern chemistry curriculum, designed the laboratory layout, and trained a large number of students from all over the world, who became leading, some outstanding, chemists.

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Introduction

"...Once again let me repeat the name of the man of whom I spoke last night, a man who knows no purpose in life other than to stand always openly for truth, who is recognised as supreme not only in his own field, but in the whole realm of thought. Justus von Liebig is his name". These were the words by a sculptress named Elisabet, spoken in some context to Ludwig, the son and successor of the Bavarian ruler Maximillian II, to whom Liebig was Advisor. The remark throws light on the high reputation Liebig enjoyed among the general public and not just his fellow scientists. Liebig's influence, his celebrity stature, fame and authority in the sciences, particularly chemistry were unmatched during his time. He is credited with the founding of many branches of chemistry and is known as the Father of Organic Chemistry, Father of Agricultural Chemistry, Father of Physiology, Founder of Modern Chemistry Curriculum, etc. Liebig was undoubtedly a leading figure in the development of chemistry during the mid-nineteenth century.

Keywords
Elemental analysis, fulminate, acids, radicals, agricultural chemistry, Liebig condenser, Kaliapparat, silver-mirroring, marmite.

Early Life

Justus Liebig was born on 10th May, 1803[1] in Darmstadt, a town then with a population of 15000 and the capital of Hesse-Darmstadt, an independent duchy about half the size of the present German state of Hesse, ruled by Duke Ludwig-I with the support of the French emperor Napoleon. Justus' grandfather was a shoemaker, and his father Johann Georg Liebig (1775–1850) had a shop that sold hardware, salts, paints, varnishes, polishes, pigments and other such articles needed by householders, local trade and business. His mother Maria Caroline Möser (1781–1855), a quick-witted woman, kept her husband's occasional unpleasant temper in check and provided good support in the business. The family belonged to lower middle class.

[1] The date of birth is uncertain. There are at least three found in different sources: 8th, 10th and 12th May, 1803.

Liebig's fascination for fulminates was so great that he was preoccupied with them for a number of years during the initial part of his research career. A good deal of early contributions to fulminate chemistry came from Liebig's laboratory.

Justus was the second among nine children, of which one boy and four girls died in their childhood, while two of his brothers lived for 30 years and another brother for 50 years. Only one of his sisters lived 17 years longer than him. Justus was considered as having inherited his mother's prominent nose and impressive eyes, and his father's occasional vehemence and impetuosity.

Johann Liebig's business did well. He had a laboratory-cum-workshop near his home, where he used to prepare some of the stuff he traded, like polishes, varnishes and such other materials. In this laboratory Justus was introduced to his father's "bucket chemistry" at an early age. His fascination to do experiments was so intense that he would search for procedures from library books and other sources and carry them out in his father's laboratory. Young Justus once witnessed a chemistry experiment in a market place. He saw a toy vendor using an explosive chemical to run his toys. The vendor prepared the explosive by mixing a few chemicals. Liebig was able to recognise these chemicals as mercury, nitric acid and alcohol, because he had handled them in his father's laboratory. He promptly repeated the experiment and obtained mercury fulminate (see equations below), which quickly caught his imagination and held his attention. His fascination for fulminates[2] was so great that he was preoccupied with them for a

[2] Fulminates are highly sensitive to heat and shock and explode spontaneously even with slight change in temperature and stress. Alfred Nobel used a fulminate as a blasting cap for his dynamite sticks.

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$$Hg + 2\,HNO_3 \longrightarrow HgNO_3 + NO_2 + H_2O$$

$$HgNO_3 + 2\,HNO_3 + C_2H_5OH \longrightarrow Hg(CNO)_2 + 4\,H_2O + NO_2 + O_2$$

Liebig attended the lectures of such great masters as Gay-Lussac, Jacques Thenard, Pierre Dulong and Jean Baptist Biot.

At the age of 16 he trained as an apprentice for one year under Gottfried Pirsch, a dispensing chemist (apothecary) in a place called Heppenheim about 35 km from Darmstadt. Then he joined the University of Bonn in 1820 to study chemistry under Wilhelm Gottlob Kastner (1783–1857), a leading professor of chemistry at that time. Soon Kastner moved to the University of Erlangen, and Liebig went there with him. Liebig worked on silver fulminate and published the results in his first paper in 1822, and continued to investigate the fulminates of silver and mercury. In the same year he had to leave Erlangen, because there was political unrest in the duchy and his activities as a member of a student unit landed him into trouble with the police. This, in a way, was a blessing in disguise for him, as he used the opportunity to study in Paris. Kastner helped him in getting a stipend from the Duke of Hesse. He stayed at the Sorbonne, (the University of Paris). Founded by Antoine Lavoisier, the Sorbonne Chemistry Centre was famous for chemistry studies. Liebig attended the lectures of such great masters as Gay-Lussac, Jacques Thenard, Pierre Dulong and Jean Baptist Biot. At the same time he continued his experiments on silver and mercury fulminates in the small laboratory of Henri-Francois Gaultier de Claubry (the discoverer of starch–iodine blue colour test). Liebig got the support of Thenard in his work.

