BOOK VI

SUMMARY AND GENERAL REFLECTIONS

1086. I intend to deal with two objectives in this book: firstly, to summarize the main properties of oils and fats as revealed to me by my research, and secondly, to establish some of the relationships that exist between fats and oils and other compounds that have already been known for a long time. These relationships demonstrate that a number of conclusions that can be drawn from my research have important implications for chemistry in general and also for some manufacturing processes.

SECTION 1

WHAT WAS KNOWN ABOUT OILS AND FATS PRIOR TO 1813

1087. Before I started my work, all that was known about oils and fats was that they were highly flammable and had a very low or even non-existent affinity for water. In other words, they were only known by properties that are totally inadequate to characterize them as an *order* of substances since these properties are also found in the same or almost the same degree in other organic materials. It was also known that several of these substances could produce soaps or a lumpy material, depending on whether they are treated with potassium and sodium hydroxide, or with lead oxide; but no one knew what these two treatments had in common, or what changes these bases cause in the composition of the fats and oils they react with.

1088. The only distinction made between the oils and fats themselves was according to their different melting points (7). On this basis, they were divided into groups called *oils, butters, fats, tallows* and *waxes*. Originally, those words only referred to a single kind of substance: they were truly *specific*. But as civilization led to novel needs and trade links were established with far-away countries[1], the number of oils and fats grew and similar substances were naturally grouped to form genera[2], each of which was given the name of the oldest known substance belonging to it. This is how specific names became generic. When scientists started to examine oils and fats, they soon observed that each of those groups, and in particular those of oils, butters and fats, encompassed such a large number of substances with a different melting point, odor, color etc. that it seemed infinite. That was the state of the art when I started to study these substances[3].

SECTION 2

GENERAL VIEWS ON THE IMMEDIATE COMPOSITION OF OILS AND FATS

Discovery of palmitic and oleic acid

1089. My first discoveries, made when examining the properties of palmitic and oleic acid, which include acidity as well as the other characteristics attributed to oils and fats, has certainly contributed to changing our understanding of the composition of organic acids, which were generally considered to be compounds containing more oxygen than required to form water with the hydrogen present in these acids[4]. These discoveries have also helped to generalize the concept of acidity by establishing the existence of a group of organic acids with an excess of combustible matter, that relate to other organic acids in the same way as hydrogen sulfide and hydrogen telluride are related to acids containing oxygen in the realm of inorganic acids[5]. Once the acidity of palmitic acid and oleic acid had been demonstrated, it proved to be an extremely valuable property on the basis of which fatty matter could be divided into two orders: acid lipids and neutral lipids. Once this distinction had been established, it opened up the way to performing a successful chemical analysis of substances that hitherto had been regarded as ‘quite simple’ because there were no adequate means to identify the immediate principles of which they consist.

Discovery of stearins and oleins

1090. As soon as I had studied palmitic and oleic acid, I tried to find out if fats could possibly be formed by two types of neutral immediate principles with different melting points. This led me to discover stearins and olein. Let us stop to consider these findings: olein is liquid at zero degrees centigrade, mutton tallow stearin is solid at 44°C and human fat stearin is still solid at 49°C; these three substances can be combined in indefinite proportions[6]. Accordingly, it is clear why oils, butters, fats and tallows, in which these substances form the total or almost total mass, can have different melting points, and that we do not have to regard each oil, butter, fat or tallow with a different melting point as a separate species in its own right.

Discovery of odorous fatty acids in phocenin and butyrin

1091. However, the discovery of olein and stearin does not fully explain all the differences shown by oils and fats in the various combinations in which they are found. Several of them, for instance butter from cows’ milk, are odoriferous and colored whereas the stearins and the olein are odorless or almost odorless and completely colorless. When you set out to examine the immediate composition of organic compounds, you cannot profess to have attained your goal until you have managed to explain the properties of those compounds by demonstrating whether they derive from immediate principles that display these properties to the highest degree when isolated, or whether these properties derive not from a particular immediate principle but from a combination of several of them, whereby the properties are the result of this combination and do not derive exclusively from any one of the immediate principles in this combination. In the latter case, the properties of the combination disappear completely when the immediate principles are isolated, instead of becoming more pronounced in one of these principles. This is certainly not the case with the properties of odor and color shown by certain odoriferous and colored oils and fats. As their liquid part is gradually isolated from the solid part, it can be observed that the aroma and the color are concentrated in the liquid part, and that when the latter is treated with alcohol, a volatile, odorous principle is obtained as well as a colored principle that is soluble in water. I must add that the amounts of these principles are small in comparison with those that remain in the fatty part[7]. It can also be observed that when colored oils and fats are exposed to light or treated with carbon, they discolor but their composition does not seem to change. If highly odoriferous oils and fats are treated with milk of magnesia[8], a significant amount of coloring principle is obtained that combines with this alkali[*]. Finally, treating dolphin oil and the liquid part of butterfat with cold alcohol splits the former into olein and *phocenin*[9], and the latter into olein and *butyrin.*

Reflections on phocenin, butyrin and hircin

1092. The discovery of odoriferous fatty acids is very important to chemistry and animal physiology since it has wide ramifications. In fact, it is remarkable to see that compounds such as phocenin, butyrin and hircin contain volatile fatty acids, or rather fully neutralized fatty acid moieties. In this respect, they have much in common with esters, which are presumed to be formed from acids and alcohol. In these two types of substances, there are no free acids but when the equilibrium between the constituent moieties is disturbed, either by alkali or by the action of air or heat, acidity appears. Accordingly, phocenin and butyrin, which are odorless when pure, acquire when exposed to hot air the strong smell that is characteristic of their acids. In this state, they turn litmus red and when treated with magnesia, an isovalerate or butyrate of that base is obtained. It is because of the stability of the phocenin and the butyrin and because only small amounts of odoriferous material are released at the same time when butterfat and dolphin oil are exposed to air, that these latter substances can release an aroma over a prolonged period. If no odoriferous material were to develop to compensate evaporation, butterfat and dolphin oil would soon cease to be aromatic when exposed to air, as happens to the kind of *artificial butter* prepared by impregnating lard with butyric acid (330).

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[*] At least that is the result I obtained when treating dolphin oil and rancid butterfat with magnesia.

1093. It is opportune to point out that before my research on cow's milk butter and dolphin oil, people had no precise idea about the nature of the odorous principles of these substances, and if they had tried to establish this by experiments carried out in an atmosphere impregnated with these principles, they would not have been successful because of the low concentration of their vapors. Let us therefore now consider the aromas given off in various circumstances by organic matter, emanations that make the air which contains them extremely harmful for living organisms. Until now, these emanations could not be examined because of the very low concentration in which they are found in the atmosphere, but now there is hope that one day, it will be possible to isolate the compounds forming that aroma from the substances from which they evolve, just as the odoriferous principles of butter and dolphin oil have been isolated from these substances in sufficient amounts to enable us to establish their nature.

1094. Today, chemical analysis can reveal the reason for the variations in melting point and aroma found in cow's milk butter. The ratio of stearin to olein and butyrin determines the melting point, and the intensity of the aroma varies according to the butyrin content. Finally, because the odoriferous fatty acids are not present in fixed ratios, the nature of the aroma varies. That is why butters that contain a higher proportion of caproic and capric acid to butyric acid display a totally different aroma from those in which the proportion is the reverse.

1095. According to a quick examination I carried out on butter made from human milk[10], this seems to me to contain the same immediate principles as butter based on cow's milk.

1096. Butter made from goat's milk contains butyric acid, caproic acid, hircic acid and perhaps capric acid (see Note 1). It is quite likely that the specific aroma of goat's milk that distinguishes it from that of cow's milk stems from the presence of hircic acid.

1097. The analysis of butter I have just described was essential to understanding the immediate principles in commercial cheeses, since their great variety of aromas is primarily due to the formation of free acids from the butter and, when the fermentation is prolonged, to changes in the capric acid. It is the latter in particular that is responsible for the aroma of Roquefort cheese. The proof is that a wet caprate or a solution of capric acid left in a bottle containing air develops exactly the same odor. I am not suggesting that the aroma of fermented cheese stems entirely from the acids in butter: 1. because during the fermentation of organic nitrogen compounds, an acid is developed that has an odor similar to that of butyric acid, and also because since cheese contains casein, there is every reason to believe that this acid is present in fermented cheeses; 2. because it is quite likely that the stearin and the olein may become rancid and thereby contribute to developing a cheesy smell by evolving volatile acids and a non-acid odoriferous principle.

1098. Finally, the disagreeable odor of leather that has been dressed with fish oil[11] is due to the decomposition of isovaleric acid present in that oil. If a few drops of isovaleric acid are added to water, this develops the same odor after a certain time (277).

1099. Since phocenin occurs in widely differing concentrations in dolphin oil[12], and butyrin is present in the milk of mammals, this should focus the attention of physiologists on the regions where they can be found.

Distinction between entities mistakenly grouped under the name of *adipocere*

1100. After establishing the immediate composition of oils, butters, fats and tallows in the above observations, I subsequently carried out a comparative study of the three entities that people have seen fit to group under the common name of *adipocere,* despite the significant differences they display. That part of the fat from human cadavers for which I reserved the name *adipocere* consists almost exclusively of palmitic acid and oleic acid; it is therefore obviously acid. In this respect, it cannot be mistaken for spermaceti or cholesterol, which exert no action on colored reagents whatsoever. On the other hand, spermaceti is transformed by the action of alkali into palmitic acid, oleic acid and cetyl alcohol; it melts at 49°C, whereas cholesterol is not changed at all by caustic potash and needs to be heated to a temperature of 137°C[13] before it melts.

Summary

1101. 1. To sum up, the discovery of a small number of species of fats that can be mixed in various different proportions explains the differences in melting point, aroma and taste displayed by the vast number of tallows, butters and oils that we encounter in organized beings, while at the same time it brings a whole class of materials back into the realm of the laws of definite proportions. It is also clear that the relationship of stearins, olein, phocenin, butyrin and hircin to the tallows, fats, butters and oils of which they are part, is analogous to that of metals like tin and lead or tin and copper to the alloys they can form, since these metals can form alloys of indefinite proportions.

2. The fatty species that I have established form a new class of species in organic chemistry that include groups[14] that are quite distinct from each other. For instance, there is fatty matter that is acid and fatty matter that is neutral. Amongst the former, there are first of all stearic, palmitic and oleic acid, which react to heat in the same way as benzoic acid. Secondly, there are the odoriferous fatty acids that are more like acetic acid. Amongst the neutral fatty matter, some do not undergo any change when treated with alkali, such as cetyl alcohol and cholesterol,

while others are converted into solid or volatile fatty acids by the same treatment.

SECTION 3

PREPARATION OF FATTY SPECIES

1102. In the chemistry of vegetable or animal matter, *an organic compound is considered to be an immediate principle species if it is impossible to separate various kinds of material from it without distinctly altering its nature* (5). But since organic immediate principles are almost always ternary or quaternary[15] compounds and their elements have a marked tendency to form more simple combinations than the compounds of which they are currently a part, it is difficult to establish whether an *organic substance* one is examining should be regarded as an immediate principle species or as a combination of several species. Moreover, the heat treatments that are so useful in unveiling the nature of inorganic compounds, cannot be used in direct organic analysis. If it is necessary to expose this *organic substance* to reagents that are likely to combine with it, to see if the resulting combination retains all the properties present in the substance before it entered into this combination, it is essential that these reagents are not able to change the equilibrium of the elements in this substance. This condition severely limits the number of reagents that can be used. Since acids and bases are only non-reactive when diluted with water and since their use is nearly always limited to immediate principles that are either alkaline or acid, the chemist has few tools at his disposal except the effect of the cold or rather the strength of the materials' tendency to solidify when exposed to low temperatures, and the solvent action of water, alcohol and ether. It is up to him to select the best of these analytical tools while varying the conditions to which he exposes the substances he aims to decompose.

1103. This discussion was necessary for two reasons: 1. to ensure a clear understanding of the way in which I used solvents to treat the organic materials, either to split them into several immediate principles or to find out if an organic substance should be regarded as a pure compound or a combination of several compounds; 2. to highlight the importance of the method I propose. This method can be described in principle as follows:

Method of applying solvents to organic materials

1104. *Take a weighed amount of an organic substance A that requires 100 parts of a liquid B to dissolve it. This amount is mixed with 10 parts of liquid B. When the solution is deemed to be saturated, it is decanted and a further 10 parts of liquid B are poured onto the residue. A second solution is obtained and this is decanted like the first one. Continue until substance A is either completely dissolved or no longer releases any material into liquid B.*

Subsequently, substance A is treated in the same way with liquids C, D, E, etc.

