CHAPTER 2

PALMITIC[1] ACID AND SOME PALMITATES

SECTION 1

PALMITIC ACID

§ 1. COMPOSITION

133. Burning free palmitic acid (from human fat) with brown copper oxide gives:

Oxygen	11.656
Carbon	76.366
Hydrogen	11.978

…134. Heating this acid with lead oxide shows that 500 mg of acid contains 17 mg of water[2].

Conclusions

1. The free acid consists of:

Acid anhydride	483	96.6	100
Water	17	3.4	3.52, containing 3.129[3] oxygen

2. The palmitic acid anhydride consists of[4]:

	BY WEIGHT		BY VOLUME
Oxygen	8.6334	8.937	1.00
Carbon	76.3660	79.053	11.55
Hydrogen[*]	11.6006	12.010	21.57
Total	96.6000		

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[*] Assuming that the water being released comes from the oxygen in the lead oxide and from the hydrogen in the acid, the portion of the acid that remains bound to the lead consists of:

	BY WEIGHT		BY VOLUME
Oxygen	11.6560	11.700	1.00
Carbon	76.3660	76.6550	8.56
Hydrogen	11.6006	11 6450	15.98
Total	99.6226		

135. 100 parts of acid anhydride neutralize an amount of base that contains 3 parts of oxygen. Consequently, the ratio of the oxygen in the acid moiety of the neutral palmitate to that in the base must be 3 : 1. Taking this into account and assuming that by volume, the acid is composed of:

Oxygen	1.00
Carbon	11.33
Hydrogen	21.67

the palmitic acid anhydride will consist of:

	AS ATOMS	BY WEIGHT	
Oxygen	3	300	9.07
Carbon	34	2602	78.67
Hydrogen	65	405.6	12.26
Total		3307.6	

§ 2. PHYSICAL PROPERTIES OF PALMITIC ACID

136. The physical properties if this acid are the same as those of stearic acid except that it melts at 60°C and that it crystallizes from the melt in intertwined needles that are closer together and less shiny than those of stearic acid.

§ 3. CHEMICAL PROPERTIES THAT ARE OBSERVED WITHOUT THE ACID BEING ALTERED

137. Like stearic acid, palmitic acid is insoluble in water. It is highly soluble in alcohol and ether. It combines with bases that can form salts and its salts are quite similar to the stearates. It colors litmus red and when heated, it decomposes potassium and sodium carbonate.

§ 4. CHEMICAL PROPERTIES THAT ARE OBSERVED WHEN THE ACID IS ALTERED

138. When palmitic acid is heated in a retort connected to a flask that is open to atmosphere, it melts and gives off white fumes that settle as a floury substance at the neck of the retort. It boils and gives off a compressible vapor that condenses as a liquid and then solidifies. At the same time, water that turns litmus red is given off together with a strong smell originating from an empyreumatic oil and perhaps also a volatile

acid. Only very little gas and liquid are formed. There is only a small carbon residue.

139. In a certain experiment, I heated 1 g of palmitic acid in a retort that contained 394 mL of air. The solid product weighed 0.9 g. It was white with a tinge of yellow and red. It was soluble in potassium carbonate except for 50 mg of a reddish fatty substance that was not acidic[*]. In addition to a lot of palmitic acid, the alkaline solution contained an appreciable amount of this material. The carbon weighed 18 mg but had only turned slightly red.

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[*] In a previous experiment using 100 parts of a mixture of palmitic acid and stearic acid, having a melting point of 56.5°C, I obtained 25 parts of the non-acidic material that was insoluble in caustic potash. It was dissolved in boiling ethanol and on cooling, it deposited small pearly crystals of a fatty nature that were slightly colored when melted. The cold alcohol still contained a dark yellow oil in solution which was liquid at 18°C

SECTION 2

PALMITATES

ARTICLE 1

POTASSIUM PALMITATE

Preparation

140. (See Table 1 at the end of Chapter 3 of this Book)

Composition

141. When 1 gram is treated with hydrochloric acid, it yields 867.9 mg of palmitic acid and 237 mg of potassium chloride, which corresponds to 150 mg of potassium oxide[5]. Therefore:

Acid anhydride…	85	100
Potassium oxide..	15	17.67, containing 2.997 oxygen

Calculated composition:

Acid anhydride………..	100
Potassium oxide………	17.81, containing 3.02 oxygen

Properties

142. It is white. I have not managed to obtain beautiful, pearly flakes as I did with the potassium stearate. Sometimes a deposit of small pearly flakes was formed from boiling alcohol in which it had been dissolved but when kept in this alcohol for some time, they lost their shine, unlike the potassium stearate**.**

Action of water

143. (See Table 1 at the end of Chapter 3 of this Book)