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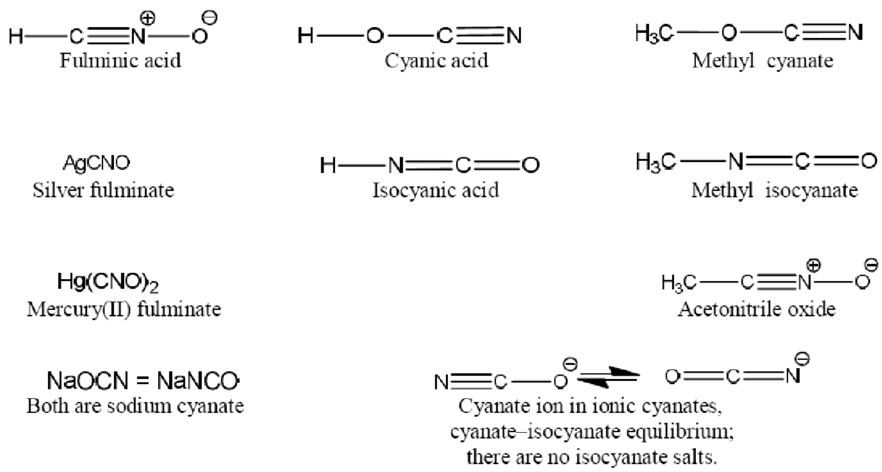
Exposure to French chemistry at that time was a great experience for Liebig. Due to Lavoisier's labour and leadership and the hard work of some of the leading contemporary scientists and Lavoisier's followers, chemistry in France then was in a better state than in Germany. Liebig was impressed by its rigor and quantitative nature. It was Lavoisier's stress on quantitative measurements which banished the alchemical phlogiston theory

Box 1. Fulminic and Cyanic Acids and their Simple Inorganic and Organic Compounds



and ushered in modern chemistry and the trend continued following him. Liebig learnt a great deal of general principles and their relationship with reactions. Perhaps from this knowledge, he was able to conclude that his fulminates of mercury and silver were the mercury and silver salts of an elusive fulminic acid which he could not isolate as a pure acid, but only as its metal salts, though he correctly speculated later that it had the same molecular formula as cyanic acid, which he had discovered in 1830 with Wöhler. The existence of free fulminic acid was shown by Heinrich Wieland in 1907 and its correct structure was determined in 1965 by its spectra by W Beck [7].

Gay-Lussac presented Liebig's work on fulminates to the Paris Academy of Science in December 1823 while Liebig demonstrated the compounds. Alexander von Humboldt, present at the meeting, was impressed by the work and recommended Liebig to his good friend Gay-Lussac, who accepted him to work in his laboratory. Till then Liebig worked in a neighbouring laboratory. From his work on gases and other achievements, Gay-Lussac was a well-known leading chemist of the day. His laboratory was well equipped and had good facility for elemental analysis, which of

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course, needed gram quantities of the analytical samples. However Liebig used it to obtain good quantitative elemental composition of substances. Entry into Gay-Lussac's laboratory gave a wonderful opportunity to Liebig to carry out his work on fulminates and determine their elemental composition accurately which enabled him to find their correct molecular formulas. The experience he gained in the analysis of elements in compounds was the beginning for Liebig to take up reforming and innovating elemental technique.

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In 1824, Liebig returned to Germany having been appointed at the age of just 21 years as Extraordinary Professor (similar to additional or adjunct professor) at the University of Giessen, thanks to von Humboldt for recommending him to this position. In 1826 he became ordinary professor (full professor) and was honoured with doctorate degree by the medical faculty of the university. Liebig remained in Giessen till 1852, and then moved to University of Munich on the invitation of the Bavarian ruler, Maximillian II, whom Liebig served as an Advisor. Much of the scientific achievements of Liebig were accomplished at his Giessen laboratory; in Munich it was essentially the continuation of that work.

Makes a Beginning at Giessen

With the rigorous training in one of the best laboratories in Paris combined with great enthusiasm to discover new vistas in chemistry research, Liebig was full of ideas as to how to develop an excellent laboratory to train a large number of students. He extended the elemental analysis procedure he had used for fulminates to organic compounds and determined their accurate elemental composition from which their correct molecular formulas could be calculated. This was basic to the development of early molecular structural theory.

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Application of chemical methods to compounds of plant and animal origin was of much interest to Liebig. He set up a pharmaceutical training institute, initially in a vacant military barracks made available to him.

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He brought about several reforms in the laboratory structure and analytical methods, which at that time were revolutionary. His description of the new laboratory plan is revealing, "An equal improvement has been accomplished in our laboratory. This is no longer the damp, cold, fireproof vault of the metallurgist, or the manufactory of the druggist, fitted up with stills and retorts. On the contrary, a light, warm, comfortable room, where beautifully constructed lamps supply the place of furnaces, and the pure and odourless gases, or of spirits of wine, supersedes coal and other fuel, and gives us all the fire we need; where the health is not invaded, nor the free exercise of thought invaded: there we pursue our inquiries and interrogate nature to reveal her secrets." The basic laboratory plan of Liebig is still found in present day laboratories. Liebig's laboratories could accommodate a good number of students. The training was well planned and systematised. The students could start learning basic experimental skills and gradually progress to the level of doing research. Liebig pioneered the system of research groups with assistants working under a professor. This practice is followed all over the world even today, in more or less the same structure and style.