1105. This will result in one of two possible cases:

First case

1106. Substance A does not dissolve completely or, if it does, the successive solutions are not identical but differ with respect to the amount that dissolved, color, odor, etc. In this case, substance A is not a pure compound. Attempts must be made to split off the immediate principles obtained by evaporating the various solutions to dryness and subjecting their residues to the same treatments that were applied to substance A itself.

Second case

1107. All the solutions of substance A in the same solvent are identical. In this case, the substance has behaved as a species and the probability that it is indeed a species becomes higher, the larger the number of solvents the substance has been treated with and the larger the number of different circumstances under which it has been treated with the same solvent.

1108. From that it can be seen that in organic chemistry, the process of establishing that an immediate principle is in fact a species is the same as the process used in inorganic chemistry to establish that a substance should be regarded as simple[16]. It is evident that the conclusion arrived at in both cases is *based on experiment and should not be considered as absolute but purely as the result of the means employed.* The only difference is that in inorganic chemistry, the conditions that can be applied to the materials are more varied and that not only can all the energy of heat and electricity be applied to isolate the elements from the material, but this energy can be used to greater effect in combination with the energy of the strongest affinities, such as the strength of an oxidizing agent, a combustible material, an acid or a base, whereas in organic analysis, you can only use neutral solvents at moderate temperatures.

1109. The method I followed is suitable to assay immediate principles that are neither acid nor alkaline as well as those that have either of these properties. The assays carried out on acid or alkaline immediate principles are more numerous than those that can be attempted on neutral immediate principles because combining an organic substance with several bases if it is acid, or with several acids if it is alkaline, multiplies the number of conditions under which the same solvent can be used to treat the same substance. Finally, the method can also be used when the solvent treatment is carried out in my distillative autoclave[17].

1110. It is equally impossible to prove that an organic substance is indeed a species as it is to prove that a substance that we call *simple* is really an element. Nevertheless, as organic chemistry progresses, we will find more reasons to support our conclusion that the immediate principles that are regarded as species really are species. It therefore seems useful to list the properties by which immediate principles and species can be recognized as such and to discuss the value of those properties as distinguishing characteristics.

1111. All the properties I will now discuss can display four orders of characteristics:

1. *The composition;*
2. *The physical properties;*
3. *The chemical properties* that can be observed when the substances do not undergo any alteration and act through the attraction of affinities;
4. *The chemical properties* that can be observed when the substances undergo a change either in the proportion of their elements or in the arrangement of their atoms or their particles[18].

Composition

1112. Differences in composition resulting from the nature of the elements or the proportions of these elements already suffice to make a distinction between immediate principles. But this characteristic is not sufficient when two substances give more or less the same analytical results or when the substances have the same composition but different properties, because the same elements combined in the same proportions can produce different compounds if their atoms or their particles can be arranged in different configurations. It is important to note that the composition will have no value as a characteristic if the experiments discussed in sub-section (1104) have not been carried out.

Physical and chemical properties that are observed when the substances do not alter

1113. These two orders of characteristics allow of a clear distinction between immediate principles that display differences in these characteristics. But there are also substances that, although distinct from each other, reveal so few of these properties that they do not suffice to characterize these substances. If the substances also have a similar composition, this makes it even more difficult to define the species.

Chemical properties that are observed when the substances change

1114. If the first three orders of characteristics are not enough to characterize the substances as species, the only course open to us is to turn to the characteristics due to the change in the nature of these substances when they are transformed into other compounds. It is therefore the chemist's task to observe these transformations of the immediate principles and to compare them to find out whether they are identical or different. He must also establish whether these new compounds are of the same nature. If this is the case, he must ascertain whether they are in the same proportion, since different species can give rise to identical products. That is how sugar and lignin behave on distillation or when treated with nitric acid. Finally, in the second case he must study the properties of the new compounds and above all, try to establish whether their composition is in accordance with the immediate principles from which they stem.

1115. These general considerations had to be set out before I go on to summarize my analytical procedures and explain my reasons for concluding that the immediate principles prepared by these procedures are species.

Preparation of fatty acids

1116. The preparation of stearic acid and palmitic acid is based on the premise that potassium stearate and potassium palmitate are less soluble in alcohol than the corresponding oleates. The separation of potassium palmitate from potassium stearate is based on the premise that the latter forms a salt with potassium that is less soluble than the palmitic acid salt of the same base. But the mutual affinity of the two salts is sufficiently strong to ensure that: 1. the compound that stearic acid forms with palmitic and oleic acid and that has a melting point of 55°C, will, after neutralization with potassium hydroxide and subsequent treatment with cold water, be split into potassium hydroxide on the one hand, and on the other hand, bistearate, bipalmitate and peroleate[19] that do not dissolve. Although potassium oleate is deliquescent, if a solution of potassium oleate is to decompose spontaneously, it must be very strongly diluted in water and exposed to a low temperature for a fairly long time; 2. that potassium oleate, which is very soluble in alcohol, cannot be separated in a single alcohol treatment from potassium stearate and potassium palmitate which are hardly soluble in cold alcohol.

1117. Potassium stearates and palmitates were considered to be pure when, after having been dissolved[20] five times in boiling alcohol, the precipitate that formed on cooling contained an acid that had the same melting point[21] as the acid that remained dissolved in the cold alcohol.

1118. I prepared oleic acid by separating potassium oleate from the stearate and the palmitate of the same base by means of cold alcohol. I then acidulated the oleate with tartaric acid and exposed the free oleic acid to lower and lower temperatures to separate it from stearic and palmitic acid that had been dissolved by the alcohol together with the oleic acid.

1119. The separation of the volatile acids present in butter is based on the premise that their barium salts are not all equally soluble in cold water. In spite of their wide differences in solubility in the pure state, these salts always have a strong mutual affinity.

1120. Although I have tested these salts as described in sub-section (1104) and although I have every reason to think that I obtained them in a pure state, when an occasion arises to subject their constituent fatty acids to a further examination, it would be useful to test other salts than those I examined.

Preparation of neutral fatty matter

1121. The preparation of spermaceti and stearins is based on the premise that these substances are less soluble in cold alcohol than the substances that accompany them, and that they crystallize under circumstances where the other substances remain liquid. But since the solubility of these substances does not differ very greatly from that of spermaceti and stearin, and since they also have an affinity for the latter that is not entirely counteracted by the force of crystallization, it is quite likely that the spermaceti and the stearin I have prepared were not quite as pure as it will one day be possible to obtain them.

1122. The preparation of olein is based on the premise that it is more soluble in cold alcohol than stearins, and that it has a lower melting point. Thus by applying an alcohol treatment and a low temperature to olein that is combined with a large proportion of stearins and subjecting olein that is combined with small proportions of stearins to a low temperature only, I managed to analyze the tallows, fats, butters and oils. In order to separate the stearin from the olein, I exposed the latter to lower and lower temperatures, separating the material that had solidified each time. For this separation to be complete, there would have to have been a point at which the stearin that solidifies with the olein formed a combination that no longer had any affinity for that part of the olein that remained liquid at the temperature at which this combination solidifies, which is not very likely since the material that solidified retained some olein[22]. Taking this into account, I think that the oleins I have studied still retained some stearin.

1123. The preparation of butyrin and phocenin is based on the premise that cold alcohol with a density of 0.822[23] (g/mL) is completely miscible with these substances whereas it dissolves only a small amount of olein. However, the mutual affinity of these compounds makes it likely that the butyrin and the phocenin I prepared still contained some olein.

1124. Because it was so difficult to separate the stearins and the olein present in a fat and to do so sufficiently accurately to be able to estimate their relative proportions, I thought it would be helpful to determine the melting points of mixtures of these three compounds[24] of known composition, just as I did for palmitic and oleic acid (208).

1125. I have described in great detail how to prepare the various species of fatty matter so that others will have a proper understanding of my methods and be able to repeat them easily, and also have a clear understanding of the basis on which I distinguish between the various species. I hope that these details will make it easier to perfect my analytical methods over the years to come, which will undoubtedly be necessary. If organic chemistry can help us to a better understanding of production processes and physiology, it will be through the improvement of analytical methods.

Summary of the species

Stearic and oleic acid

1126. The samples of stearic acid that we have studied may well have retained some oleic acid and the samples of oleic acid some stearic acid. Nevertheless, they have been properly characterized as species.

1. Although their compositions are quite similar with respect to the type and proportions of the elements, stearic acid has a higher hydrogen to carbon ratio than oleic acid.

2. They have very different melting points: oleic acid is still fluid below zero degrees centigrade, whereas stearic acid melts at 70°C.

3. There is little significant difference between their equivalent weights[25] since they contain about the same proportion of oxygen and the ratio between that oxygen and the oxygen in the bases that they neutralize is the same for both the stearates and the oleates. The great differences observed between the compounds they form with potassium and sodium respectively suffice to distinguish the one from the other very clearly.

1127. Although the properties I have described characterize stearic and oleic acid, it is evident that the differences will become more striking in the future if and when oleic acid can be separated from the former and stearic acid from the latter.

Palmitic acid

1128. The existence of palmitic acid as a separate species has not been as clearly established as the previous species, given the numerous similarities between this acid and stearic acid. However, I had to make a distinction between them because: 1. the melting point of palmitic acid is 10°C lower; 2. when treating potassium palmitate with alcohol, I found it to be impossible to split this salt into stearate and oleate; 3. palmitic acid has a higher oxygen content than stearic acid and oleic acid.

Isovaleric and butyric acid

1129. The designation of these acids as separate species is based on their very different properties, such as composition, density, odor, solubility in water, equivalent weight, and the properties of their salts, which make it impossible not to recognize them as such. All the attempts I made to split these acids into an *acid principle* and a *neutral odorous principle* were in vain. Several of their salts were gently heated, treated with a stream of carbon dioxide[26] and with alcohol. Finally, they were exposed to the atmosphere for more than five years without my being able to observe any significant reduction of the intensity of the odor of the acid that remained attached to the bases.

Caproic and capric acid

1130. The acids have a similar odor and density but capric acid is solid at 11°C and caproic acid is still liquid at 9°C below zero[27]. The acids also have a different composition and their salts also have different properties.

Cholesterol

1131. This substance is not only characterized by its composition, its melting point of 137°C, and because it forms an astringent compound with nitric acid, but also by its property of not undergoing any change when treated with potassium hydroxide. Consequently, we must conclude that it does not contain any species of saponifiable fatty matter.

Cetyl alcohol

1132. Although this substance differs substantially from all the other species by its melting point of 52°C, its failure to react with potassium hydroxide and the similarity of its composition to that of alcohol and ether, I must confess that I have not made many attempts to split it into a number of immediate substances.

Spermaceti

1133. I think that spermaceti is a species that is sufficiently characterized by its saponification products, because when potassium hydroxide splits it into palmitic acid and oleic acid, it does not yield glycerin as all other types of saponifiable fatty matter do but instead, it yields cetyl alcohol, which other species never do.

Stearins and olein

1134. The two stearins cannot be distinguished from the olein on the basis of their color, taste, odor, vapor pressure or the effect of water, nor can they be characterized by the effect of alcohol or ether, since this effect is too similar in the three substances; furthermore, the differences between their oxygen and hydrogen contents are too small to be taken into account. Nevertheless, it is quite evident that the two stearins are sufficiently different from the olein: 1. with respect to their melting points, since olein melts at 4°C below zero and the stearins do not melt until 43°C and 49°C; 2. because of the way they react with potassium hydroxide; all three are converted into glycerin, a high-melting acid material and oleic acid but the stearins yield a high proportion of high-melting acid whereas the olein which yields a high proportion of oleic acid. If somebody succeeded in proving that the samples of stearin I studied contained some olein and that the olein sample contained some stearin, these differences would not prove to be absent in pure samples but would in fact be even more marked.

Stearin from human fat and from mutton tallow

1135. The distinction between the two stearins is based on the differences that I have established between palmitic acid and stearic acid. If two samples of these stearins with the same melting point are saponified, the soap formed from the stearin from human fat consists of palmitic acid and oleic acid in a proportion such that their mixture melts at 51°C, whereas the soap formed from the mutton tallow stearin consists of stearic acid, palmitic acid and oleic acid in a proportion such that their mixture melts at 53°C. If the two stearins were identical, their saponification products would also have been identical.

Phocenin, butyrin

1136. The distinction between these species cannot be doubted since we know of no saponifiable material that yields isovaleric and butyric acid on saponification. If anyone were to suggest that phocenin and butyrin contained enough olein and stearin from human fat to explain the origin of the palmitic acid and oleic acid that I found in the saponification products of the samples of phocenin and butyrin I studied, these products in the pure state would have been characterized by the property of being converted into glycerin and volatile acids. Consequently, the distinctions I have made still hold.

