

How Chevreul (1786-1889) based his conclusions on his analytical results

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Abstract: In 1811, when Chevreul started to study animal oils and fats, organic chemistry was still very much in its infancy because it had to rely on natural products and these tended to be mixtures or impure. Some organic compounds like alcohol and tartaric acid were available as pure compounds but they were exceptions in an otherwise chaotic world. How to create some order in this chaos? In the Introduction to his monograph, Chevreul argues strongly in favour of a painstaking and systematic approach to experimentation. His own work is a prime example of this approach and this could well be the reason why his monograph was still reasonably up to date when it was reprinted on the occasion of the centenary of the author, the reason why he is the father of lipid chemistry

Key words: Chevreul, analytical chemistry, elemental analysis, fatty acids, glycerol

Introduction

In 1811, Nicolas-Louis Vauquelin (1763-1829) asked his pupil and assistant Michel Eugène Chevreul to study fatty materials by giving him a piece of lard based soap, at a time when all that was known about these materials was that they felt greasy, were highly flammable and had no affinity for water. Consequently, the range of fatty materials Chevreul came to study was wider than just oils and fats [1]. It included spermaceti, adipocere and cholesterol and if mineral oil had been available at that time¹, this greasy material would no doubt have been included in the range. At that time Chevreul² [2] was 25 years of age and he had already some experience in chemical research. He had studied cork and isolated several dyes from wood products but fatty materials were to become his main challenge [3-5].

Some work had been done before Chevreul started, since oils and fats were already used industrially in making soap and candles. Carl Wilhelm Scheele (1742-1786) had discovered that on saponification, oils and fats release glycerol and in 1741, Claude Joseph Geoffroy (1685-1752) had discovered that the fatty material that results from acidulation of soaps was soluble in alcohol, whereas the oil used to

make the soap was not but these observations had not received the attention they deserved. On the other hand, various theories were doing the rounds such as that acetic acid was an inevitable by-product of saponification, that carbon dioxide was produced during saponification and that no saponification could take place in the absence of oxygen. There was a tendency to regard oils, fats, butters, tallows etc. as different compounds and there were no theories on why oil is liquid and fat is solid.

State of the art in the early 1800s

In the field of inorganic chemistry, much progress had already been made in the early 1800s. More than half the elements had been discovered and most of their atomic weights had been determined quite accurately. The term "atomic weight" did not yet exist³ [6] but people had a quite accurate idea how much metal oxide corresponded to a given amount of a salt of that metal. Table 1 illustrates this by comparing data derived from Chevreul's monograph on animal oils and fats [7] with modern data and shows them to be quite close.

Less progress had been made in organic chemistry and only a few organic compounds had been isolated in a pure state. These comprised several organic acids such as acetic acid made

by bacterial oxidation of ethyl alcohol, tartaric acid obtained from the cream of tartar deposit in wine casks, citric acid that was isolated from fruits, and oxalic acid and muric acid, both of which are produced by nitric acid oxidation of sugars.

These acids all have an oxygen content that exceeds the amount required to produce water from the hydrogen present in the molecule and at the time, this was considered to be a characteristic of organic acids and likened them to inorganic acids like sulphuric acid and phosphoric acid that can also be regarded as combinations of an oxide and water. When Chevreul then discovered that fatty acids contain much more hydrogen than required to make water with the oxygen present, he likened them to acids like hydrogen sulphide or telluride, which also have an "excess" of hydrogen. In fact, Chevreul started with the well-established idea that salts are formed because the oxygen in the acid reacts with the hydrogen in the base to form water. He gradually started to toy with the idea that the hydrogen in the acid could perhaps react with oxygen in the base or an alcohol like glycerol or cetyl alcohol, in line with the reaction of acids like hydrogen sulphide.

Table 1. Metal oxide contents of various salts.

Salt	Chevreul	Current
Sodium chloride	53.29	53.26
Potassium chloride	63.25	63.14
Calcium sulphate	41.53	41.19
Strontium sulphate	56.36	56.40
Barium sulphate	65.62	65.68

¹ According to <http://www.little-mountain.com/oilwell/>, the petroleum industry began with the August 1859 drilling of the Drake Well near Titusville, Pennsylvania and/or, simultaneously, an unnamed well near Petroleum, West Virginia.