The seeds of organic synthesis had just been sown by Friedrich Wöhler in 1828 and it had yet to become a regular practice of chemists. However, analysis, both qualitative and quantitative, was very important. Based on the known properties of acids, alkalies, metals and salts, Liebig systematically organised the available information to separate and identify substances present in unknown samples. We still follow his basic ideas in inorganic and organic qualitative analysis by classifying a substance in a solubility group. The methods and procedures were written and published as textbooks by Liebig's assistants, Fresenius[3] and Will.

[3] Fresenius became professor of chemistry, physics and technology and later the first director of the chemical laboratory at Wiesbaden Agricultural Station, Hesse.

Attention to Accuracy in Analysis – the Balance and the Kaliapparat

Liebig gave even greater attention to quantitative analysis. In this regard, he is all praise for Lavoisier and the balance. It is fascinating to hear his passionate description of the important role the balance plays in quantitative analysis, and the difference it made in the reliability of results. See his remarks in 'Familiar Letters on Chemistry':

"*...to these simple means (laboratory furnishings) must be added 'The Balance' and then we possess everything required for the most extensive research. For all great discoveries chemists are indebted to the 'balance' – the incomparable instrument which gives permanence to every observation, dispels all ambiguity, establishes truth, detects error and guides us in the true path of inductive science.*

The balance, once adopted as a means of investigating nature, put an end to the school of Aristotle in physics. The explanation of natural phenomena by more fanciful speculation, gave place to a true natural philosophy. Fire, earth, air and water could no longer be regarded as elements... the notion of the elementary nature of air, earth and water, so invariably held, was now discovered to belong to the errors of the past.

The great distinction between the manner of proceeding in chemistry and natural philosophy is, that one weighs, the other measures. The natural philosopher has applied his measures to nature for many centuries, but only for fifty years (since Lavoisier) have we attempted to advance our philosophy by weighing."

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– Liebig

Liebig's emphasis on determining the accurate elemental composition of chemical samples of inorganic or organic origin, led him to develop innovative analytical procedure to achieve the desired accuracy.

Determination of the elemental composition of a sample comprises three steps, namely weighing the sample, its combustion and weighing the quantity of gases after absorbing them in suitable solutions. Liebig introduced modifications in all the three components. He brought about considerable improvement in the working of the balance, with which he could achieve a weighing accuracy of 0.3 mg per 100 g of a substance. (Liebig

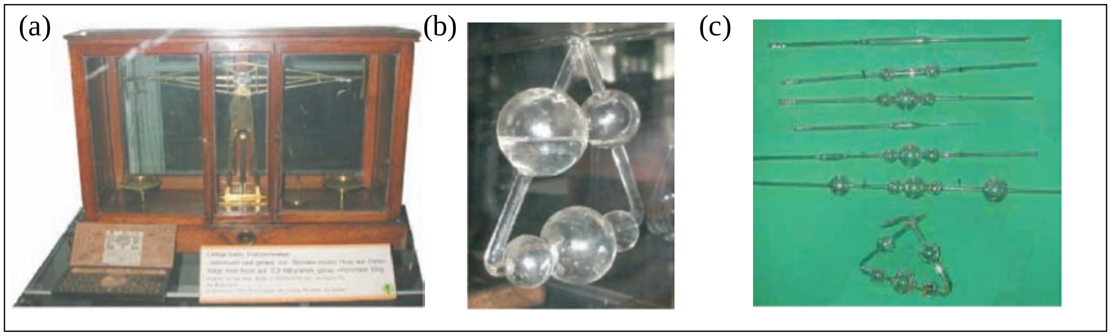

Figure 1. (a) A balance.
(b) Kaliapparat in an elemental analysis unit (unit is not shown).
(c) Kaliapparat at different stages of its fabrication.
Source: Liebig Museum,Giessen.

used about 50–200 mg sample for combustion analysis and hence with the use of his balance the elemental percentages were very accurate). For combustion he introduced a modified chamber, better heating system and better oxidising chemicals for smooth and complete combustion. For efficient absorption of carbon dioxide, he invented (in 1831), 'Kaliapparat' or caustic apparatus. It is a triangular glass tube with each limb of about 4" length, two limbs of which had one bulb each and the third limb had three bulbs blown into them. The bulbs were filled with caustic potash solution. The combustion gases, after being freed from water vapours by absorbing them in calcium chloride placed in an earlier tube, passed into Kaliapparat and carbon dioxide was absorbed by the alkaline solution. The difference in weight of the Kaliapparat before and after passing the gases gave the weight of carbon dioxide from which the percentage of carbon present in the sample was calculated.

In Giessen, Liebig took up, along with the study of fulminates, also the study of the oxidation or decomposition reactions of chlorine with various chemical substances. In one such reaction he studied the action of chlorine on silver cyanide, expecting to get Friedrich Wöhler's cyanic acid with additional oxygen atom, which was reported by Georges Serallus. However, accurate elemental analysis by Liebig showed that Serulla's analytical results were erroneous, and the compound was indeed cyanic acid. At this point, knowing that fulminic acid and cyanic acid had the same C, H, N and O composition, Liebig collaborated with Wöhler, who concluded that the two acids were isomers, following Berzelius' recognition of isomerism earlier.