SECTION 4

VARIOUS PROPERTIES OF POTASSIUM AND SODIUM STEARATES, PALMITATES AND OLEATES WITH RESPECT TO SOLVENTS

1137. The properties of stearic, palmitic and oleic acid of being totally insoluble in water and soluble in alcohol and ether prompted me to give particular attention to the action of these solvents on stearic acid, palmitic acid and oleic acid soaps and in particular on their potassium, sodium and ammonium soaps. For quite some time, I have wanted to draw some general conclusions about the action of these solvents on the combinations of the entities they dissolve, because these solvents are the main instruments of analytical chemistry, as I have mentioned before (1102). I felt it was especially important to determine up to what point combinations of immediate principles with opposite properties could resist the action that a neutral solvent exerts unequally on each of these principles.

1138. Investigation of the action of water, alcohol and ether on potassium stearate.

Effect of water

1139. When cold water is mixed with 1/10th of its weight of potassium stearate, it does not decompose the latter. It is absorbed and the soap forms a thick mucilage.

1140. When cold water is mixed with 1/1000th of its weight of stearate, it starts to compete with the stearic acid (which it cannot dissolve, as we know) for the potassium. But the poor solubility of potassium bistearate limits this kind of action and only half of the potassium dissolves, while the other half remains combined as bistearate with the total amount of acid.

1141. If the temperature is raised to 100°C, the poor solubility of the bistearate no longer suffices to counterbalance the affinity between the water and the dissolved potassium, and the stearate used in the experiment dissolves completely.

1142. The proof that potassium bistearate is more soluble in hot water than in cold water is that the addition of boiling water to bistearate extracts a significant amount of potassium hydroxide and acid in a proportion such that the amount that is not dissolved shows a higher ratio of acid to alkali than the bistearate itself. If this residue is collected and again treated with boiling water, it loses more potassium hydroxide and changes into a material with a melting point of 72°C that contains four times as much acid as the neutral stearate. This material therefore appears to be a *quadrostearate*, analogous to a *potassium quadroxalate*[28].

Effect of ether

1143. Since ether has much more effect on stearic acid than on potassium, it should produce the opposite effect to that of water, if it has enough energy to change the position of the dissociation equilibrium of the potassium stearate[29], and this is exactly what the following experiment shows. If you treat potassium bistearate with boiling ether, collect the liquor by filtration after it has cooled completely and repeat this treatment several times, this will yield ethereal solutions of stearic acid that contain almost no potassium, and a residue that could contain more base than the neutral stearate since this will have released acid to the boiling ether.

Effect of alcohol

1144. Since alcohol dissolves both potassium hydroxide and stearic acid, it tends to maintain the compositions of the potassium stearate and bistearate with which it is brought into contact, as observed. The fact that a solution of potassium quadrostearate in boiling alcohol splits on cooling into potassium bistearate that crystallizes and stearic acid that remains in solution, is above all due to the cohesive force of the bistearate competing with the affinity of the alcohol for the stearic acid, an affinity that is further favored by the low potassium content of the quadrostearate.

1145. This shows that treating potassium stearate successively with cold water and boiling ether causes the successive separation of potassium hydroxide and stearic acid; the affinity of the two opposite principles in this compound is thus reduced by the neutral solvents.

1146. Potassium palmitate behaves towards solvents in the same way as potassium stearate.

1147. Although potassium oleate is soluble in cold water, it nevertheless has a tendency to decompose into an insoluble acid salt and potassium hydroxide when it is dissolved in a large amount of water.

1148. When sodium and ammonium stearates and palmitates are mixed with water, they also decompose into free alkali and insoluble acid salts.

Conclusions

1149. These decompositions are remarkable in several respects:

1. They show that when seeking to explain the decomposition of a salt by a solvent, you should not consider the cohesive force of the undissolved matter in absolute terms but in relation to the solvent. If liquid A dissolves the base present in a salt but does not dissolve the acid part, liquid B may dissolve the acid of this salt but not the alkaline part, whereas a third liquid may dissolve both the acid and the alkaline parts

without decomposing the salt. The stability of the latter is thus relative to the liquids with which it is brought into contact.

2. They show that, if there are cases where a salt fails to dissolve when in contact with a liquid that is able to dissolve it, you may conclude that the affinity of the liquid is not strong enough to overcome the cohesive energy of this salt, but it would not be correct to extend this conclusion to all such cases. Thus potassium stearate dissolves in boiling water but because this solution decomposes on cooling into potassium hydroxide and bistearate that precipitates, it is highly likely according to the law of continuity that the transition of the moieties in the neutral stearate to this second equilibrium does not take place abruptly but gradually. Consequently, there is a moment when the solution does not contain just neutral stearate but dissolved potassium hydroxide that is combined with potassium bistearate. It is also likely that amongst the solutions of neutral salts, there will be basic and acid salts that are combined with the rest of the acid or base that together constituted the neutral salt before it was dissolved.

1150. With respect to the influence that solvents can have on the separation of the immediate principles of salts, the only investigations carried out so far are on the action of water on bismuth nitrate[30], antimony chloride[31], mercuric nitrate[32], mercuric sulfate[33] and copper sulfate[34]. Although I was right to attribute these decompositions to: 1. the affinity of water for the acid; 2. the cohesive force of the base; and 3. the weak alkalinity of the latter, I also admit that before I started my work, I overrated the influence of the third cause in comparison with the first one. The following seems to me to support that opinion: "If substances that are highly oxidizing are allowed to react with combustible compounds and substances that are acid are allowed to react with alkalis, they form reaction products that are subject to the law of definite proportions and provide the most striking examples of an energy-based affinity since they present the phenomena of combustion and neutralization. On the other hand, when reagents that do not show opposite properties react with each other, the reaction products usually have indefinite proportions. This can be observed: 1. when a solid is dissolved by a liquid; 2. when an elastic fluid[35] is absorbed by a liquid; 3. when liquids are mixed and mutually dissolve each other. In these combinations that are called *dissolutions,* the characteristic properties of the constituent entities are not lost *and since quite a large number of them are obviously formed by reagents that interact only weakly, I am inclined to regard all these combinations* WITHOUT DISTINCTION *as the result of much weaker affinities than those that give rise to well-defined reaction products. Accordingly, I think that salts that can be decomposed by solvents are formed by principles that interact only weakly."*

1151. Nowadays, I think that the fact that a salt is decomposed by a solvent is not a reason to conclude *in general and for all cases without* *distinction* that the acid and the base forming that salt only interact weakly. The following arguments prove that solid[36] fatty acids are quite strong and that, if several of their compounds succumb to the action of water and ether, it is because they have a relatively strong affinity for the potassium or the fatty acid moiety in these salts. It is indeed so that: "stearic acid, palmitic acid and oleic acid decompose potassium carbonate, sodium carbonate and barium carbonate at a temperature of 100°C. When these acids are dissolved in alcohol and added to alcoholic solutions of various salts, the bases of which are able to forms soaps that are insoluble in alcohol, the salts are decomposed. This is what can be observed with silver nitrate in particular."

1152. *The property displayed by potassium butyrate dissolved in a small amount of water, of forming a liquid with a significant amount of free butyric acid that is neutral to blue litmus paper but turns it red when water is added* (370), demonstrates the influence that solvents can have in experiments made with litmus paper to see if a salt has an excess of acid. *It is clear that an excess of acid in a salt will only be indicated by the litmus when this excess acid has a stronger affinity for the alkali in the litmus than the coloring principle in the litmus has for this alkali.* Thus the cohesive force of the coloring principle, which is combined with the potassium as well as with the paper, is such that the excess of butyric acid present in the concentrated alcoholic solution of potassium butyrate cannot capture any alkali from the coloring principle. But the addition of water weakens the cohesive force between the alkali and the coloring principle sufficiently for the potassium hydroxide to neutralize the excess of butyric acid. If the red litmus paper is then heated, the alkali that was combined with the butyric acid migrates from the latter to form a strong compound with the coloring principle, and the paper turns blue again. I concluded that it is chiefly the cohesive force of the litmus extract that prevents its alkali from reacting with the excess butyric acid present in the concentrated potassium butyrate solution, because when dry litmus extract is added to this solution, which has no effect on litmus paper, this dry extract dissolves and turns red. By evaporating this red liquid in a glass dish, it is possible to obtain a blue residue that turns red again when dissolved in water. However, this result is more difficult to obtain this way than when using litmus paper. It is possible that the affinity of the potassium butyrate for the excess butyric acid, which increases as the amount of water that keeps these compounds in solution decreases, joins the cohesive force of the litmus to restore the blue color to the litmus that had previously been turned red by the less concentrated acid solution of potassium butyrate.

1153. If the amount of water in which the potassium butyrate with an excess of acid had been dissolved has such an effect on the behavior of litmus paper, then the kind of colored reagent in general use to establish neutrality in salts is bound to have a very substantial effect on the results, as I have already observed a long time ago[37]. Since the facts that prove this are linked to the previous observation, I feel I should repeat them here. One and the same salt solution can be acid according to one indicator and alkaline according to another. For instance, when litmus paper is immersed in a solution of lead acetate or stannous chloride, it turns red whereas the addition of a solution of campeachy[38] extract makes these solutions turn blue, indicating an excess of alkali. These results appear to be contradictory if neutrality is seen as something absolute, but they can be explained quite easily by taking into account the tendency of bases to precipitate and the affinity of the alkali in the litmus for acetic acid and hydrochloric acid in the first case, and in the second case, the tendency of lead oxide and tin oxide to form compounds with hematin that are insoluble in water.

1154. It is thus clear that: 1. *a salt with an excess of acid can be indicated as neutral by litmus paper;* 2. *a neutral salt can be indicated as acid by one colored reagent and alkaline by another.*

SECTION 5

GENERAL VIEWS ON THE INTERACTION BETWEEN BASES THAT CAN FORM SALTS, AND OILS AND FATS

1155. After having described each species of fatty matter and how to prepare them, I examined the changes that take place in stearins, olein, butyrin, phocenin and spermaceti when they produce soaps by reacting with bases that can form salts.

1156. It is now possible to give a more exact definition of *saponification,* which originally meant *the process of making soap* or *the phenomenon shown by fatty matter when it reacts with an alkali to produce soap.* Since soaps are combinations of stearate, palmitate and oleate and since they are always produced on a large scale from oils and fats that consist of stearin and olein, neither of which are shown to be acid by colored reagents, it follows that *saponification is a process that by means of alkali produces acid fatty matter from certain fatty material that is not acid, or the phenomenon that non-acid fatty material presents when it becomes acid after having been subjected to the action of alkali.* But if soaps were made by allowing an alkali to react directly with stearic acid, palmitic acid or oleic acid, the latter definition would no longer be applicable. In fact, that would not be a true saponification but the same process as the reaction between any acid with a base to form a salt; moreover, in a soap works, soap has never been produced by direct reaction with potassium or sodium hydroxide. Consequently, the true meaning of *saponification* is not so much the production of soap that results from it, but of the acidity shown by a fatty material after it has been subjected to the action of an alkaline base.

1157. We have seen that three kinds of material are needed for saponification: 1. a fatty material like the two stearins, olein, spermaceti, phocenin, butyrin and hircin[39]; 2. a base that can form salts; 3. water. We have also seen that the process proceeds without contact with atmospheric oxygen. I have studied saponification from two angles: 1. with respect to the fatty material; 2. with respect to the bases that can form salts.

A. SAPONIFICATION WITH RESPECT TO THE FATTY MATERIAL

1158. When comparing the elementary composition of human fat, lard, mutton tallow and spermaceti with the composition of their saponification products, it is clear that the amount and the proportion of the elements in those products reflect as exactly as can be hoped in the current state of the art, the composition that I have ascribed to the material from which they originate.

1159. It is also clear that on saponification, fats are split into two highly unequal parts: 1. one that amounts to at least 92 % of the fats by weight and that consists of oxygen, carbon and hydrogen, whereby the ratio between the latter two is almost the same as the ratio in which they occur in the fat, while their proportion with respect to oxygen is much higher than in the latter; 2. the other part also consists of oxygen, carbon and hydrogen, and binds water to form glycerin with a density of 1.27 (g/mL).

1160. The elementary analyses of the mutton tallow stearin and olein that I carried out are in accordance with the above. Consequently:

1. The mutton tallow stearin contains less oxygen and a higher proportion of hydrogen to carbon than the olein.
2. On saponification, the mutton tallow stearin yields more fatty acids and less glycerin than the olein, and the stearin gives much less oleic acid than the olein.