² For a biography in French see: <http://hdlboy.club/fr/Chevreul.html>.

³ This term should not be used any more either. It has been replaced by the term "relative atomic mass".

This way of thinking may well show that Chevreul did not yet regard water as being composed by two hydrogen atoms and a single oxygen atom and that, in other words, Avogadro's law did not yet form part of his thinking. This is not surprising since this law was only published in 1811 and it was half a century before it was revived by Cannizzaro in 1858 and accepted at the Karlsruhe congress in 1860 [6].

Various compounds that could be purified by crystallisation were known, such as several sugars, and similarly, purification by distillation had led to the isolation of ethyl alcohol. When this was treated with sulphuric acid, it could form diethyl ether which at that time was called "sulphuric ether" or "vitriolic ether" to distinguish it from ether made with nitric acid as acatalyst, which was called "nitric ether". In this context, the term "ether" stood for almost anything volatile, including esters. This generic meaning is still present in terms like "ethereal oils" and "petroleum ether". The treatment with sulphuric acid could also lead to the formation of ethylene and if chlorine was added to this gas, ethylene dichloride was formed, a compound generally known as the "oil of the Dutch chemists". Because ethylene was a starting material of this oil, it was referred to as "olefiant (= oil making) gas".

Quantitative elemental analysis of organic compounds had been started by Lavoisier but his method of analysis had subsequently been much improved by *i.a.* Gay-Lussac, who introduced the use of copper oxide as oxidising agent for the organic compound to be analysed and a horizontal glass tube to carry out the oxidation. Berzelius introduced the use of calcium chloride to absorb the water formed during the oxidation and Chevreul made use of both these improvements. All these developments and improvements were quite recent when Chevreul started his work and understandably, he describes the particular method of analysis he used himself in great detail. He also mentions which specific weights he uses for the gases concerned. As shown in *table 2*, his values deviate only very little from current values.

In his description of the analytical method used, Chevreul starts by describing a rather cumbersome method but near the end of the section, he describes the method whereby the water formed during the combustion of the sample is absorbed by calcium chloride and

Table 2. Weights of 1 litre of gas in grams at 0 °C and 760 mmHg.

Type of gas	Values used by Chevreul	Current values
Carbon dioxide	1.98033	1.9630
Hydrogen	0.08937	0.0899
Oxygen	1.43228	1.4376

Table 3. Water content of compounds "consisting of water and ethylene".

Compound	Chevreul		Current	
	Parts of water per 100 parts compound	Ratio	Parts of water per 100 parts compound	Ratio
Ethyl alcohol	63.23	8.31	64.28	8.00
Diethyl ether	31.61	4.15	32.14	4.00
Cetyl alcohol	7.61	1.00	8.04	1.00

also provides an evaluation of this improvement. It could therefore be that Chevreul started with the old method and described it for future inclusion into his monograph and then switched to the improved method, a description of which was then inserted into the manuscript.

Chevreul was well aware of what went on around him. In 1814, de Saussure finally managed to obtain good analyses of ethyl alcohol and diethyl ether which, being quite volatile, were difficult to analyse according to the method developed by Gay-Lussac for solid compounds. He concluded that alcohol contained twice as much water as diethyl ether for a given amount of olefiant gas⁴. When Chevreul discovered cetyl alcohol (1-hexadecanol) as a saponification product of spermaceti and determined its elementary composition, he noted that this product formed part of this range by having eight times as much olefiant gas per water molecule as alcohol. His analytical data are shown in *table 3* and expressed as parts of water per 100 parts of compounds, just as Chevreul did to arrive at his conclusion.

How were compounds characterised? Smell and taste played an important role since Chevreul put every compound he made into his mouth and reported its taste. Glycerol was found to be sweet, and would not have been given this name if it had not been tasted. Compounds could be bitter, astringent, or have an aftertaste or not. Colour and appearance were used to characterize a compound and if a compound was coloured, this raised the question of whether the colouring principle was part of the compound or just an impurity. For crystalline compounds the crystal morphology was used so Chevreul always reports whether a compound formed flakes, needles or some other shape and most importantly, Chevreul intro-

duced the melting point of the crystal as an indication of purity and means of identification.