Liebig studied the reaction of chlorine with uric acid, (French, *urique* = urine). Under the reaction conditions he employed, he obtained oxalic acid, (Greek, *oxalis* = sharp, acrid), cyanic acid and ammonia, and attempted, in a reverse reaction to synthesise uric acid, inspired by Wöhler's recent urea synthesis, but failed. We see here, the naive thinking of early organic chemists with regard to synthesis. Their synthetic plans were based only on the molecular formulas of the target compound and of the starting compounds, as structural chemistry was yet to be born. So much so that only a miracle could intervene to deliver the anticipated compound. Sometimes the results could be unexpectedly extraordinary by producing highly useful substances, as in the case of Perkin's mauve[4] in 1856. The methodology was much akin to the one followed by alchemists. The scene changed only after proper understanding of molecular structures, like in the case of Adolf von Baeyer's synthesis of indigo after elucidation of its structure[5] for which he got the Nobel Prize in 1905. What we witness today in the area of organic synthesis would not have been dreamt even by von Baeyer in his wildest dreams. Continuing his studies with chlorine, Liebig chlorinated alcohol and obtained chloral. His interest in the composition of uric acid led him to study an acid found in horse urine. When he distilled this acid he obtained benzoic acid which was different from the former and he called it hippuric acid, (Greek, *hippose* = horse).

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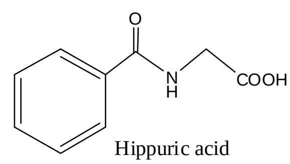
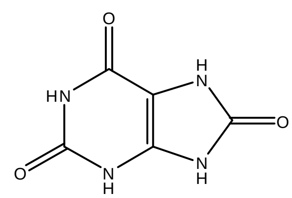
[4] See, *Resonance*, Vol.15, No.9, pp.779–793, 2010.

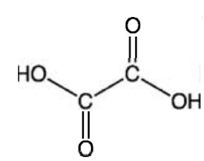
[5] See, *Resonance*, Vol.8, No.3, pp.42–48, 2003.



Hippuric acid



Uric acid



Oxalic acid

(These structures were unknown to Liebig)

During the studies on uric acid and hippuric acid, Liebig found that the elemental analytical procedure he was using was not giving satisfactory data, particularly for nitrogen. In order to overcome the difficulties encountered in these cases, he designed Kaliapparat. The analytical system developed by Liebig greatly enhanced the pace of organic research, especially in the area of alkaloids, which contain nitrogen in small quantities, relative to carbon and hydrogen, in their molecules.

Kaliapparat's high efficiency of CO_2 absorption, (preceded by absorption of H_2O vapours by $CaCl_2$, along with improvements in combustion process), eliminated the practice of measuring CO_2 by volume. This made the analysis quicker and introduced

Box 2. Nitrogen Estimation: Dumas' Method

The nitrogen containing organic compound is decomposed at red hot copper oxide yielding nitrogen and some nitrogen oxides which are reduced to nitrogen with copper present in copper oxide. Nitrogen is swept with pure carbon dioxide and collected over potassium hydroxide. Its weight is calculated from its volume at atmospheric pressure and room temperature. In modern instruments, the quantity of nitrogen is measured using thermal conductivity detectors (TCDs).

higher accuracy in the determination of carbon and hydrogen. As a consequence, Liebig, with persistence and patience, was able to get more reliable analytical values for alkaloid nitrogen using the procedure of Dumas and Pelletier (*Box* 2). With these modifications the analysis did not need Liebig's skill and supervision, and his assistants could perform it independently. In fact one of his assistants, a Mexican by name Ortigosa became so highly skilled that he could correct even Liebig's values. By involving many students Liebig was able to analyse hundreds of samples in a year. (This of course is a ridiculously miniscule number compared to the number of samples analysed by automated instruments these days).

The consequences of the new analytical technique were far reaching in organic research. Since more number of samples could be analysed in a short time, organic chemists could now analyse not only the main compound isolated from a source, but the products of their degradation by various reagents under different conditions. This gave a great push to structural determination of organic compounds, and organic chemistry made rapid progress. (For this reason, Giessen University's Liebig Museum has this slogan, "Liebig, the father of modern organic chemistry").

The Kaliapparat's impact was so much that the American Chemical Society adopted it as a symbol in its logo, which every user of its journal is familiar with. Liebig's analytical method, with some minor modifications ruled the world of chemistry for nearly eight decades until Fritz Pregl (1869–1930), a medical doctor who got interested in chemistry, came on the scene and made revolutionary improvements in C, H, N analysis, for which he was awarded the Nobel Prize in 1923.

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Foundation for Modern Chemistry Curriculum

The system of teaching and research developed by Liebig was novel. In this, a senior scientist heads and mentors a research group of junior scientists who work as assistants and students.