1161. These results are both in accordance with the compositions of glycerin and of fatty acids and with my observations concerning the saponification of fats.

1162. The elementary analysis of spermaceti is likewise in accordance with that of its saponification products. In this process, *all its oxygen binds carbon and hydrogen in the ratio in which these are found in palmitic and oleic acid, while the remainder of these combustibles form cetyl alcohol in which the elements are present in the same ratio as in ethylene, while binding enough water to keep the potassium in solution.* I considered the production of a small amount of soluble matter amounting to less than 1 % of the spermaceti that was saponified to be incidental to the process. The major part of the material that does not become part of the acids but forms cetyl alcohol, that is to say a substance that does not neutralize fatty acids and does not dissolve in water, could at a certain point explain why spermaceti is saponified more slowly than the stearins and olein under the same experimental conditions.

1163. I will end my summary of saponification with respect to the fatty matter by recalling that the fact that cholesterol cannot be saponified is probably due to the small amount of oxygen it contains and also because the ratio of carbon to hydrogen is much higher than in ethylene. In fatty matter that can be saponified, the carbon to hydrogen ratio is very close to the ratio found in ethylene.

B. SAPONIFICATION WITH RESPECT TO THE BASES THAT CAN FORM SALTS

1164. When studying saponification with respect to the alkalis that cause it, I investigated which bases that can form salts are capable of converting the stearins and the olein into soaps, the amounts of those fatty materials that a given amount of potassium hydroxide can saponify, and finally, whether it is possible to carry out a saponification by using carbonates[40].

1165. The first investigation allowed me to observe that all the bases that can form salts that I used in my experiments, can be classified in three groups according to the way they react with the stearins and the olein. The first group contains bases like alumina, which form no bond with these substances in moist conditions; after having mixed these two reagents, the addition of boiling water causes most of the stearins and the olein to float to the surface while the alumina remains at the bottom of the water. The second group comprises bases that combine quite strongly with the stearins and the olein, since they cannot be separated when the materials are heated in boiling water. This is the case with magnesia when it has not reacted long enough to cause saponification. Finally, the third group comprises bases that are able to convert the stearins and the olein into soaps and glycerin in a short period of time. We have seen that potassium and sodium hydroxide, baryta, strontium hydroxide and lime, that is to say the alkaline bases regarded as the strongest[41], lead to saponification and produce the same amount of glycerin and the same proportion of bound fatty acids. Zinc oxide and lead oxide, which are also alkaline since they can neutralize acids, show similar results. This indicates that the lumps formed by lead oxide are actually due to saponification. It is remarkable that saponification is equally well induced by bases that form soluble soaps as by those forming insoluble soaps. But what is most surprising is that magnesia only causes saponification with difficulty although it has strongly alkaline properties. Liquid ammonia behaves similarly but this is less surprising since it is too volatile to permit heating.

1166. Let us now consider these two elements of saponification together.

1167. On the one hand there are the stearins and the olein, either as separate compounds or mixed in the form of tallows, fats or oils, and on the other hand there is the spermaceti; none of these are acid to colored reagents, and all of these have only a very slight affinity or none at all for bases that can form salts and cause saponification. However, the elementary analysis of these substances when compared with that of their saponification products shows that it is possible that 9/10th of the stearins and the olein are converted into soaps with the remaining 1/10th being glycerin, whereas 6/10th of the spermaceti is converted into soaps, while the remainder of the spermaceti combines with water to form cetyl alcohol. Accordingly, *the action of an alkali is to be understood as changing the state of equilibrium in which certain proportions of oxygen, carbon and hydrogen constitute compounds that have no affinity for those alkalis, to a new equilibrium where the same proportions of elements form acid compounds.*

1168. I would add that in a saponifiable substance, a given quantity of alkali can only develop an amount of acid material such that the resulting combination with this alkali is neutral. Thus when potassium hydroxide is heated with an amount of fat that would yield a 'persoap' on complete saponification with this alkali, it in fact only produces a neutral soap. Therefore, only half the amount is saponified and the other half remains unsaponified, thereby demonstrating that the alkalinity is the cause of the saponification.

1169. Finally, a strange result is that although the alkalinity of potassium carbonate is partially weakened by the carbon dioxide, it is still sufficiently strong to develop acidity in fats that it is brought into contact with. If the temperature is not too high, only half of the potash takes part in the saponification. The other half retains all of the carbon dioxide in the form of neutral bicarbonate.

SECTION 6

APPLICATIONS OF MY RESEARCH

Combustion application

1170. The analyses I carried out on a large number of oils and fats showed that those fats with the highest stearin content contain the most combustible material.

1171. Since some of the olein can be easily separated from fats with a high stearin content, this provides a means for improving the quality of tallow. By losing some of its olein, it also loses some color and odor, since the color and odor principles are concentrated in the olein. The removal of some olein also raises its melting point, which makes it less likely to stain any textiles on which it is spilled. But even if all the olein were to be separated from the stearin, the latter would still not display the properties of a wax; I will demonstrate below that this substance is totally different from the materials in the class to which it is generally thought to belong. Many people told me they hoped to convert tallow into wax by means of nitric acid, but this possibility is not borne out by my experiments (46), which showed that nitric acid simply oxidizes carbon and hydrogen, thereby making the oxygen content more dominant in the compounds thus treated. This result is the opposite of what would be required to convert tallow into wax.

1172. My experiments on the conversion of cadavers into fat as suggested by the nature of adipocere, have shown that there is little or no advantage in conducting this conversion on a large scale because the *adipocere* is formed from the fatty parts of cadavers only, without any contribution from other components of the cadavers. I found that the amount of adipocere that can be obtained from albumin[42], yellow elastic tissue, sinews, muscle fiber, etc. is smaller than the amount of fatty material that can be separated from these same substances by means of alcohol and ether. I also established that these solvents simply extract fatty matter and keep it in solution. Consequently, they do not determine the formation of the fatty matter as has been claimed. The same holds when nitric acid is heated with the nitrogenous substances listed above and gluten. It liberates the fatty matter contained in these substances by changing it to a certain extent.

These experiments and the numerous conclusions that can be drawn from them will be set out in detail in my monograph[43] on nitrogenous material of animal origin. I will prove that in living organisms, muscles do not change into adipocere or even into fat.

Application to the art of soap making

1173. When I discovered that the fatty matter in soap is acidic and in fact consists of three different acids: stearic, palmitic and oleic acid, I realized that this knowledge would enable soap makers to conduct their operations with greater precision than was possible before the nature of the soaps was perfectly understood. In fact, once these compounds were recognized as salts, this placed them in the category of compounds that are subject to the law of definite proportions and from then onwards, it could be hoped that studying the soap manufacturing process in the light of science would one day raise it to the same level as the manufacture of alum[44], iron sulfate etc. But to arrive at this point, it would be necessary to determine the properties of the fats and oils before their saponification and the proportion of the products resulting from this process, and to describe all the essential process conditions. After this research has been carried out on one fatty material, it must be repeated on other samples of the same material to explain the differences observed in the properties of soap. There are two main ways in which these materials can differ: 1. they may be hard or soft; 2. they may have a more or less strong odor or no odor at all. I will now examine these two aspects.

A. SOAPS CONSIDERED WITH RESPECT TO THEIR DEGREE OF HARDNESS OR SOFTNESS

1174. *Hard soaps* are obtained by the saponification of olive oil and above all animal fats by means of sodium hydroxide. *Soft soaps* are obtained by using potassium hydroxide for the saponification of seed oils in general and more or less fluid animal oils.

1175. When investigating what exactly it is that makes soaps hard or soft, it becomes clear that these properties depend on how the soaps react with water. *Hard soaps* lose most of the water used to manufacture them when exposed to the air. Once they have lost this water, they only dissolve very slowly in cold water without absorbing any of it. *Soft soaps,* on the other hand, cannot be dried by exposure to air. They retain a varying amount of water that makes them soft or gelatinous. If they are dried by heating and then mixed with cold water, they dissolve in this water or are diluted by it to a greater or lesser extent.

1176. Experiments to find out why a soap is soluble or less soluble in water reveal two causes: 1. *the nature of the alkaline base*; 2. *the nature of the fatty matter that is combined with this base*. Let us now examine the effect of those two causes.

1. Effect of the alkaline base

1177. The effect of the alkaline base is demonstrated by the following experiments. When one of two samples of the same fat is saponified by potassium hydroxide and the other by sodium hydroxide, it will always be observed that the sodium soap is less soluble in cold water than the potassium soap.

2. Effect of the fatty matter that is combined with the base

1178. If the alkaline base alone determined whether a soap is hard or soft, all fatty materials should give soft soaps when saponified by potassium hydroxide and hard soaps when saponified by caustic soda. This is not what happens since olive oil and high melting animal fats in particular give soaps with sodium hydroxide that are much harder than sodium soaps made from seed oils and animal oils. Secondly, these same oils produce soaps with potassium hydroxide that are much softer than potassium soaps based on olive oil and high melting animal fats. My research explains these results. But let us first of all remind ourselves of the effect of cold water on soaps or rather on the salts that stearic acid, palmitic acid and oleic acid form with sodium and potassium.

1179. Sodium stearate can be considered to be a typical hard soap since it does not seem to change at all when treated with ten times its own weight of water. Potassium stearate produces a thick mucilage when mixed with this amount of water. Sodium oleate is soluble in ten times its own weight of water. Potassium oleate forms a gel with twice its weight of water and a solution with four times its weight. It is sufficiently deliquescent for 100 parts of soap to absorb 162 parts of water when exposed to air that is saturated with water vapor at 12°C.

1180. Sodium and potassium palmitate soaps differ from the stearate soaps of the same bases only in that water has a stronger effect on the former than on the latter.

1181. The stearates, palmitates and oleates of sodium and potassium can be mixed in all proportions.

1182. The different degrees of hardness and softness found in soaps can be explained by the above concepts and the following analytical results I obtained:

1. Soaps from human fat and vegetable oils[*] consist of oleates and palmitates mixed in widely varying proportions. It was observed that the soaps are softer when they contain more oleate and thus less palmitate.

2. Apart from the odorous salts that they may also contain, soaps made from mutton tallow, beef tallow, lard and butter consist not only of palmitate and oleate like the above soaps, but also stearate. They were found to be harder with an increasing proportion of stearate to oleate.

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[*] I am only referring here to soaps formed from *vegetable oils* that were more or less fluid.

1183. On the other hand, since my experiments have shown that the stearins are the main source of stearic acid and palmitic acid and that olein yields oleic acid, it follows: 1. that on the basis of the ratio of stearin to olein in the saponifiable fatty raw material, which ratio can be determined from the melting point of these materials, it is possible to predict the degree of hardness or softness of the soaps these materials will produce; 2. that it is easy to imitate a *given soap* by starting with stearins and olein in such proportions that the resulting ratios of the stearic, palmitic and oleic acid they will produce on reaction with the alkali are the same as in the soap to be imitated. So by adding to oils that only yield soft sodium soaps a raw material that is rich in stearin such as the wax of the *Myrica cerifera, a substance produced* abundantly by an African tree[45] and that was sent to me by an English traveler and scientist, it is possible to imitate soap from olive oil, a soap which does not differ fundamentally from soaps based on seed oils[*] in that it contains less oleic acid.

1184. It is evident that these concepts form the basis of the art of soap making and allow it to attain a degree of precision that would have been impossible if soap makers were still not aware that there were three acids in the fatty part of soaps, or why saponifiable fatty raw materials produce either hard soaps or soft soaps.

B. SOAPS CONSIDERED WITH RESPECT TO ODOR

1185. Soaps are either *odorless,* like those made from human fat and lard, or *odorous,* like those made from butter, dolphin oil or beef tallow. The odors of the soaps originate from principles that are totally distinct from stearic acid, palmitic acid or oleic acid; I concluded this because:

On the one hand, when these soaps are dissolved in water, acidulated with tartaric acid or phosphoric acid, filtered and distilled, it can be observed that: 1. the product yielded by butter soap contains butyric acid, caproic acid and capric acid; 2. the product yielded by dolphin oil soap contains isovaleric acid[†]; 3. the product yielded by beef tallow soap contains hircic acid.

On the other hand, by washing the stearic, palmitic and oleic acids sufficiently, these acids can finally be obtained in such as state of purity that when they are combined with potassium or sodium hydroxide, they form totally odorless soaps. I have noticed this particularly with soap made from butter[‡].

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[*] I refer here only to seed oils that are commonly used in the manufacture of soft soaps, since I have also come across oils extracted from vegetable seeds that I found to contain other fatty materials than stearin and olein.