Main achievements by Chevreul in the field of edible fats

Perhaps Chevreul is best known for his discovery of a number of different fatty acids, most of which still bear the names he gave them: stearic acid, butyric acid, capric acid caproic acid. We also owe names like glycerin, cholesterol, stearin, olein, and cetyl, to Chevreul. He also discovered palmitic acid which he called margaric acid because of its pearly potassium soap, and the acid we now call isovaleric acid, which Chevreul called phocenic acid after its source: dolphin oil. He also describes a fatty acid he called hircic acid but his sample was quite small so his description is quite rudimentary and from the description it is not clear which acid he meant, if any.

He concluded that the alkali used to saponify the fat has no influence on the types of fatty acids that are formed. He based this conclusion on his observation that all the different metal soaps yield the same fatty acids on acidulation. He also observed that the sum of the weights of the fatty acids and the glycerol formed during saponification exceeded the weight of the fat by a few percent. He introduced the titre (melting point) as a means to characterise a mixture of fatty acids as obtained by the saponification of an animal fat. He purified his compounds by recrystallization and was the first to control their purity by measuring their melting point, which he also introduced as a means of characterising chemical compounds. He was the first to use solvent fractionation of edible fats to purify them and he also used the difference in the solubility of their soaps to arrive at reasonably pure samples.

Chevreul also proposed a theory according to which oils and fats consisted of mixtures of various compounds comprising a single fatty acid and glycerol and explained the differences between these fats and oils by assuming that these mixtures had different compositions. A liquid oil for instance would contain relatively more of the oleic acid compound and a solid fat more of the stearic acid compound and/or the

⁴ According to Costa (see references), a paper by Theodore de Saussure: "New Observations on the Composition of Alcohol and Sulfuric ether" was published in *Annals of Philosophy* 1814; 4: 34-47, but when I went to <http://scholar.google.com> to see if I could read the paper, I was referred to "Nouvelles observations sur la composition de l'alcool et de l'éther sulfurique" in *Des Annales de chimie* 1814; 89: 273-305.

palmitic acid compound. This explanation greatly simplified what was hitherto an unknown area of organic chemistry, and gave it some structure.

Analysis of fatty acids

Before analysing a fatty acid, it had first of all to be prepared, isolated and purified. In the case of palmitic acid, Chevreul describes the following steps:

- The fat originating from a prisoner who had been tortured to death is first of all separated from membranes and other tissue material;
 - Then it is washed with cold water to remove blood and the like;
 - It is melted on a water bath;
 - The molten fat is filtered several times to remove the last traces of cellular tissue.
- Then the fat had to be saponified so that the soaps could be acidulated:
- Take 4 parts of fat, 4 parts of water and 1 part of potassium hydroxide, place them in a porcelain dish and heat on a water bath for some 10 hours while replenishing the water;
 - Saponification is complete when the mass has become homogeneous, semi-transparent and forms a clear solution when mixed with boiling water;
 - The soapy mass is treated with tartaric or phosphoric acid and the oily layer floating on top is separated;
 - This oily layer is washed with water until the washing liquid is no longer acid.
- This yielded a mixture of free fatty acids from which the palmitic acid had to be isolated:
- The fatty acid mixture is then converted into potassium soaps by allowing it to react with aqueous potassium hydroxide;
 - These soaps are treated while cold with twice their weight of alcohol containing 9.7% water by weight for a period of twenty-four hours;
 - The solid soaps are isolated by filtration and the filter cake is washed with cold alcohol;
 - Then the filter cake is dissolved in hot alcohol and on cooling a deposit of potassium palmitate is formed;
 - The deposit is allowed to drain, dissolved again in hot alcohol and a new deposit is formed on cooling;

⁵ Modern literature on edible oils and fats like *The Lipid Handbook* no longer provides data on the composition of human fat but in the past, authors were less squeamish. A book printed in 1948 (H.A. Boekennoogen, *De Scheikunde der Oliën en Vetten*, N.V. A. Oosthoek's Uitgeversmaatschappij, Utrecht) mentions that human fat contains some 36% saturated fatty acids: C14:0 2.6-5.9%; C16:0 24.0-25.7%; C18:0 5.2-8.4%. However these data were obtained before analysis by GLC became available.

Table 4. Determination of elemental composition of palmitic acid.