This is the model followed even today, perhaps with minor variations, in universities and research organisations the world over. It was highly efficient in providing good training, spreading scientific knowledge and thereby speeding up the advancement of science. Liebig's success lay in his great administrative skill and excellent teaching ability. Because of Liebig's authority in chemistry and reputation, a little known university at Giessen became a famous centre for chemistry education and students came from all over Europe, the US and Mexico to be trained in his laboratory. We can count among Liebig's students such great names as August Wilhelm von Hofmann, Friedrich August Kekule, Edward Franklin, Carl Schmidt, Hermann von Fehling, Emil Erlenmeyer, Adolf Strecker and J L Smith, one of the founders of the American Chemical Society and who was instrumental in adopting the Kaliapparat in the Society's logo.

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Strengthening the Berzelius' Concept of Isomerism

Liebig's and Wöhler's work on fulminic acid and isocyanic/cyanic acid, which have the same elemental composition of one atom each of carbon, hydrogen, nitrogen and oxygen, posed a new question: if both acids have the same elements in the same proportion, how do we account for the differences in their properties? As answer they concluded that the two compounds must be having different arrangement of elements in their molecules. Sometime earlier (in 1830) Berzelius had proposed the idea of isomerism to describe the phenomenon of different compounds having the same elemental composition, but it was not accepted by most chemists then (*Box* 1). However, the fact that tartaric acid (optically active) and racemic acid (inactive) had identical elemental composition gave support to the idea of isomerism; but more importantly the thoroughness of Liebig–Wöhler investigation of fulminic acid, cyanic acid and their salts convinced everyone of the existence of isomerism. This sowed the seeds of structural organic chemistry and a little later the theory of valency emerged (Frankland, Couper, Kekule).

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Work on Organic 'Radicals'

Now we are familiar with clusters of atoms called groups/radicals that appear as one unit, e.g., methyl (in methyl alcohol, methyl chloride, dimethyl sulphate, dimethyl ether), ethyl, phenyl, benzoyl, etc. (This should not be confused with the present concept of organic free radicals, though both refer to an atom or group that behaves as one unit). This concept evolved over a period of several years during the late 1820s and 1830s through the efforts of many scientists, with Berzilius, Dumas, Liebig and Wöhler in the forefront. There used to be conflicts, arguments, and disagreements among them. The concept of organic radicals gained acceptance slowly, supported by the emergence of organic structural theory and organometallic chemistry (e.g., preparation of $Zn[(C_2H_5)]_2$ by Edward Frankland in1848).

Defining Acids

Another important topic Liebig tackled was the nature of acids, particularly organic acids. There was too much of confusion among the leading scientists in 1820s and 1830s with regard to the problem of their classification and chemical properties, especially about the displaceable hydrogen by bases. The work of Thomas Graham (of the law of diffusion) had shown that phosphoric acid had three hydrogen atoms that could be successively replaced by alkali metals, but it was not much noticed. However, Liebig was able to see the merit of Graham's concept and applied it to his own studies on a number of organic acids and their derivatives such as oxalic acid, tartaric acid, citric acid, malic acid, meconic acid and several others, and some of their pyrolysis derivatives. Liebig noticed that during pyrolisis either carbon dioxide or water or both are lost. He also noticed that when carbon dioxide is lost no hydrogen is lost, but the number of replaceable hydrogens is reduced. Based on a large number of such experiments, he came to the conclusion that acids can have one or more hydrogen atoms which can be successively replaced by alkali metals or other metals under suitable conditions. These findings, which suggested the notion of basicity of acids without explicitly

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mentioning it, added substantially to the progress in the proper understanding of acids.

Considerable cause for confusion in understanding the nature of organic substances in general had its roots in using wrong atomic weights and not very accurate elemental analysis. Many scientists, including Dumas, were taking the atomic weight of carbon as 6, while others, like Liebig took it as 12. The problem of atomic weights was resolved only in 1860 after the Karlsruhe Chemistry Congress, whereupon, due to strong persuasion by Cannizzaro, Avogadro's hypothesis was adopted for determining atomic weights[6].

[6] See *Resonance*, Vol.11, No.1, pp.2–5, 2006.

Contribution to Agricultural Chemistry

By 1840, Liebig turned his attention to the study of the chemistry of soils, plants and animals, which could help agriculture to become more profitable. His first important hypothesis in this area was that the carbon used by plants is extracted from the atmosphere and not from the soil humus. This idea was based on his observations that the total carbon composition of plants grown each year in a given land area remained the same. Secondly, he assumed that the plants get their nitrogen requirement from the ammonia dissolved in rain water. It was his pure imagination, because his investigation of plant material had shown the presence of some definite quantity of ammonia. However, he later became unsure of the rain water as the source of ammonia, because of its very low concentration, but was sure that plants needed some ammonium salt.

Liebig came to the conclusion that ammonia, potassium, calcium, magnesium, phosphate, etc., are essential for the growth of plants and by applying proper fertilizers, the depleted nutrients are replenished.