[†] When this acid deteriorates, it gives the product or rather the soap an odor of leather that has been dressed with fish oil.

[‡] It is difficult to remove all odor from the fatty matter of soap made from dolphin oil because its liquidity and low density in comparison with water obstruct an intimate intermingling of the two liquids.

1186. The applications I have described show how research that may appear to be purely speculative can lead to a better understanding of the processes involved in various manufacturing processes and how necessary it was to carry out this large number of experiments on the saponifiable fatty matter and their saponification products before applying my findings as described above.

SECTION 7

CONJECTURES ON THE COMPOSITION OF VARIOUS SPECIES OF FATTY MATERIALS

Conjectures on the properties of saponifiable species of fatty materials in what is presumed to be a pure state

1187. In everything that I have said so far, I have tried to establish as many links as possible between the facts I have observed. In the few explanations I have given, I have endeavored to stay within the scope of the experiments. Now it could be useful to expound a number of conjectures on the nature of various species of fatty materials, some of which spring to mind so naturally that the reader would be surprised if they were not included in this monograph.

1188. The saponification products of 100 parts of stearin and 100 parts of olein from human fat are as follows:

	STEARIN	OLEIN
Glycerin…………………………………..	8.5	9.8
Palmitic acid (melting point 55°C)…….	80.0	22.08
Oleic acid, liquid at 0°C…………………	16.4	73.92

The products are the same except that the stearin yields slightly less glycerin and a much higher proportion of palmitic to oleic acid than the olein. On the other hand, we have seen (1121) that it is quite likely that the stearin sample I used for my experiments still contained some olein just as the olein retained some stearin (1122). *Consequently, we can conclude that, when absolutely pure,* 1. *the stearin would only yield glycerin and palmitic acid*[*]; 2. *the olein would only yield glycerin and oleic acid.*

1189. *For the same reason, pure mutton tallow stearin would yield only glycerin and stearic acid.*

1190. On saponification, 100 parts of phocenin and butyrin yielded:

	PHOCENIN
Glycerin…………………………………………	15.00
Isovaleric acid anhydride……………………	32.82
Oleic acid………………………………………..	59.00

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[*] If palmitic acid is truly different from stearic acid, the stearin that provides palmitic acid should be called *palmitin* and the name *stearin* should be kept for mutton tallow stearin.

	BUTYRIN
Glycerin	12.50
Volatile acids	13.68
Palmitic acid (melting point 55°C)	16.90
Oleic acid, liquid at 0°C	63.60

1191. Similarly, given the arguments expressed above, it would be logical to assume that:

1. The *phocenin* described consists of *olein* and another substance that is characterized by the property of being converted into glycerin and isovaleric acid by alkali; this would therefore be *pure phocenin*.

2. The *butyrin* described consists of five immediate principles: 1. *olein*; 2. *stearin*; 3. a compound that is converted by alkali into glycerin and butyric acid; this would be *pure butyrin*; 4. a substance that is converted by alkali into glycerin and caproic acid; this would be *caproin*; 5. a substance that is converted by alkali into glycerin and capric acid; this would be *caprin.*

1192. Finally, according to the same hypothesis, spermaceti would consist of two immediate principles, one of which is characterized by the property of being converted on saponification to palmitic acid and cetyl alcohol while the other would have the property of forming oleic acid and cetyl alcohol. The purification of spermaceti presents the same difficulties as the purification of stearin and olein (1121).

Conjectures on the immediate composition of saponifiable species of fatty material

1193. The previous conjectures are of a type that can be confirmed by experiment because it is not unthinkable that one day, absolutely pure stearins, olein, spermaceti etc. will be found in organized beings or that it will be possible to obtain these substances in a pure state by chemical means. However, I must admit that the following conjectures about the arrangement of the elements that make up several types of fatty matter are hypotheses that cannot be fully proven. I will nevertheless set them out here because I believe that they could point the way to further research.

1194. We have seen that phocenin and butyrin, which are not acid, yield acids and glycerin when treated by potassium hydroxide. We have also seen that when exposed simultaneously to air and heat, they become odorous and able to pass on their odorous principle to magnesia. Esters[46] and ethyl nitrate, which are considered to be reaction products of acids and alcohol, show similar properties: they are not acid but when treated with caustic potash, they split into alcohol and acids. When exposed to air and heat, part of their acid is liberated. In view of these analogies, surely we have reason to regard phocenin and butyrin as reaction products of odoriferous acids and anhydrous glycerin, or rather a substance consisting of oxygen, carbon and hydrogen that changes into glycerin on reacting with water?

1195. If we accept the similarity I have pointed out between the immediate composition of esters and that of phocenin and butyrin, we are bound to extend this to stearins and olein, because they are extremely similar to phocenin and butyrin in the way they behave, not only when exposed to alkali but also when exposed to air and sulfuric acid:

(A) In the presence of alkali, the stearins and olein are converted into glycerin and non-volatile fatty acids, just as phocenin and butyrin change into glycerin and volatile fatty acids.

(B) When stearins and olein are exposed to oxygen, they become acid and although volatile acids and a non-acid aromatic compound are produced, non-volatile acids are also formed just as isovaleric acid and butyric acid are formed when phocenin and butyrin are exposed to oxygen (see note 2 at the end of this work).

(C) When stearins and olein are mixed with concentrated sulfuric acid, non-volatile acids are formed and perhaps also some glycerin (see note 3 at the end of this work). Similarly, when phocenin and butyrin are exposed to concentrated sulfuric acid, isovaleric acid and butyric acid are formed and perhaps some glycerin (see note 4 at the end of this work).

1196. In truth, there are a number of arguments against the validity of this opinion that I feel I should set out here, especially since when I discussed this subject in 1814, in my third paper on oils and fats,* these objections seemed to me to be sufficiently strong to persuade me that it was more logical to regard the glycerin and the non-volatile fatty acids produced by the saponification of stearins and olein as newly-formed compounds rather than as the immediate principles of stearins and olein. But at that time, I had no knowledge as yet of phocenin and butyrin and I was unaware of the analogy between the effect of oxygen on these saponifiable fatty compounds and the effect of alkalis on the same compounds. Below I will list the arguments I raised at the time against an opinion that I now consider to be the most likely to be valid, together with the counterarguments that seem to me to disprove them.

(A) Stearic acid, palmitic acid and oleic acid are insoluble in water. Glycerin dissolves quite readily therein. Why does water not remove this principle from the acids with which it is combined? It is because cold water does not remove potassium from the bistearate or the persilicate of this base.

(B) Why is it that stearic acid, palmitic acid and oleic acid, which are completely miscible with boiling alcohol with a density of 0.821 (g/mL), form together with anhydrous glycerin, which is soluble in the same liquid (at least when it has been hydrated), compounds that are

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* *Annales de chimie,* volume XCIV, page 113.

hardly soluble in it at all? This is because sulfuric acid and potassium hydroxide form a neutral salt that is not very soluble in water, and because acetic acid and alcohol form an ester that is not very soluble in the same liquid, even though sulfuric acid, potassium hydroxide, acetic acid and alcohol are highly soluble in water.

(C) Stearic acid, palmitic acid and oleic acid, etc. turn litmus strongly red. Glycerin has a significant affinity for potassium hydroxide and would therefore also appear to be acid rather than alkaline; why, then, does it counteract the effect of these acids on litmus? Because the esters alcohol forms with nitrous acid, acetic acid and citric acid, are not acid themselves.

(D) Why is it that when stearic acid, palmitic acid, oleic acid etc. are brought into contact with glycerin, they do not form stearins, olein, etc.? That is because when these compounds are brought together, they are in the form of hydrates. As such, their mutual affinity is not sufficiently strong to release the amounts of water in excess of what is present in the stearins, olein, etc. Furthermore, when acetic acid, benzoic acid etc. are brought into contact with alcohol, be it cold or hot, they never react to form an ester in the absence of[47] an inorganic acid.

(E) Why is saponification not instantaneous[48] when saponifiable materials are brought into contact with a base? Without pretending to provide a conclusive answer to this objection, the difficulty of establishing an intimate and sufficiently long contact between two immiscible liquids could be a significant obstacle to the saponification reaction.

1197. Finally, I would like to add that the properties of anhydrous glycerin could well be quite different from those we are familiar with after it has reacted with water. Organic compounds are capable of reacting with water in well-defined ratios in two ways: 1. by maintaining more or less their original properties, like for example an anhydrous inorganic salt that can bind water of crystallization; 2. by acquiring properties that are totally different from those they had before reacting with water, like for instance starch, which is converted by weak sulfuric acid into glucose[49] by binding water.

1198. Regardless of which of these two opinions is to be preferred, I will now summarize the explanation of the saponification reaction according to two hypotheses: (A) by assuming that saponifiable fatty matter is formed directly by oxygen, carbon and hydrogen, and (B) by assuming that they are formed by a direct combination of fatty acids and a compound that forms glycerin or cetyl alcohol after binding water.

SAPONIFICATION ACCORDING TO THE FIRST HYPOTHESIS

1199. The stearins, olein, phocenin, butyrin and hircin are formed from oxygen, carbon and hydrogen in such proportions that one part of their elements represents a volatile or non-volatile acid, while the other part +

water represents glycerin. Spermaceti is formed from the same elements in such proportions that one part represents a non-volatile fatty material and the other part consisting of carbon and hydrogen (in the same ratio as in ethylene) + water represents cetyl alcohol. When these saponifiable fatty materials are allowed to react with a base that can form salts and that is sufficiently strong, the equilibrium between the elements is disturbed and the alkaline force determines the acidity of one part of the mass of saponifiable materials, while the remainder of this mass binds water to form glycerin or cetyl alcohol. According to this hypothesis, saponification is a phenomenon similar to that of metals dissolving in an acid while they oxidize at the expense of water. The only difference is the nature of the force that comes into play: during saponification, it is the alkaline force which determines the development of the acid force, while during the dissolution of metals, it is the acid force that determines the development of the alkaline force. In both cases, salts are formed from materials that contain only one of the immediate principles of the salts being produced.

SAPONIFICATION ACCORDING TO THE SECOND HYPOTHESIS

1200. Stearins, olein, phocenin and butyrin are types of salt formed by the anhydride of a volatile or non-volatile fatty acid and glycerin anhydride. Similarly, spermaceti is also a kind of salt but the base that neutralizes the acid part is not glycerin but an ethylenic compound[50]. This composition makes spermaceti similar to esters, which are also considered to consist of an acid and ethylene. According to this hypothesis, the saponification reaction is just the decomposition of a fatty salt by a base that can form salts and replaces the anhydrous glycerin or the ethylenic compound, whereby these latter compounds form syrupy glycerin or cetyl alcohol by reacting with water.

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[1] This is what we now call ‘globalization’.

[2] Here the author skips the family that comes between order and genus. See also endnote 2 on page 4.

[3] Now that the author has reviewed the state of the art with respect to oils and fats, it may be opportune to review the state of the art with respect to organic chemistry and to focus this review on oils and fats:

- Elemental analysis was already quite advanced and the author also introduced several improvements, so he was able to determine the carbon, hydrogen and oxygen contents of fatty acids, glycerin, cholesterol etc. He also distinguished between stearic acid and oleic acid on the basis of such elemental analyses.
- However, molecular weights were as yet unheard of so the results of these analyses were expressed as the number of carbon atoms per oxygen atom and the number of hydrogen atoms per oxygen. Other methods of expression were also used but they were all based on ratios.
- How the various atoms were arranged within a molecule was a subject that had not yet been addressed at all. It was only in 1858 that Archibald Scott Couper (1831-1892) started drawing bonds between atoms. (His paper is available at:

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http://web.lemoyne.edu/~giunta/couper/couper.html) However, his contribution was brushed aside and it was Friedrich August Kekulé (1829-1896) who is credited with the concept of equivalency, which he formulated in 1860.

- The only alcohol that was known at the time was ethanol and it was only in 1834 that Jean Baptiste André Dumas (1800-1884) and Eugène Melchior Péligot (1811-1890) concluded that wood spirit constituted another alcohol: methanol. Consequently, alcohols were not regarded as a group of different compounds with some similar properties at the time when Chevreul studied oils and fats.
- Chevreul discovered a number of fatty acids; common ones like stearic acid, oleic acid and palmitic acid but also less common ones like for instance isovaleric acid.
- Glycerin had been discovered and described by Carl Wilhelm Scheele (1742-1786) in 1779 but he mistakenly thought that this 'sweet principle' was a constituent of the acidulated soaps as well as of the original oil.
- Fatty acids were also known since Geoffry had observed that acidulated soaps were soluble in alcohol whereas oils were not. It was Chevreul who established the relationship between fats, soaps and glycerin. However, it took until 1860 before Marcellin Berthelot (1827-1907) suggested that fats and oils might consist of triglycerides in which a single glycerin moiety was combined with perhaps even three fatty acid moieties.
- Accordingly, Chevreul considered oils and fats to be mixtures of stearin and olein whereby their ratio determined the physical properties such as melting point. Some fats contained volatile fatty acids and thus contained butyrin, caprin etc.