	A	B	C	D	E
Oxygen	11.656	8.634	8.938	1.0	3
Carbon	76.366	76.366	79.054	11.8	34
Hydrogen	11.978	11.600	12.008	21.5	65
Total	100.000	96.600	100.000		

– This procedure is repeated until the soap yields an acid with a melting point of 60 °C.

Chevreul assumed this palmitic acid to be pure since it had a constant melting point but it probably contained some 20% of stearic acid⁵ since the above purification method does not separate it from the palmitic acid.

This supposedly pure sample was then analysed by combusting it with copper oxide and measuring the amount of carbon dioxide that was evolved. By using a sample of known weight and measuring the weight loss of the tube in which the combustion took place, two more independent data resulted giving a total of three known values from which three unknowns: the amounts of oxygen, carbon and hydrogen in the sample, can be calculated. In column A of table 4, the analytical results of the elemental analysis of palmitic acid have been given as percentages.

Subsequently, a sample of 500 mg of this free palmitic acid was heated with lead oxide and the amount of water that was formed was determined to be 17 mg. So 100 parts of the free acid would yield 3.4 parts of water and according to the assumption that all of this water originates from the free acid⁶, the acid in the soap would amount to 96.6 parts. This assumption is analogous to the reaction of sulphuric acid with calcium oxide to form calcium sulphate. Now, in the early twenty-first century, we regard calcium sulphate as consisting of a calcium ion and a sulphate ion but in the early nineteenth century, it was considered to be the sum of calcium oxide and sulphur trioxide [6], the latter being the actual acid and sulphuric acid being the “hydrated acid”. In this context, it is interesting to go to a garden centre and look at a bag of fertiliser. It still quotes the phosphorus content of the fertiliser as P₂O₅ and its potassium content as K₂O.

Knowing the water content of the “hydrated palmitic acid” (the free acid), allows us to calculate the elemental composition of the ‘actual palmitic acid (the anhydride)’. The 3.4 parts of water stand for 3.022 parts of oxygen and 0.378 parts of hydrogen and by deducting

⁶ Because it requires 2 fatty acid molecules to form 1 molecule of water, 100 parts of palmitic acid (MW=256) can liberate $0.5 \times (18 : 2.56) = 3.5$ parts of water.

these values from those in column A, the values in column B result. Normalising those to percentages leads to column C and by setting the oxygen content to an equivalent of 1.00, it follows that the carbon equivalent equals:

$$\frac{79.054}{8.938} \times \frac{16}{12} = 11.8$$

Similarly, the hydrogen equivalent equals 21.5. These values have been tabulated in column D of table 4.

When 100 parts of free acid were treated with lead oxide and 3.4 parts of water were liberated, these 3.4 parts contained 3 parts oxygen and since the 100 parts of acid contained almost 9 parts of oxygen, a ratio of 1:3 is observed. Accordingly, a “molecular formula” of the acid anhydride can be arrived at by multiplying the values in column D by 3 to arrive at column E. Chevreul analysed all the acids he isolated like the palmitic acid discussed above. However, his method is quite sensitive to small analytical errors. So he concluded that for some acids, the ratio that was found to be 1:3 for palmitic acid was in fact closer to 1:2.5, and the “acid anhydride” would contain 5 oxygen atoms whereas it contained only 3 oxygen atoms in the case of palmitic acid. He did not comment on these anomalies. To eliminate such anomalies, table 5 summarises the molecular formulae for the fatty acids Chevreul analysed. These formulae have been arrived at by using his analytical results and setting the number of oxygen atoms per acid at 2. Table 5 shows that in general, the carbon content is somewhat overestimated. The hydrogen content on the other hand, is quite accurate, presumably since this was determined in a less indirect manner by measuring the weight increase of a tube with calcium chloride.

Analysis of soaps

Chevreul also prepared a large number of soaps from the fatty acids he isolated and purified. He analysed these soaps and reported the results as a percentage of the metal oxide and a percentage of “dry acid”, which has been translated [7] as acid anhydride. When analysing a barium soap, Chevreul acidulated the soap with sulphuric acid and determined the weight of the barium sulphate. This allowed him to calculate the oxide content in accordance

Table 5. Molecular formulae of acids analysed by Chevreul.