By further investigation of plants, he found that they contained alkali and alkaline earth metals in some combined form, e.g., potash, soda ash, etc. However, he found that their quantities depended on the soil type. From such results, he concluded that these metals are essential for plant growth and that if one metal is not available in a particular soil, the plant would absorb another metal of similar characteristic, e.g., sodium for potassium, calcium for magnesium. Liebig drew support for his proposition not only from his own work, but also from the related work

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done by other chemists. From these studies Liebig came to the conclusion that ammonia, potassium, calcium, magnesium, phosphate, etc., are essential for the growth of plants and by applying proper fertilizers, the depleted nutrients are replenished. He argued that such studies greatly help farmers to practice profitable agriculture. He wrote a book, *Organic Chemistry in application to Agriculture and Physiology* in which he has described the importance of nutrients such as carbon, nitrogen and other elements for plant growth. An important argument he put forth was that the plants get their carbon from the carbon dioxide of the atmosphere and not from the humus in the soil. He also argued that the carbon dioxide used up in the process is replaced through its exhalation by animals, which otherwise would cause its build-up in the atmosphere and this would go against the fact that the atmospheric carbon dioxide is constant. He opined that plants utilise carbon dioxide for synthesising sugars, starch and other chemicals containing carbon, and release oxygen. However, he did not know how all this is done by plants.

As for the source of phosphorus, Liebig thought that pulverised bones were the best. Regarding the other elements, like sodium, potassium, calcium, magnesium, he advocated the use of plant ashes and human and animal wastes. To conserve soil fertility, he advocated rotation of crops instead of repeating the same crop year after year, because each crop uses different alkali and alkaline earth metals. This would give time for natural replenishment of elements used by one crop.

Based on whatever little knowledge of organic synthesis was available at that time, and his own observations on nutrients and plants' elemental composition, Liebig tried, with considerable imagination, to explain the chemical processes that could be taking place in plants. With such arguements he underscored the importance of chemistry in relation to plant physiology.

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The English version of the book, translated from German by Liebig's former student, Lyon Playfair, made particularly impressive impact in English speaking countries. The hypothesis put forth in the book as to the nutrient requirements of plants and how they can be met by applying chemical fertilizers, quickly attracted the attention of all those interested – farmers, administrators, traders and industrialists – in improving agricultural production and increasing their nation's prosperity. Adopting Liebig's ideas in agriculture gave a push not only to food production, but to fertilizer production as well. (Liebig foresaw industries producing fertilizers). It also influenced the direction that agricultural research took, particularly in soil science and plant physiology. Though several chemists, including Antoine Lavoisier in France and Humphrey Davy in England, had attempted to apply chemistry to agriculture, the impact of Liebig's views was more powerful. Although there were some contradicting results from the experiments carried out in England, Liebig was able to refute all of them by pointing out the flaws in their methodology. From further studies, Liebig proved that his original views regarding the need for nutrient metals for plant growth were correct.

The studies involved experiments on sterile fallow land, which he was able to convert into a fertile land over a period of time by applying a combination of nutrient salts in proportion to that found in plant ashes. In these experiments he found that the plant's growth would be stunted even if one of the needed elements is in deficient supply and all others are in excess supply. The results led to the conclusion that every nutrient element is essential and the deficiency of any one of them will have an adverse effect. Therefore, a minimum of every nutrient must be available for the healthy growth of plants. This concept is known as Liebig's 'Law of Minimum'. *Table* 1 illustrates how the combination of two nutrients, nitrogen and sulphur boosts the crop yield, while either one of them has no effect if the other is absent.

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Considering the fact that the knowledge of chemistry was very limited during the time Liebig carried out this research, we realise what a visionary he was to have applied that limited knowledge to another area with such great success. Some of his

Table 1. Effect of N and S on yield of canola and barley.

Yield (cwt/A)				
Fertilizer Applied[1]	Canola	Barley	Canola	Barley
None	2.2	13.1	3.5	15.6
Sulphur	3.3	14.4	5.2	20.4
Nitrogen	0.3	13.0	0.8	12.2
Nitrogen + Sulphur	17.2	39.5	16.0	35.6

[1] N rate = 100 lb/A; S rate = 20 lb/A; cwt/A = hundredweight per acre or centum weight per acre. (1 cwt ~ 50.8 kg).

ideas in this area hold good even today. For all these achievements and contributions, he is considered as the 'Father of Agricultural Chemistry'.

In a similar manner, Liebig made attempts to apply chemistry to physiology. "One of the most remarkable effects of the recent progress of science is the alliance of chemistry with physiology, by which...light has been thrown upon the vital processes of plants and animals" – Liebig in *Familiar Letters on Chemistry*. "We have now no longer any difficulty in understanding the different actions of aliments, poisons and remedial agents – we have a clear conception of the cause of hunger, of the exact nature of death..."

"The oxygen of the atmosphere received into the blood...acting upon the elements of the food, is the source of animal heat." "All living creatures...possess a source of heat..." – these are some of the other remarks of Liebig.

Liebig reasoned that the heat produced in the body is through the burning of food to carbon dioxide and water.

Liebig reasoned that the heat produced in the body is through the burning of food to carbon dioxide and water. He argues that the heat produced in the body by burning of carbon and hydrogen in food is exactly the same as that produced if the same amounts of these elements are burnt directly in oxygen.