[4] Tartaric acid (2,3-dihydroxybutanedoic acid) is a good example of the organic acid the author refers to; it is also an acid the author uses quite frequently, for instance to acidulate soaps. Its molecular formula is: $C_4H_6O_6$. To form water from the hydrogen present in the molecule, only three of the six oxygen atoms are required. The other three are the excess referred to. On the other hand, an acid like acetic acid ($C_2H_4O_2$) has no excess oxygen.

[5] On paper, it is possible to compare for instance hydrogen sulfide (H_2S) with sulfuric acid (H_2SO_4) and look for similar relationships between organic acids with a relatively low oxygen content such as fatty acids and those with relatively more oxygen such as citric acid or tartaric acid. In practice, this comparison is rather meaningless since the organic acids considered here are acid because of their carboxyl groups.

[6] The word 'indefinite' has been chosen here to make a clear distinction with compounds that are formed in accordance with the law of definite proportions.

[7] It looks as if the author contradicts himself here. I had a look at this sentence in another edition of the book and that is exactly the same.

[8] Milk of magnesia is a suspension of magnesium oxide in water. The oxide hardly reacts with water so the suspension is almost neutral. However, it reacts with acids including fatty acids.

[9] See endnote 1 in Chapter 15 of Book II.

[10] This illustrates that at that time, chemists investigated everything they could lay their hands on.

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[11] This is a somewhat undue generalization. Isovaleric acid is peculiar to certain marine mammals and does not occur in fish oil.

[12] According to the literature (H.N. Koopman, S.J. Iverson and D.E. Gaskin, Stratification and age-related differences in blubber fatty acids of the male harbour porpoise *(Phoecena phoecena)*, J Comp Physiol B, (1996) **165**, 628-639), the isovaleric acid concentration in dolphin blubber can vary between wide limits. In the outer layers of old animals, it can approach 20 % but in the blubber of young animals and blubber that takes an active part in metabolism, the percentage can be negligible. Accordingly, it is impossible to estimate how much tri-isovalerin a blubber sample is likely to contain. The translator hereby expresses his thanks to Dr Koopman for sending him an electronic reprint of her article.

[13] Modern literature invariably gives 148.5°C as the melting point for cholesterol.

[14] Here the author does not adhere to the Linnaean classification.

[15] In the present context, 'ternary' and 'quaternary' mean that the principles or compounds contain atoms from three or four different elements respectively. These are presumably C, H, and O or C, H, N and O.

[16] In sub-section (1110), the author clarifies what he means with the word 'simple'.

[17] See page xxxiii in the Introduction.

[18] At the time of writing there were hardly any ideas about how atoms were arranged in molecules and getting an idea of what the author means entailed some inevitable guesswork and hoping for the best. As the translator, I had a first go. Then my wife corrected my efforts but in the margin of this sub-section she scribbled in Dutch: "Joost mag weten wat dit betekent." (Heaven knows what this means), whereby it is interesting to note that the Dutch "Joost" stands for the Devil, which in this case is more appropriate than "Heaven".

[19] See Book II, Chapter 3, Section 2, Article 2, sub-sections (220) and (221), page 61.

[20] Presumably, the author recrystallized his material several times in fresh alcohol and discarded the mother liquor each time but the text does not say this in so many words.

[21] The author has also used the lack of change in melting point on subsequent recrystallization as an indication of purity. See also sub-section (182) in Book II, Chapter 2, Section 2, page 50.

[22] To understand this argumentation, we must remember that the author regards each fat or oil as a combination of the compounds olein and stearin and that the properties of the oil and fat depend solely on the ratio of these two compounds. When a fat is fully molten, the temperature is so high that the stearin dissolves completely but when the temperature is lowered, some stearin may no longer dissolve and thus crystallize. So to get pure olein, the temperature must be lowered to such an extent that the solubility of the stearin is almost negligible.

In practice, it is not possible to obtain pure crystals by filtration so the stearin filter cake contained olein, which the author felt was 'combined' in the form of some mixed crystal (?).

[23] Alcohol with a density of 0.822 (g/mL) contains 90.3 % ethanol by weight or 93.5 % by volume.

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[24] The three compounds are the olein, a stearic acid based stearin and a palmitic acid based stearin.

[25] The text refers to 'saturation capacity' but since this applies to the behavior towards bases, this term has been translated as equivalent weight. Nowadays, we would say 'molar equivalent' but that notion did not yet exist at the time of writing.

[26] If a small amount of an odorous compound had been dissolved in the fatty acid or its soap, the carbon dioxide might have stripped it from its solution. Since this did not happen, the odor must come from the acid itself.

[27] The original indicates this values as: 9° - 0.

[28] The *Handbook of Chemistry and Physics* lists three potassium salts of oxalic acid. There is potassium hydrogen oxalate (KHC_2O_4), which can have 1 H_2O water of crystallization. Then there is potassium oxalate ($K_2C_2O_2.H_2O$) and finally the potassium tetraoxalate ($KHC_2O_4.H_2C_2O_4.2H_2O$). The latter was formerly referred to as quadroxalate.

[29] The author does not mention a dissociation equilibrium or potassium stearate but talks about the equilibrium of the potassium combined with the stearic acid.

[30] According to Ostwald (G*rundlinien der Anorganischen Chemie*, 1912, page 744), bismuth nitrate ($Bi(NO_3)_3.5H_2O$) can be prepared by crystallizing a solution of this salt in nitric acid. If water is poured on these crystals, they decompose while forming a basic nitrate: $Bi(OH)_2NO_3$, whereby the liberated nitric acid keeps some of the nitrate in solution. The hydrogen ion concentration of the liberated acid keeps the hydroxyl ion concentration so low that it meets the requirements of the solubility product of the basic salt.

[31] Antimony trichloride, once called "butter of antimony", is decomposed by water to form various poorly soluble oxychlorides, including SbOCl and $Sb_4O_5Cl_2$.

[32] In *A Textbook of Theoretical and Inorganic Chemistry* (F.A. Philbrick and E.J. Holmyard, J.M. Dent & Sons, London, 1932) I read: "Mercuric nitrate, $Hg(NO_3)_2$ is obtained by the action of nitric acid on mercuric oxide, or by boiling mercury for some time with concentrated nitric acid in excess and thereby oxidizing the mercurous nitrate first produced. It is a colourless hygroscopic substance which crystallizes as $2Hg(NO_3)_2.H_2O$ and $Hg(NO_3)_2.H_2O$. It is very soluble in water and the solutions are dissociated and strongly hydrolysed: unless free acid is added to them they deposit basic nitrates on evaporation."

[33] The book quoted in the previous reference also mentions that mercuric sulfate is converted to a basic salt by water.

[34] It is not clear why copper sulfate has been included in this series of salts that are decomposed when dissolved in water.

[35] It is not clear what is meant by and 'elastic fluid'; this is the only time this term is used.

[36] 'Solid' is a translation of 'fixe' but it is again not clear what is meant.

[37] Manufacturers of indicator paper are quite happy to make use of this by supplying indicators that cover a wide pH range.

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[38] The campeachy (*Haematoxylon campechianum)* is a spiny shrub or small tree of Central America and West Indies having bipinnate leaves and racemes of small bright yellow flowers and yielding a hard brown or brownish-red heartwood used in preparing a black dye. See also endnote 46 on page 39.

[39] This sentence is a perfect illustration of the conclusion reached by the author that fats are a mixture of compounds like stearin, etc. that are formed by a single fatty acid and glycerin. All such compounds do not occur in all fats and the ratio of the compounds present determines the physical properties of the fat.

[40] The text refers to 'sous-sels' meaning salts with a low content of acid moieties. Since the only such salts reported are carbonates, I used this description as translation.

[41] The text describes these bases as "the most energetic" but nowadays bases are classified according to their strength.

[42] According to my Oxford English Dictionary, albumen is a simple form of protein that is soluble in water and coagulable by heat, such as that found in egg white, milk, and (in particular) blood serum.

[43] No mention is made of this monograph in Albert Bernard Costa's PhD. thesis by . It therefore looks as if Chevreul never got round to writing it.

[44] This salt can also be called potash alum. Its formula is $AlK(SO_4)_2.12H_2O$.

[45] However, according to Wikipedia, ***Myrica cerifera*** is a small tree or large shrub native to North America. Its common names include Wax myrtle, Bayberry, Candleberry, Bayberry tree, and Tallow shrub. It sees uses both in the garden and for candle making, as well as a medicinal plant.

[46] For quite some time, the French language did not distinguish between ether and ester. They were both called ether. However, some esters were called 'vegetable ethers' and 'nitrous ether' is the reaction product from ethanol and nitric acid and thus also an ester.

[47] A literal translation of the original reads: ".... when they were not under the influence of ...", which is quite an elegant way to describe catalysis.

[48] Many inorganic reactions are instantaneous, such as for instance the formation of a precipitate of barium sulfate when a solution containing barium ions is added to a solution containing sulfate ions. Why this difference?

[49] The original does not use the name 'glucose' but refers to 'sugar from grapes'.

[50] Sometimes, 'hydrogène percarburé' can be translated as ethylene but in this instance, this would be too precise; a more general formulation has therefore been chosen.

[51] See also: Dumas, J.-B. and E. Peligot, Recherches sur la nature de lé´thal, tendant à prouver que cést un corps à analogue lalcool, *Ann. Chim. Phys.*[2], **62**, 5-22, 1836.

NOTES

FIRST NOTE

ON THE ANALYSIS OF GOAT'S MILK BUTTER

(a) I had only 4.5 g barium salts originating from the decomposition of soaps made from goat's milk butter. This amount was mixed with 12.5 g of water at 22°C. At the moment of contact, a mixed odor of caproic acid and hircic acid was released.

A *1st solution* was obtained consisting of:

Water	100
Salt[1]	16.62

1st residue: mixed with 14.64 g of water, this gave a *2nd solution* consisting of:

Water	100
Salt	9.19

2nd residue: mixed with 11.50 g of water, this gave a *3rd solution* consisting of:

Water	100
Salt	3.25

3rd residue: mixed with 21.45 g of water, this gave a *4th solution* consisting of:

Water	100
Salt	0.755

4th residue: mixed with 50 g of water, this gave a *5th solution* consisting of:

Water	100
Salt	0.50

5th residue: its solution yielded crystals that were very similar to those of the 5th solution; they were therefore combined.

(b) The crystals of the 5th and 6th solutions were very similar to the crystals of impure caprate and if they had not released a strong odor of hircic acid, they could have been mistaken for them.

Since I only had 0.4 g of crystals for my experiments and also because I had only been able to gain a glimpse of some of the properties of barium hircate and was not sure about the solubility of its acid, it was impossible to ascertain whether these crystals were really a mixture of barium caprate and barium hirciate. But what is important is that *I could establish that the odorous principle that distinguishes goat's milk from cow's milk is found in the barium salts originating from the analysis of soap made from goat's milk butter.* Today, all known facts seem to indicate that this odoriferous principle is an acid with the odor of hircic acid.

SECOND NOTE

THE EFFECT OF OXYGEN ON LARD

(a) Some lard was spread out over the walls of a flask with a ground stopper; the flask was filled with oxygen and left in a place out of the sun. After three years, most of the gas had been absorbed and if any carbon dioxide had been formed, this was in an extremely small proportion. The melting behavior of the fat appeared to have changed because after it had been melted, it started to become cloudy at 35°C but did not solidify until 27°C. Before the fat had been exposed to oxygen, its solidification point was also 27°C, but cloudiness did not appear until 31°C. When it solidified, it produced a more uneven surface than before it was exposed to oxygen. It was white and had a strong rancid odor that was obviously aromatic and acid.

(b) The fat was washed several times with water. Each time, the water was removed by filtration after having been in contact with the fat for twenty-four hours. I will now examine: 1. the washing liquor from the rancid fat; 2. the washed rancid fat.

§ 1. WASHING LIQUOR FROM THE RANCID FAT

(c) It was acid and smelly and the odor it gave off was exactly the same as that of the rancid fat.

(d) It was distilled.