Fatty acid	Current molecular formulae	Values derived from Chevreul data		
		Oxygen	Carbon	Hydrogen
Stearic acid	C ₁₈ H ₃₆ O ₂	2	20.3	39.2
Palmitic acid	C ₁₆ H ₃₂ O ₂	2	17.5	32.9
Oleic acid	C ₁₈ H ₃₄ O ₂	2	19.3	33.7
Isovaleric acid	C ₅ H ₁₀ O ₂	2	6.5	9.9
Butyric acid	C ₄ H ₈ O ₂	2	5.6	7.4
Caproic acid	C ₆ H ₁₂ O ₂	2	8.0	12.7
Capric acid	C ₁₀ H ₂₀ O ₂	2	12.1	19.2

with the data in table 1. The same method was used for the calcium and strontium soaps. Since potassium and sodium sulphates are water-soluble, another method was used for their soaps. They were acidulated with hydrochloric acid and the aqueous phase was then evaporated to dryness, the potassium chloride was weighed and its oxide content was calculated. Finally, the metal oxide content of the magnesium, lead, zinc and copper soaps was determined by just calcining the soaps and weighing the ash.

In his monograph [1, 7] Chevreul analysed almost all the soaps he made and reports the metal oxide content as parts per 100 parts of acid anhydride. With current knowledge of the relative molecular masses of these metal oxides, relative molecular masses of the fatty acids can be calculated as follows:

$$\left(\frac{\text{parts acid anhydride}}{\text{parts metal oxide}} \times MW_{\text{metal oxide}} + 18 \right) : 2$$

This has been done and the results have been summarised in table 6. This table leads to the following observations:

- The values reported for each fatty acid are remarkably close together;
- The values for stearic acid are on the low side. This could be because the stearic acid used by Chevreul still contained some palmitic acid;
- The values for palmitic acid are on the high side, since the sample of palmitic acid still contained some stearic acid;
- The values for oleic acid are more scattered than for the other acids. The fact that the oleic

acid sample used by Chevreul will have contained some linoleic and palmitoleic acids may explain the low average value but does not explain this scatter, unless he used different samples to prepare the different soaps;

- The values for isovaleric and butyric acid are most impressive: close together and close to the current value;

- The two values for capric acid are so different from the current literature value that it is more than likely that the sample isolated and analysed by Chevreul is in fact the fatty acid we now call caprylic acid [8]. The melting point, density and solubilities in water and alcohol reported by Chevreul also point in this direction.

However, the most remarkable observation that can be made in connection with table 6 is that Chevreul did not arrive at it (or something similar) himself. After all, he knew how many parts of metal oxides combine with 100 parts of sulphur trioxide, chlorine or carbon dioxide. So why did he not make a list of these combinations and include the various fatty acids in this list? Then he would have concluded that stearic acid anhydride is more or less equivalent to seven sulphur trioxides or that caproic acid anhydride is more or less equivalent to five carbon dioxides.

As is only to be expected, Chevreul does not give an answer to this question and since the question may not have been asked before, subsequent literature does not give an answer either. So we can only speculate why a coherence that nowadays (in retrospect?) is so self-

Table 6. Relative molecular masses of various fatty acids derived from the composition of their metal soaps.

	Current value	K	Na	Ba	Sr	Ca	Pb	Mg	Zn	Cu
Stearic acid	284.5	271	260	276	265	263	267			
Palmitic acid	256.4	276	249	267	274	262	276			
Oleic acid	282.4	272	270	269	273	300		277	283	294
Isovaleric acid	102.1	97		102	99	96	100			
Butyric acid	88.1	86	86	87	85	85	82		86	84
Caproic acid	116.2	120	120	115	116	116				
Capric acid	172.3			145	147					
Hircic acid	?			107						

evident, was not perceived at a time when all necessary data were available.