He discusses about the elements of nutrition, about their sources, their conversion to blood and through that the formation of tissues and body parts. He talks of composition of blood, its central role in living; he talks of the chemistry of starvation, normal state of health, pathology and even death.

"...of these substances which are adapted to the formation of blood, are formed all the tissues. The other class of substances, in the normal state of health, serve to support the process of respiration. The former may be called the plastic elements of nutrition; the latter, the elements of respiration."

"Among the former we reckon – vegetable fibrin, vegetable albumen, vegetable casein, animal flesh, animal blood. Among the elements of respiration in our food, are – fat, pectin, starch, bassorine, gum, wine, cane sugar, beer, grape sugar, spirits, sugar of milk."

Liebig's views attracted great commendations as well as intense criticism, and in effect drew everyone's attention.

It is amusing to go through Liebig's books *Animal Chemistry in its Application to Physiology and Pathology*, and *Familiar Letters in Chemistry and Its Relation to Commerce, Physiology and Agriculture*. But perhaps, during his time much of what he propounded was acceptable. Some of his assertions were based on observations of others and his own, but to a large extent they emerged from his speculative intellect. His views attracted great commendations as well as intense criticism, and in effect drew everyone's attention.

Liebig Condenser and *Liebig's Annalen der Chemie*

Most of the present-day chemists seem to be unaware of the great influence Liebig wielded and the fact that he was considered as the authority in chemistry and other areas of knowledge during his time, through his contributions to analytical, organic and inorganic chemistry, chemical education, research methodology, chemical industry, agriculture, physiology, medical field and several other areas. He, with Wöhler, was responsible for shifting the primacy of France in chemistry to Germany, which as we know, dominated chemistry research for the whole of the next century till the end of WW-II. However, every student of chemistry knows about Liebig in connection with a condenser bearing his name and every chemist would have referred the journal *Justus Liebig's Annalen der Chemie*.

Liebig, with Wöhler, was responsible for shifting the primacy of France in chemistry to Germany.

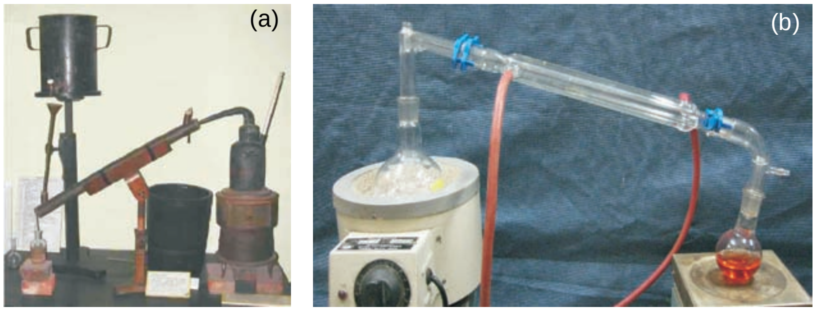

Figure 2. (a) Liebig's original condenser.
(b) Modern Liebig condenser.
Courtesy: (for (b): Raja Mitra)

Ironically, both the condenser and the *Annalen* are not his original creations. The condenser, in its earlier form was described by a German chemist Christian Ehrenfried Weigel (1748–1831) in his 1770 MD thesis submitted in Göttingen. Liebig modified and used it in his Giessen laboratory. The present day Liebig condenser is of course far more sophisticated (see *Figure* 2). All his students and assistants referred to it as Liebig condenser. Since many of these students became eminent chemists, they continued to attach Liebig's name to the condensation device later in their laboratories. In any case, it is to the credit of Liebig that it became part of the set-up for distillation of volatile liquids since the eighteen thirties.

Annalen der Chemie was the leading journal of chemistry for a long time. It was started as *Magazin für Pharmacie*... in 1824 by Philip Geiger. Liebig joined as its editor in 1832. During the period of its existence, *Annalen*... underwent several changes, including its name, until 1998, when it finally became part of the new *European Journal of Organic Chemistry*. These transformations are quite interesting and are briefly traced in *Box* 3.

Something for Everyday Life: Silvering of Mirror, and Extracts of Meat and Yeast

Liebig used his scientific knowledge not only in tackling profound issues, but sometimes in solving mundane problems. A few of them are mentioned here.

Box 3.

The form and format of *Annalen der Chemie* underwent many transformations during its life. In 1824 Phillip Lorenz Geiger (1785–1836) started editing the *Magazin für Pharmacie und die dahin einschlagenden Wissenschaften* (Magazine for Pharmacy and the Related Sciences). This was renamed as *Magazin für Pharmacie und Expermentalkritik* and merged with *Ärchivs des Apothekerverein im nordlichen Teutchland* (Archives of the Apothecars Association of northern Germany) in 1832 to form the new journal *Annalen der Pharmacie* under the editorship of Rudolf Brandes, Phillip Lorenz Geiger and Justus Liebig. The first volume had papers from Berzelius, Gay-Lussac, Liebig and other well-known chemists. In 1840 the journal name was again changed to *Annalen der Pharmacie und Chemie* and was edited jointly by Liebig and Wöhler. After the death of Liebig, it was called *Justus Liebig's Annalen der Chemie und Pharmacie*. In 1875 *und Pharmacie* were dropped. Till 1978 the journal carried the name *Justus Liebig's Annalen der Chemie*, but again in 1979 it was further shortened to *Liebig's Annalen der Chemie*, which became *Liebig's Annalen* in 1995. In 1997 it was merged with the Dutch journal *Recueil des Travaux Chimiques des Pays-Bas*. In 1998 these two and *Chemische Berichte* were merged and the combined journal was given an entirely new name *European Journal of Organic Chemistry*.