Distillation residue

(e) This residue was yellow, acid and bitter. Its surface was covered with *orange oily droplets that looked very similar to the oleic acid yielded by the adipocere of cadavers* (945). The droplets were separated from the liquid on which they floated. When this liquid was evaporated to dryness and mixed with cold water, more oily drops appeared and they were separated. After this treatment, the aqueous liquid was less colored and less bitter. Its acid flavor was more pronounced and also mixed with an empyreumatic[2] taste. When this liquid was evaporated it gave an orange colored extract that was quite different from glycerin and seemed to consist of a fatty substance and a non-crystallizable substance. The extract was dried by exposure to air; when dissolved in water it only formed a slight precipitate with barite water. When it was evaporated to dryness and the residue treated with alcohol, the latter only dissolved a trace of a barium salt and an orange oil that could be liberated from the alcohol by the addition of water.

(f) From the above experiments I concluded that the distillation residue *(d)* was a compound of *oleic acid,* an *orange coloring principle,* a *non-volatile acid that is water-soluble and perhaps combined with a non-acid organic substance.*

Distillation product

(g) The distillation product *(d)* had the odor of rancid fat. After having been neutralized with baryta water, it was distilled. This yielded: 1. a *volatile product;* 2. a *barium salt residue.*

Volatile product

(h) It smelled like rancid fat but without the acid odor of this substance. The odor was exactly the same as that of the non-acid product obtained when distilling fats in contact with air. When the aqueous solution of the non-acid, odoriferous principle of the rancid fat was kept for several months in a closed flask, it acquired the odor of Roquefort cheese.

Barium salt residue

(i) This residue was given three successive water washes:

The 1st aqueous washing liquor consisted of:

Water	100
Salt	9.99

The 2nd washing liquor consisted of:

Water	the amounts were not determined
Salt	

The 3rd washing liquor consisted of:

Water	100
Salt	1.01

(k) It looks as though that there were two barium salts in the salt residue. However, since I did not separate them, I cannot present this as a firm conclusion. I can only add that the acid component of the barium salts as isolated from the barite, looked like a free fatty acid, similar to free caproic acid. And if there were two volatile acids in the rancid fat, it would be worth investigating if one of them stems from the stearin and the other from the olein[3].

§ 2. EXAMINATION OF THE WASHED RANCID FAT

(m) It was treated with three times its weight of boiling alcohol with a density of 0.821[4] (g/mL). After cooling, the liquid was filtered and allowed to evaporate. This left an oily extract that was still liquid at 15°C, viscous below this temperature, very acid and totally miscible in all proportions with cold alcohol with a density of 0.821 (g/mL). I did not study the residue that did not dissolve in the alcohol. But it seemed to me to consist of stearin and olein, at least for the most part.

(n) The oily extract *(m)* released a *yellow material* in boiling water, similar to the yellow material described in *(e)*. When no more was released, the extract was dissolved in alcohol and precipitated again by the addition of water. The water again dissolved some *yellow material*.

(o) After the above treatment, the oily extract was viscous at 15°C. It seemed to consist of a liquid substance and a solid substance dispersed in it. It was treated with magnesia in boiling water, which left hardly anything in solution. The oily matter that had formed a paste with the magnesia was first treated with cold alcohol and then with boiling alcohol.

(p) The washing alcohol contained a *neutral fat* with a little *magnesia soap*. Alcoholic washing liquor

(q) This residue consisted of *magnesium palmitate* and *magnesium oleate* and probably some *stearate of the same base.* When the acids had been separated from the magnesium at a temperature of 18°C, these acids were partially in the form of needles and partially in a liquid state. I ascertained that this material could react with potassium hydroxide without losing any weight or changing its melting point, and that in water, the potassium soap changed into a *pearly material* and an *oleate*. Alcohol-insoluble residue

(r) When lard is exposed to oxygen gas at ambient temperature, it absorbs a considerable amount of this gas.

The olein and the stearin change into:

1. an *orangey coloring principle;*
2. a *non-volatile acid that is soluble in water;*
3. a *non-acid substance that is soluble in water;*
4. a *neutral, volatile principle;*
5. one or two *volatile acids* that belong to the 2nd genus of the species described in this work.

The rancid fat owes it odor both to the neutral, odoriferous principle and to the volatile acid material. It is quite likely that all these volatile principles are formed during the distillation of fats as commonly carried out.

6. *non-volatile fatty acids.*

THIRD NOTE

THE EFFECT OF SULFURIC ACID ON STEARINS AND OLEIN

SECTION 1

THE EFFECT OF SULFURIC ACID ON LARD

(a) 6.5 g of lard were mixed with 6.5 g of concentrated sulfuric acid and the mixture was exposed to 100°C for several minutes. The material became slightly brown and a small amount of sulfur dioxide was liberated.

(b) After a week, the materials were diluted with 50 g of water and an *acid liquid* was separated from a *fatty material.*

(c) When the *fatty material* was mixed with 100 g of water, it formed a homogeneous emulsion that broke as soon as the sulfuric acid was neutralized with magnesia after heating. The *fatty material* was at first fluid and gradually became more solid when it combined with the magnesia, which had been added in excess. The magnesium soap was washed with boiling water.

(d) I will now investigate 1. the *acid liquid (b);* 2. the *aqueous liquid* in which the fatty material reacted with the magnesia; 3. the *magnesium soap*. The water that had been used to wash this soap was added to the aqueous liquid.

§ 1. THE ACID LIQUID *(b)*

(e) It was mixed with a slight excess of barite water and then filtered. I did not investigate whether the precipitate contained any other insoluble salt apart from barium sulfate. When the filtrate was evaporated to dryness, it left a residue that was treated with alcohol. This yielded an *undissolved material* and an *alcoholic solution.*

(f) Non-dissolved material (e). This was a barium salt, the acid of which seemed to be very similar to sulfovinic acid[5]*, which is why I gave it the name SULFOADIPIC*[6] *ACID*. This acid is probably formed by a reaction between hyposulfuric acid[7] and an organic material. The barium sulfoadipate weighed 330 mg after correction for the barium carbonate that was mixed with it. It was highly soluble in water, and almost insoluble in alcohol. When it was distilled in a tube that contained some air, it yielded *inter alia*: 1. an acid, empyreumatic and extremely pungent vapor[8] in which the presence of sulfur dioxide and hydrogen sulfide could be detected; 2. sulfur; 3. barium sulfide mixed with carbon. The barium solfoadipate had a sharp taste at first and a slightly sweetish aftertaste.

I did not manage to get it to crystallize. When the barium present was precipitated by sulfuric acid, it yielded a syrupy acid with a very sharp odor; its distillation products were similar to those of the salt, except that they were more pungent and oilier. The distillation left a large residue of carbon.

(g) Alcoholic solution (e). When evaporated to dryness, it left a residue of 200 mg that contained *barium sulfoadipate* and an *organic material* that was soluble in both water and alcohol. It was syrupy and sweetish and could have been glycerin.

§ 2. THE AQUEOUS LIQUID *(d)*

(h) It was neutral toward colored tinctures. After it had been evaporated, the residue was treated with alcohol, which caused magnesium sulfate to separate out. The alcoholic solution was diluted with water and concentrated and then mixed with barite water; this precipitated magnesia and an amount of organic material that was too small to be investigated. The aqueous solution seemed to me to consist predominantly of *barium sulfoadipate* since when this solution was evaporated to dryness, it left 70 mg of a residue that was insoluble or hardly soluble in alcohol, soluble in water and gave the same distillation products as the salt *(f)*.

§ 3. THE MAGNESIUM SOAP *(d)*

(i) It was washed three times with fifteen times its weight of boiling alcohol. The washing liquors yielded a deposit that was separated by filtration.

ARTICLE 1

UNDISSOLVED RESIDUE

(k) It was decomposed by hydrochloric acid. This yielded 1.9 g of a *brown fatty material with a melting point of* 48°C that dissolved immediately in highly diluted caustic potash. When this material was separated from the caustic potash after having been boiled in it, it had the same melting point and the same weight as before. This proves that it was an entirely acid material. It formed an emulsion in water that had been acidified with either sulfuric acid or hydrochloric acid. The emulsion could be broken by either: 1. concentrating it; or 2. by neutralizing the sulfuric or hydrochloric acid; or 3. by adding an excess of sulfuric or hydrochloric acid. The fatty material consisted mainly of *palmitic acid, oleic acid* and probably *stearic acid* and a *substance* that provided these three acids with the ability to form emulsions with acidified water. This substance probably contained dithionic acid, since on distillation it released a large amount of hydrogen sulfide and its barium salt yielded a great deal of sulfur when heated red hot[9].

ARTICLE 2

DEPOSIT *(i)*

(l) This deposit was a magnesium soap containing 0.95 g of fatty acids of which melted at 47°C and did not have the property forming emulsions with acidified water, either hot or cold. On distillation, the acids did not form any sulfur-containing product, or hardly any.

ARTICLE 3

MATERIAL THAT STAYED IN SOLUTION IN THE ALCOHOL AFTER COOLING

(m) When the material was separated from the alcohol, it did not dissolve in water except for a trace of a magnesium salt. When treated with cold alcohol, it left an insoluble residue weighing 180 mg with a similar composition to that of the deposit *(l)* described above. The alcoholic solution left a residue after evaporation of 1.6 g of a *reddish substance*, from which hydrochloric acid extracted 30 mg of magnesia. I did not investigate whether the acid had dissolved anything else besides the magnesia.

Properties of the reddish material, which weighed 1.57 g after the removal of the magnesia

(n) It was orangey in color; it formed an emulsion with acidified warm water and it absorbed cold water. When it was melted and then allowed to cool, it congealed to a certain extent at 29.5°C, but without becoming totally solid.

(o) When 500 mg of this substance were heated in water, they melted without the water seeming to play any part. On the sudden addition of baryta water, the fatty material became more solid because it combined with the alkali. The reaction product became fluid before the water boiled. The baryta water that was in excess was decanted and the insoluble material was washed first with boiling water and then with boiling alcohol.

(p) Residue that was not dissolved by water or alcohol. When the barium was separated from this residue by hydrochloric acid, an *orangey red material* was obtained with the following properties: it melted at 28°C; it absorbed cold water; with acidified water it formed an emulsion that could be broken by concentration, acids and magnesia. It was soluble in aqueous caustic potash and reacting with this alkali did not cause its melting point to change. Potassium bipalmitate, probably mixed with potassium bistearate, precipitated from this alkaline solution. The orangey red material released a larger amount of hydrogen sulfide on distillation; I think it differed from the *brown fatty material with a melting point of 48°C (k),* in that it contained a much larger proportion of oleic acid and of the substance that I thought was composed of dithionic acid and an organic material. I am not aware of any relationship that this substance may have with sulfoadipic acid.

(q) Aqueous washing of the residue (p). It contained baryta that was bound to a material that yielded sulfur-containing products on distillation.

(r) Alcoholic washing of the residue (p). It contained some material that was similar to residue *(p).*

Results

When lard was treated with its own weight of sulfuric acid, it yielded:

1. *Sulfoadipic acid*, which does not crystallize but dissolves in water and alcohol. On distillation it gives sulfur-containing products and with barium hydroxide, it forms a salt that is soluble in water but almost insoluble in alcohol.
2. *A material that is soluble in water and alcohol,* does not crystallize and has a sweetish taste. I am all the more inclined to believe that this material was glycerin because lard treated with half its weight of sulfuric acid yielded a substance with the greatest similarity to glycerin. Like the latter, it remained fluid under a dry vacuum; it had a sweet taste, and also a sharp aftertaste due to a small amount of barium sulfoadipate, the presence of which was established on distillation. If I had not found that salt in this material, I would not have hesitated to say it was glycerin.
3. *Palmitic acid.*
4. *Oleic acid.*
5. *Stearic acid*; but I did not separate this from the previous two acids.

6. *An organic substance that is probably bound to dithionic acid.* This is the substance that provides the above acids with the property of forming emulsions with acidified water. I did not have time to separate it from these acids, although I would have liked to have found out if it really is a different substance from sulfoadipic acid, as it seemed to be since: *when the substance is treated with barium hydroxide in the presence of the fatty acids, the compound formed by this substance and the barium hydroxide remains for a large part bound to the barium soaps formed by the fatty acids.* If the substance is not sulfoadipic acid, it cannot be regarded as a reaction product of non-volatile fatty acids and dithionic acid, whereas sulfoadipic acid can be regarded as a reaction product of glycerin and dithionic acid.

Treating lard with sulfuric acid splits this material into two very unequal parts, just as in saponification: 1. one part that is *soluble in water* and consists of sulfoadipic acid and a substance that appears to be glycerin; 2. another part that is *insoluble in water* and consists of non-volatile fatty acids and a substance that has a composition similar to that of sulfoadipic acid.