Acid soaps

Chevreul prepares potassium stearate by dissolving equal weights of potassium hydroxide and stearic acid in hot water and allowing the solution to cool. He therefore used a large molar excess of alkali and consequently, all the fatty acids must have been dissociated. He reports the analysis of the precipitated potassium stearate by saying that treating 1 g of the potassium stearate with hydrochloric acid yields 0.86 g of free stearic acid and 0.237 g of potassium chloride and continues by reporting the composition of this salt in terms of oxides by converting the free acids to 0.8308 g of dry acid and the potassium chloride to 0.1499 of potassium oxide equivalent. These values allow the molecular weight of the stearic acid to be calculated to 278, which compares very well with the actual value of 284.5

When this potassium stearate is then dissolved in hot water and the resulting solution is added to a large amount of cold water, a precipitate is formed that contains only 9 parts of potassium oxide per 100 parts of stearic acid, unlike the original potassium stearate, which contained 18 parts of potassium oxide per 100 parts of stearic acid. Fully in line with Dalton's law of definite proportions, Chevreul concluded that he had isolated potassium bistearate. When he dissolved this bistearate in water and boiled it for a long time, he even prepared a perstearate that contained more acid than the bistearate but he did not report the analysis of this acid soap.

The fact that the bistearate contained half the potassium is just coincidence. In order to crystallise potassium stearate, an excess of potassium hydroxide is necessary but if the excess is smaller even a shortfall, the ratio in which the potassium stearate and the stearic acid crystallise is a matter of wait and see.

Analysis of glycerine

Chevreul prepared a sample of pure glycerol by allowing lead oxide to react with pure olive oil, treating the aqueous solution of the glycerol formed with hydrogen sulphide to remove any lead present in the solution and concentrating it on a water bath. It had a pleasant, sweet taste and when 1 gram was heated in a platinum crucible, it only left a residue of 1 mg alkaline ash. At 17 °C, it had a density of 1.252 (g/mL). This sample was analysed but a 25 g aliquot was also exposed to vacuum for several months. During this period, the sample lost 1.5 g of water and its density increased to 1.270 (g/mL) at 10 °C. This sample was also

Table 7. Molecular formulae of glycerol samples characterised by their densities.

Density	1.252	1.270
Oxygen	1	1
Carbon	0.92	1.02
Hydrogen	2.72	2.81

analysed and the results have been summarised in *table 7*.

The data show that eliminating 6% of water does indeed lead to a significantly higher carbon content of the sample and hardly affects the hydrogen content. According to the literature, glycerol has a density of 1.2613 (g/mL) at 20 °C so the second sample (density 1.270 (g/mL) at 10 °C) must have been quite pure. This is also clear from the molecular analysis the result of which is close to the actual value of C₃H₈O₃.

Chevreul used the results of his analysis of glycerol when attempting to arrive at some kind of mass balance of the oxygen, carbon and hydrogen involved during the saponification reaction. So he started with the elemental analysis of for instance mutton tallow. He knew how much glycerol this had yielded on saponification (8.0 parts per 100 parts of tallow) and how much water the fatty acids liberated when heated with lead oxide and given the elemental analyses involved, he could work out how much he had found and he compared this with the amount he felt he should have found for each of the three elements. The differences were quite sizeable (up to 2.8% absolute). Chevreul mentions analytical errors and losses of glycerol and fatty acids as likely causes and indeed, the determination of the amounts of glycerol was far from accurate. For mutton tallow he finds 8.0 parts per 100 parts of tallow, for lard he finds 8.82 parts and for human fat, he finds 9.66 parts. All these values are on the low side since 100 parts of trioleate (MW = 884) yield 10.4 parts of glycerol (MW = 92).

However, there is a fundamental reason for the discrepancies in the mass balance and this has been illustrated in *table 8*. The left half of the

table lists the analytical data and values derived from them as published by Chevreul and the right half lists the values that would result for trioleate. So in row A, the analytical results Chevreul obtained for human fat have been given next to the values calculated for trioleate. Chevreul then goes on to state that 100 parts of human fat yielded 96.18 parts of free fatty acids and 9.66 parts of glycerol; on hydrolysis, the 100 parts of trioleate yield 95.70 parts of FFA and 10.41 parts of glycerol by reacting with 6.11 parts of water; the elemental composition of these parts of FFA has been listed in row B. For the trioleate, the oxygen content does not change since the triglycerides and the FFA contain the same number of oxygen atoms. However, the data from Chevreul are analytical results and so his values show some variation.