He developed with the help of an engineer, a method for making cheap and nutritious beef extract from the worthless parts of slaughtered animals and marketed it under the banner of Liebig Extract of Meat Company. Similarly, Liebig was successful in making yeast extract as another nutritious food. Both the meat extract (now called 'Oxo') and the yeast extract (called 'Marmite') are common concentrated food items today.

Liebig developed a method for making mirrors by coating the glass surface with silver by spraying diammine silver(I) solution and then reducing it to a thin coating of silver by spraying sugar solution on the surface. It was a simple, but great improvement over the then existing methods for making mirrors.

Publications

Liebig was a prolific writer. Apart from editing *Annalen der Chemie*, he published 317 scientific papers and several books. His books had great influence on not only science, but on commerce, industry, education, agriculture and even politics. Among them are *Animal chemistry*, *Chemistry in its Application*

Leibig's efforts to popularize the importance of chemistry in its application to physiology, agriculture, commerce, industry and other aspects.

to Agriculture and Physiology, *Familiar Letters on Chemistry, Instructions for Chemical analysis of Organic Bodies, Agricultural Chemistry, Chemistry of Food*, *Researches on the Motion of the Juices in the Animal body,* etc. *Familiar Letters on Chemistry* was the product of his efforts to popularize the importance of chemistry in its application to physiology, agriculture, commerce, industry and other aspects, and were first published in instalments in the newspaper, *Augsburger Algemeine Zeitung*.

Awards and Honours

The list of awards, honorary degrees, medals and recognitions occupy a full page. Some of them are mentioned here. The Grand Duke of Hesse conferred on him the Baronetcy in 1845, whence he became von Liebig. He was honoured with Prussian Order of Merit for Science and Art and the French Legion d'Honneur. He was awarded Copley Medal of the Royal Society, London, (then the highest honour for science in the world), Albert Medal of the Society of Art, London. He was made the Freeman (a person who is entitled to full political and civil rights) of the cities of Glasgow, London and Munich. He was an elected member of many learned societies including Royal Society of London, Royal Swedish Academy of Sciences and Foreign Associate of the French Academy of Sciences. He was President of the Academy of Sciences, Munich. After his death the University of Giessen was renamed as Justus Liebig University, Giessen. Many universities in Germany have streets named after him (Justus von Liebig Weg). Germany issued a Liebig commemorative stamp in 1953. In 2003 Britain's Royal Society of Chemistry installed a Landmark Plaque to honour him on his 200th birth anniversary, as he was the inspiration to start the Royal College of Chemistry and Imperial College, London.

There are many awards and medals given in his name: Justus von Liebig Award for World Nutrition, Liebig Applied Soil Science Award, Liebig Medal of International Union of Soil Sciences, Liebig–Wöhler Freundschaft Preis, Liebig Medal of Gesellschaft

Deutscher Chemiker, Liebig Professorship Award and several others.

Personal Life

Liebig married Henriette Moldenhauer (1807-1881) in 1826. They had two sons and three daughters, named Georg (1827-1903), Agnes (1828-1861), Hermann Georg (1831-1894), Johanna (1836-1926) and Marie (1845-1920).

Georg von Liebig became a medical doctor. Apart from practicing in Britain and Germany, he worked in India in the service of the East India Company between 1853 and 1858. He served in Bombay (Mumbai) for three years and then taught in Hindu College in Calcutta (Kolkata) for two years. After going back to Germany he did considerable amount of research in the medical field. Hermann Georg von Liebig studied Agricultural Technology in University of Giessen (he was a student of his father) and worked in agricultural institutions and estates. Some of Liebig's grandchildren became scientists, some got into legal and other professions.

Liebig passed away in Munich on the 18th of April, 1873.

Suggested Reading

[1] W H Brock, *Justus von Liebig: The Chemical Gatekeeper*, Cambridge University Press, 1998.

[2] J Liebig, *Animal Chemistry or Organic Chemistry in Its Application to Physiology and Pathology*, John Owen (Publisher), Cambridge, 1843.

[3] J Liebig, Familiar Letters on Chemistry and its Relation to Commerce, Physiology, and Agriculture, *Chemical Society*, London, 1844.

[4] K J Etherington, A Rodger and P Hemming, *LabPlusinternational*, February/March, pp.26–27, 2001,

[5] http://www.chem.yale.edu/~chem125/125/history/Analysis/Liebiganal.html

[6] http://www.chem.yale.edu/~chem125/125/history99/4Radicals Types/Analysis/Kali/kaliapparat.html

[7] W Beck, *Eur. J. Inorg. Chem*. pp.4275–4288, 2003.

[8] W B Jensen, *J. Chem Educ.*, Vol.83, p.23, 2006.

[9] Numerous websites on Liebig.

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