I established that during the above treatment, no noticeable amounts of acetic acid were produced. I did not investigate whether any alkaline substance was formed.

SECTION 2

THE EFFECT OF SULFURIC ACID ON MUTTON TALLOW STEARIN

(a) 6.68 g of mutton tallow stearin with a melting point of 43°C were treated with 6.68 g of sulfuric acid, just as the lard had been. The phenomena observed were the same.

(b) After a week[10], the materials were mixed with water and split into an *acid liquid* and a *fatty material* that formed an emulsion with water after having been separated from the acid liquid. This emulsion was then split by magnesia into an *aqueous liquid* and a *magnesium soap.*

§ 1. THE ACID LIQUID *(b)*

(c) This liquid was mixed with an amount of aqueous barium hydroxide sufficient to precipitate all the sulfuric acid present. After filtration, the filtrate was distilled. The distillation products seemed to me to contain a trace of *acetic acid.* The distillation residue contained: 1. *sulfoadipic acid*; 2. an *organic material* that was soluble in alcohol and water, had a syrupy consistency and a sweetish taste and could have been glycerin. The sulfoadipic acid corresponded to 450 mg of barium sulfoadipate. The second material weighed 200 mg but it still retained some barium sulfoadipate.

§ 2. THE AQUEOUS LIQUID *(b)*

(d) It was evaporated to dryness. Alcohol was used to isolate magnesium sulfate from the residue; it dissolved some magnesium sulfoadipate and perhaps an organic material.

§ 3. THE MAGNESIUM SOAP

(e) It was treated five times with cold alcohol and then twice with boiling alcohol. I shall now examine: 1. the *residue that did not dissolve in the alcohol;* 2. the *material dissolved by cold alcohol*; 3. the *material dissolved by boiling alcohol.*

ARTICLE 1

RESIDUE THAT DID NOT DISSOLVE IN ALCOHOL

(f) It was decomposed by sulfuric acid and it yielded a *yellow fatty material with a melting point of 57°C* that weighed 2.95 g and did not form an emulsion with pure water or acidified water. This fat was completely saponified because when it was mixed with a weak, warm aqueous potash solution, it dissolved immediately. After the liquid had been boiled and acidulated with phosphoric acid, it yielded a *fat with a melting point of 57°C* and a weight equal to that of the material that had been allowed to react with the potash. This fat consisted of *stearic acid, palmitic acid* and *oleic acid;* stearic acid with a melting point of 69°C was isolated from it. It was very shiny and did not release the slightest trace of sulfur-containing gas on distillation.

ARTICLE 2

MATERIAL DISSOLVED BY COLD ALCOHOL

(g) It weighed 1.73 g. It was yellow. When mixed with 100 g warm water, it did not form an emulsion but became partially flocculent. Water only dissolved a trace of its magnesium salt. Since the material was acid, it was neutralized with milk of magnesia and the resulting water hardly contained any soluble material.

(h) By treating the soap with alcohol, I split the organic material it contained into:

1. An *acid fatty material* that weighed 190 mg, melted at 44°C, did not form an emulsion with water and was completely saponified;
2. An *acid fatty material* that weighed 1.54 g, melted at 36°C and had a slight tendency to form an emulsion with acidified water. It had not been entirely saponified, since after having been boiled in caustic potash and then separated from this alkali, it melted at 37°C. This product formed an emulsion with acidified water as previously. On distillation, it yielded products containing sulfur.

(k) The substance that provided the above material with the property of forming emulsions with water, was similar to the one discussed in Section 1 of this note *(k)*.

ARTICLE 3

MATERIAL DISSOLVED BY BOILING ALCOHOL

(l) The solution became very cloudy on cooling; it was filtered.

(m) Material precipitated on cooling. It was a mixture of acid fat, magnesium soaps and a neutral fat. Neutralization with magnesia followed by an alcohol treatment yielded:

1. 0.7 g of *fatty acids with a melting point of 55°C;*
2. 0.2 g of *a neutral fat with a melting point of 42°C* (this material was stearin that had not been in contact with the sulfuric acid).

(n) Material that stayed in solution in the cold alcohol. This was completely acid and had a melting point of 44°C. It did not form an emulsion with water, or only very slightly. It weighed 0.37 g. On distillation, it yielded products containing sulfur.

(o) After treating beef tallow with half its weight of concentrated sulfuric acid at 50°C and washing the materials with water, a washing liquor was obtained containing *hircic acid* and a *substance* that looked very much like glycerin. The material that did not dissolve contained non-volatile fatty acids.

Conclusion

(p) It can be seen that the effect of sulfuric acid on stearin is totally analogous to the effect it has on lard and that by this treatment *well-characterized stearic acid* is obtained, amongst other products.

(q) Before me, Mr Braconnot[11] observed that beef tallow treated with half its weight of sulfuric acid changed into a *material that has a strong tendency to react with alkali.*

FOURTH NOTE

SECTION 1

EFFECT OF SULFURIC ACID ON PHOCENIN

(a) 1.5 g of phocenin were mixed with 1.5 g of sulfuric acid at 66°C. The mixture was heated to 100°C and left to stand: after a week, it released an aroma of isovaleric acid and sulfur dioxide. 40g of water were added to the mixture. Gradually, an *oily material* rose to the surface of the water. When this had collected as a transparent layer on the surface, it was drawn off with a pipette. It will be examined under the name of *acid liquid.*

(b) The *oily material* formed an emulsion with 50 g of water. This emulsion was broken by magnesia and a *neutral aqueous liquid* and a *magnesium* soap were obtained.

§ 1. ACID LIQUID AND NEUTRAL AQUEOUS LIQUID

(c) The sulfuric acid in the *acid liquid* was precipitated by a slight excess of baryta water and the liquid was then filtered to remove the barium sulfate*.

(d) The *neutral aqueous liquid* was evaporated to dryness and the residue was treated with alcohol: this left some magnesium sulfate. The alcoholic extract was evaporated to dryness and the residue dissolved in water and then mixed with baryta water to separate the magnesium from it. The filtrate was combined with liquid *(c).*

(e) The two liquids *(c)* and *(d)* which contained barium were distilled in the presence of phosphoric acid. This yielded isovaleric acid corresponding to 700 mg of dry barium isovalerate but some of it was lost. On distillation, this barium isovalerate did not yield any sulfur. The residue, when mixed with hydrochloric acid, released a trace of hydrogen sulfide that could not be detected by its smell but blackened a paper impregnated with lead acetate. This product was probably accidental.

(f) Apart from the phosphoric acid, the distillation residue contained: 1. an *organic material that was soluble in water and alcohol,* which might have been glycerin; 2. *sulfoadipic acid.* These materials weighed 250 mg.

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* I did not investigate whether the barium sulfate was pure.

§ 2. THE MAGNESIUM SOAP

(g) This soap was treated with cold alcohol and then twice with boiling alcohol. The latter yielded only a slight deposit on cooling

ARTICLE 1

RESIDUE THAT DID NOT DISSOLVE IN ALCOHOL

(h) This residue was treated with hydrochloric acid. It yielded 0.3 g of an acid that showed all the properties of colored oleic acid. It did not contain any sulfur or only very little.

ARTICLE 2

THE DEPOSIT FROM THE ALCOHOLIC SOLUTION

(i) When this deposit was treated with hydrochloric acid, it yielded 70 mg of oleic acid that did not form an emulsion with water and that was dissolved completely by aqueous potassium hydroxide.

ARTICLE 3

THE COOLED ALCOHOLIC SOLUTION

(k) When the alcoholic solution was evaporated to dryness, it left an orangey yellow residue that was treated with hydrochloric acid. The fatty matter weighed 510 mg. It was only slightly colored. It had only a very slight tendency to form an emulsion with acidified water. It dissolved in cold aqueous caustic potash. However, the solution was not completely transparent and certainly contained a very small amount of neutral, saponifiable fatty matter since on boiling, the solution became perfectly transparent. When this material was mixed with baryta and distilled, it released a small amount of a gas containing sulfur, and a trace of barium sulfate.

Treating phocenin with sulfuric acid thus yields isovaleric acid, oleic acid and sulfoadipic acid, and other products.

SECTION 2

THE EFFECT OF SULFURIC ACID ON BUTYRIN

When butyrin was treated in exactly the same way as phocenin, it gave exactly the same results except that instead of isovaleric acid, butyric acid was obtained, probably combined with other volatile acids from the butter, and it seemed to me that there were larger proportions of the sulfoadipic acid and the emulsifying material than in the same materials originating from phocenin.

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[1] This is a literal translation of a compound we would now call soap. In general, the author only uses the word 'soap' when discussing potassium or sodium soaps, probably because they are used as soaps.

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[2] See endnote 18 on page 37.

[3] Since these degradation products are apparently acids themselves, it would seem to be more logical to see whether they stem from stearic acid and/or oleic acid but to the author, this distinction is irrelevant since he regards stearin as a combination of glycerin and just stearic acid, and olein as a combination of glycerin and just oleic acid.

[4] This density corresponds to 90.7 % by weight or 93.7 % by volume.

[5] According to *Éléments de chimie, appliquée à la médecine et aux arts* (Matthieu Joseph Bonaventure Orfila, Librairie de Crochard, 1835) 'acide sulfovinique' (sulfovinic acid) is diethyl sulfate. It is made by allowing alcohol to react with concentrated sulfuric acid. He even gives a formula: C^8H^8, 2 SO^3 H^4O^2, which is somewhat short on hydrogen and corresponds to the compound divinyl sulfate, which did not exist at the time. Nowadays we express diethyl sulfate as: $(C_2H_5)_2SO_4$. The name 'sulfo*vinic* acid may originate from the fact that ethyl alcohol was obtained from wine, *vinum*.

[6] Adipic acid (hexanedioic acid) was formerly made from unsaturated fatty acids; hence its name. The use of this name by the author must be regarded as generic rather than specific. When later authors mention sulfoadipic acid, it is only when they quote Chevreul.

[7] This is a literal translation of 'acide hyposulfurique'. Searching for the latter in Google reveals that this acid was discovered in 1819 by Welter and Gay-Lussac and is composed of 44.44% sulfur and 55.56% oxygen. Its molecular formula is therefore S_2O_5. The acid has the formula: $H_2S_2O_6$ and it is the lowest member of the group of polythionic acids and is called 'dithionic acid'.

[8] This 'extremely pungent vapor' may well have contained acrolein (2-propenal, CH_2=CHCHO). It is a dehydration product of glycerin and this explains the odor given off by burning candles made from fat. The name is derived from the Latin *acer* (sharp) and *olere* (to smell).

[9] The author is not very specific about how red the heat should be. According to Ernst (*Dictionaire Général de la Technique Industrielle,* Oscar Brandstetter Verlag, 1982), a dark red heat corresponds to 775 K, a red heat to 925 K, a bright red heat to 1025 K, a low cherry red heat to 1125 K, a cherry red heat to 1125 K and a bright cherry red heat to 1225 K.

[10] The original says : 'eight days', this being the Roman way of counting.

[11] Henri Braconnot ((1781-1855) was director of the botanical gardens in Nancy. In 1820, he isolated the amino acid leucine from muscle fiber and wool. He also obtained glycine from gelatin. See also: Braconnot, H. Extrait du mémoire sur la nature des Corps Gras, *J. Pharm.*, **1**, 385-401, 1815.

Fig. 1.

Fig. 2

Fig. 5.

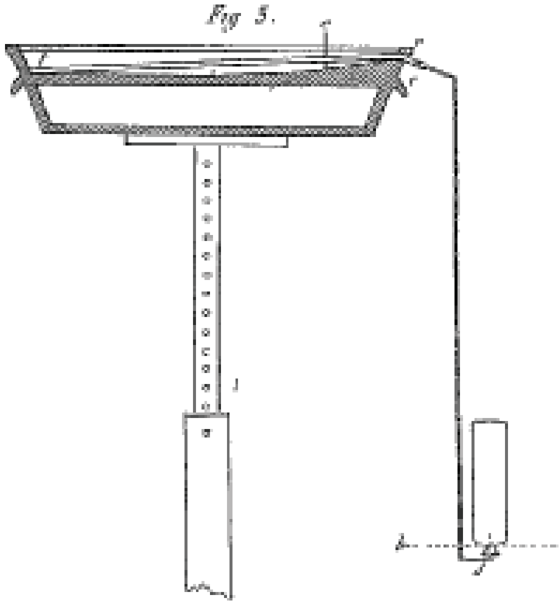

Fig. 3.

Forme de Batonets de cuivre

Fig. 4.

Adam sculp