In a previous sub-section, Chevreul mentioned that 100 parts of free fatty acids from lard and 100 parts of free fatty acid from human fat each released 3.65 parts of water when heated with lead oxide. This means that the 96.18 parts of FFA release 3.51 parts of water containing the amounts of oxygen and hydrogen listed in row C. Accordingly, subtracting the values in row C from those in row B gives the elemental composition of the anhydrides (row D). In row E, Chevreul lists the contents of the elements of the 9.66 parts of glycerol and in row F those of glycerol without water.

Then he adds the values of the acid anhydride (row D) to the values of the glycerol (row E) to arrive at row G and he compares this with his analytical data in row A and tabulates the differences in row H. But there are similar discrepancies for the trioleate, so they are of a fundamental nature rather than merely the result of analytical errors. Apparently, adding the anhydrides to the glycerol does not reconstitute the original triglycerides. For the carbon it does but for the oxygen and hydrogen it does not because two free fatty acid molecules liberate only one molecule of water when forming an anhydride but liberate two molecules of water when reacting with glycerol. The water shortfall in the Chevreul mass balance is also illustrated by the trioleate discrepancies: the oxy-

gen surplus of 2.715 parts and the hydrogen surplus of 0.340 parts correspond exactly to a surplus of water equalling 3.055 parts, which also equals the amount of water listed in row C. This raises the question of whether Chevreul himself could have noticed that his mass balance was flawed. His findings and mass balance discrepancies have been summarised in *table 9* with the relevant trioleate data. He reports that 100 parts of mutton tallow, lard and human fat yield about 96 parts of free fatty acids and around 9 parts of glycerol, so hydrolysis causes an increase in weight of 5 parts. The trioleate increases by 6.1% on hydrolysis. The amount of water Chevreul takes into account is only 3.51 parts which is significantly less than 6.1% but perhaps the difference with 5 parts is not significant. However, the discrepancies are systematic and should therefore have alerted him that something was not right. The fact that this did not strike him as odd may well be because he had become convinced that the acid anhydride was the actual acid

Saponification of spermaceti

The same discrepancy also caused the mass balance Chevreul reports for to be flawed. Spermaceti is a wax containing C₁₂-C₂₂ fatty acids, 77 mol% of which are monounsaturated and C₁₄-C₂₀ fatty alcohols, 60 mole% of which are monounsaturated. The molecular formula can be written as C_{15.9}H_{30.3}COOC_{17.0}H_{33.8} [9] and the relative molecular mass can be calculated as 520.9. Accordingly, 100 parts of spermaceti require 3.5 parts of water for their hydrolysis and this is where the difficulties with Chevreul's mass balance start: his weight gain on hydrolysis is only 1.6 parts. A second difficulty is that his reported fatty alcohol content is very low. He reports only 40.64 parts whereas the above molecular formula would lead to 48.9 parts. On the other hand, his analysis of "éthral", the neutral hydrolysis product, which we now know to be a mixture of fatty alcohols, is surprisingly accurate. He arrives at a molecular composition of C_{16.6}H_{35.54}O which compares very well with the C_{17.0}H_{34.8}O determined by

Table 8. Comparative mass balances based on the analytical data obtained by Chevreul on human fat and theoretical data for trioleate.

		Chevreul (human fat)			Trioleate (C ₅₇ H ₁₀₄ O ₆)		
		Oxygen	Carbon	Hydrogen	Oxygen	Carbon	Hydrogen
A	Triglycerides	9.584	79.000	11.416	10.860	77.376	11.764
B	FFA	10.633	74.507	11.040	10.860	73.302	11.538
C	Water	3.120		0.390	2.715		0.339
D	Anhydrides	7.513	74.507	10.650	8.145	73.302	11.199
E	Glycerol	4.927	3.871	0.862	5.430	4.073	0.905
F	Anh. glycerol		3.871	0.247		4.074	0.226
G	D + E	12.440	78.378	11.513	13.575	77.376	12.104
H	G-A	+2.856	-0.622	+0.097	+2.715	0	+0.340

Table 9. Differences between elemental compositions.

	Chevreul's results			
	Mutton tallow	Human fat	Lard	Trioleate
Water released by 100 parts fatty acids	3.65	3.65	3.65	
Glycerol released on saponification (%)	8.0	9.66	8.82	10.41
Difference in oxygen content	+ 1.777	+ 2.856	+ 1.885	+ 2.715
Difference in carbon content	- 0.976	- 0.622	- 1.151	
Difference in hydrogen content	+ 0.176	+ 0.097	+ 0.476	+ 0.340

mass spectrometry [9]. Similarly, his analysis of the fatty acids formed by saponification is surprisingly accurate: $C_{8.38}H_{15.96}O$ reported by Chevreul, versus $C_{8.45}H_{15.65}O$ arrived at by setting the oxygen content at unity.

By determining the above molecular composition of the free fatty acids and subtracting the water formed when these free fatty acids react with lead oxide, Chevreul arrived at the composition of the "acid anhydride". Adding the éthal data should then lead to the values found for the spermaceti but as we now understand quite easily, it didn't because the amount of water Chevreul took into account was only half of the amount required for hydrolysis. However, in this instance, the alcohol content of the hydrolysis products is so much less than expected that the differences Chevreul works out do not give any indication as to why they have arisen. So the conclusion by Chevreul that: "This difference is due to losses during the analyses, the production of the soluble material and perhaps to the formation of a small amount of water and carbon dioxide by reaction with atmospheric oxygen" is fully understandable.

Saponification by various bases

When different bases are used to saponify a given oil or fat, different soaps results. Sodium soaps tend to be firm, whereas potassium soaps are much softer. This raises the question of to what extent the reaction products originating from the fat or oil are responsible for this difference. Could it be that potassium hydroxide forms different saponification products than caustic soda? With our present knowledge, we would not bother to ask such a question but at the time, when a distinction was made between "sulphuric ether" and "nitric ether", the question was fully justified.

Chevreul tackled this problem by saponifying lard with a number of different bases: potassium hydroxide, sodium hydroxide, barium, strontium and calcium hydroxide, all of which were found to saponify the lard and form soaps. When these soaps were acidulated, they yielded free fatty acids, the titre of which was always the same. Moreover, when the free

fatty acids were dissolved in alcohol and their solution was cooled, all solutions yielded the same kind of crystals. It was therefore concluded that all bases make the lard undergo the same changes in composition.

Not all bases turned out to be capable of saponifying lard. When lard was heated with an aqueous suspension of magnesium oxide for a period of twenty-four hours, nothing much happened and no glycerol was detected. When the heating was continued, some glycerol was observed and finally, magnesium soaps were formed that on acidulation yielded fatty acids with the same melting point as those obtained with different bases. When lard was treated with ammonia for a period of fourteen months, it was only partially saponified. Aluminium oxide did not lead to any saponification, zinc oxide and lead oxide did but copper oxide did not.

Discussion

The early part of the nineteenth century must have been a most interesting period for the relatively few people who were actively involved with chemistry. New observations were regularly reported, new theories were put forward and new analytical methods were developed. However, in the Introduction to his monograph [1], Chevreul warns against a certain kind of literature and argues strongly in favour of a painstaking and systematic approach to experimentation. His own work is a prime example of this approach and this could well be the reason why his monograph was still reasonably up to date when it was reprinted on the occasion of the centenary of the author.

The monograph is also an example of creating order in what at first sight looks most chaotic indeed. Chevreul's efforts to introduce a kind of Linnaean system of classification of organic compounds which started with the kingdoms of inorganic compounds and of organic compounds and included a "Family of acid lipids", incorporating a 1st genus of fats and oils with "fatty acid species" that do not evaporate when mixed with boiling water, was bound to

fail by lack of knowledge/understanding of functional groups.

On the other hand, the theory regarding all fats and oils as mixtures of compounds between a fatty acid and a glycerol molecule was very much to the point since it explained the diversity of their properties by assuming different mixture compositions. Chevreul was not able to prove this theory experimentally but his experiments point in this direction. If only he could have achieved a further purification, then the stearin obtained would have yielded pure stearic acid on saponification.

Nevertheless, Chevreul put his theory forward, and this is the way that true science works: some observations are made; first of all, they make little sense but when looked at in a certain, probably original way, there is a kind of pattern; this may lead to a theory that calls for experimental verification which in its turn may cause the theory to be rejected outright or to be accepted, but more often the experimental results lead to some form of amendment. The latter is also the case with the explanation of the properties of fats and oils. We still explain them on the basis of their glyceride composition but we now attach three fatty acid moieties to a glycerol molecule instead of just one.

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