Effect of alcohol

144. *(idem)*

Effect of ether

145. *(idem)*

Effect of palmitic acid on potassium carbonate

146. It is the same as that of stearic acid.

ARTICLE 2

POTASSIUM BIPALMITATE

Preparation

147. This salt is prepared by treating neutral potassium palmitate with a suitable amount of water[6].

Composition

Acid anhydride	91.935	100
Potassium oxide	8.065	8.70

The calculated composition is:

Acid anhydride	100
Potassium oxide	8.9

Properties

148. It occurs in small pearly flakes that never have the silvery sheen of bistearate flakes.

Effect of water

149. Cold water removes some traces of alkali.

150. Boiling 1 part in 75 parts of water released 1/200th part consisting of potassium hydroxide and a trace of palmitic acid[7].

Effect of alcohol

151. 100 parts of alcohol with a density of 0.834 (g/mL) dissolve 31.37 parts of bipalmitate at 67°C. At 20°C, 100 parts of this alcohol only dissolve 0.31 parts.

152. When an alcoholic solution of potassium bipalmitate is added to water, an appreciable amount of potassium is released, just as with the bistearate. In one of my experiments, the precipitate contained 7.8 parts of potassium oxide for every 100 parts of acid; for 1 part of bipalmitate, 340 parts of water were used.

Effect of palmitic acid on litmus

153. It is the same as for stearic acid[8].

ARTICLE 3

SODIUM PALMITATE

Preparation

154. (See Table 2 at the end of Chapter 3 of this Book).

Composition

155. The decomposition by hydrochloric acid of 265 mg of perfectly dry sodium palmitate yielded 244 mg free palmitic acid and 55 mg sodium chloride, which corresponds to 29.3 mg sodium oxide[9].

Palmitic acid	2357	100
Sodium oxide	293	12.43, containing 3.179 oxygen
Total	2650	

The calculation of the composition gives:

Acid anhydride……	100
Sodium oxide………	11.82, containing 3.003 oxygen

Properties

156. It consists of small, semitransparent flakes. At first it has no taste but after a while, it tastes alkaline. It melts when exposed to heat.

157. When 1 part of sodium palmitate is added to 600 parts of water at a temperature of 12°C, it looks no different after soaking for one week. After two weeks, it has lost its transparency. When the water is evaporated, only a trace of palmitate remains.

158. When 2 g of sodium palmitate are heated in 100 parts of water, they dissolve before the water starts boiling. The solution is perfectly clear. By diluting this solution with 3 liters of cold water, a pearly precipitate was obtained. This was filtered off after three days[10]. The filtrate was evaporated to dryness and left a small alkaline residue that only contained a negligible amount of palmitic acid. The pearly residue was a true sodium perpalmitate.

159. Sodium palmitate occurs in all sodium soaps. It is this material in the opodeldoc ointment[11] that produces the *vegetations* that appear in it when it is exposed to a low temperature.

ARTICLE 4

SODIUM BIPALMITATE

Preparation

160. It was obtained by dissolving the neutral palmitate in a large amount of warm water, collecting the pearly deposit on a filter, drying it and dissolving it in boiling alcohol. The bipalmitate precipitate was drained on paper and then dried in the sun.

Composition

161. An amount of 223 mg was decomposed by hydrochloric acid. This yielded 217 mg of free palmitic acid and 232 mg of sodium chloride, which corresponds to 125.2 mg of sodium oxide.

Acid anhydride.	0.20962	100
Sodium oxide…	0.01252	5.973 containing 1.528 oxygen
Total…….	0.22214	

The calculated composition is:

Acid anhydride.…………………………………….	100
Sodium oxide….……………………………………	5.91

Properties

162. It has a lower melting point than the neutral palmitate and is white, tasteless and odorless.

163. It does not dissolve in water.

164. It is quite soluble in alcohol and the solution turns litmus red. After adding water, the solution turns blue[12].

ARTICLE 5

BARIUM PALMITATE

Preparation

165. It is the same as for barium stearate.

166. When 100 mg are burned in a platinum crucible, an ash results that corresponds to 34 mg[13] of sulfate. Accordingly:

Acid anhydride.	77.69	100.00
Barium oxide….	22.31	28.72, containing 3.001 oxygen

The calculated composition is:

Acid anhydride……………………………………..	100
Barium oxide………………………………………..	28.92

ARTICLE 6

STRONTIUM PALMITATE

Preparation

167. It is prepared the same way as barium stearate.

Composition

168. When 100 mg are burned, the strontium oxide ash corresponds to 29 mg[14] of sulfate.

Acid anhydride..	83.655	100
Strontium oxide..	16.345	19.54, containing 3.0638 oxygen

The calculated composition gives:

Acid anhydride……………………………………..	100
Strontium oxide…………………………………….	19.56

ARTICLE 7

CALCIUM PALMITATE

Preparation

169. It is prepared like calcium stearate.

Composition

170. Burning 100 mg leaves an ash with a lime content that corresponds to 24 mg of sulfate[15].

Acid anhydride.	90.033	100
Calcium oxide…	9.967	11.07, which contains 3.1095 oxygen

The calculated composition gives:

Acid anhydride…….……………………………	100
Calcium oxide…….………………………………...	10.76

ARTICLE 8

LEAD PALMITATE

Preparation

171. It is the same as that of lead stearate.

Composition

172. Burning 900 mg in a glass dish yields 265 mg of lead oxide.

Acid anhydride.	635	70.55	100
Lead oxide…….	265	29.45o	41.74, containing 2.993[16] oxygen

The calculated composition gives:

Acid anhydride………………………………………	100
Lead oxide……………………………………………	42.16

ARTICLE 9

BASIC LEAD PALMITATE

Preparation

173. It is prepared is the same way as basic lead stearate.

Composition

174. On burning, 1.7 g yields 775 mg[17] of lead oxide. Therefore:

Acid anhydride.	925	54.41	100
Lead oxide ……	775	45.59	83.79 containing 6.008 oxygen

The calculated composition gives:

Acid anhydride……………………………………..	100
Lead oxide…………………………………………..	84.33

ARTICLE 10

AMMONIUM PALMITATE

175. The free palmitic acid reacts with ammonia just like the stearic acid but reacts more slowly; nevertheless it absorbs more or less the same volume of ammonia. Preparation

176. Palmitic acid also reacts with liquid ammonia. If the acid is heated in a closed flask that is completely filled with liquid ammonia, the acid dissolves completely if the ammonia has been sufficiently diluted. If not, a gelatinous, more or less transparent palmitate is formed.

177. When heated under vacuum, it reacts like ammonium stearate. Properties

178. It dissolves in warm water, or at least in water containing ammonia. The solution deposits pearly perpalmitate on cooling, and no measurable amount of acid is left in the mother liquor.

179. When ammonium palmitate (or at least the palmitate resulting from an aqueous solution) is exposed to air at 13°C, it releases part of its alkali.

OBSERVATIONS CONCERNING STEARIC AND PALMITIC ACID

180. On 5 July 1813, I presented a fatty material with acid properties under the name of *margarine* at the Institute[18]. In 1816, I named it *palmitic acid*[19]. I had isolated it back in 1811 from a soap I had been given for analysis. In fact, it is this analysis that made me start the work that is the subject of the present monograph. In 1816, when I was investigating whether or not there were any differences between the acids of potassium bipalmitate obtained from the soapy waters resulting from the fat of various animals, that I found that the palmitic acids from human fat, lard, jaguar fat and goose fat have almost the same physical properties and a melting point between 55 and 56.5°C. I also noted that the acids obtained from mutton and beef tallow stearins differed from the former in this respect since the acids from mutton tallow melted at 64.8°C and those from beef tallow at 62°C. I did not express any opinion as to

whether the acids from mutton and beef tallow were essentially different from the other acids.

181. On 17 July 1820, I presented some analytical data at the Institute from which it follows: 1. that palmitic acid from mutton tallow contains less oxygen than the palmitic acids from man or pig: 2. that there is virtually the same ratio of carbon to hydrogen in these acids. These results led me to name the palmitic acid from mutton tallow *margarous acid*[20].

182. I have recently carried out many experiments on this acid.

1. I treated potassium bipalmitate obtained from mutton tallow in exactly the same way as potassium bipalmitate obtained from human fat, the acids of which have the same melting range. This is described in detail in Book III, Chapter 1, Section 3. From the former material, I obtained an acid with a 70°C melting point and from the latter an acid that melted at 60°C. I also noted that repeated recrystallization from alcohol tended to lower the melting point rather than raise it.

2. Having some reason to suppose that it would be easier to purify the neutral potassium palmitates of mutton tallow and human fat than to purify their respective bipalmitates, I recrystallized these from alcohol. (The method is described in detail in Book III, Chapter 1, Section 3.) I arrived at the same results as reported above. The acid in potassium palmitate obtained from human fat melted at 60°C and even after five successive recrystallizations from alcohol, it was still found to melt at 60°C.

3. From a given quantity of mutton tallow based potassium soap I could only obtain an oleate and a palmitate, the acid of which melts at 70°C. I always obtained significant amounts of an acid that melted at 56 to 60°C and had similar properties to those of the human palmitic acid. The melting point of this acid tended to drop rather than rise when treated repeatedly with boiling alcohol.

4. By treating potassium soaps of beef tallow and lard in the same way, I obtained an acid with a melting point of 70°C and an acid melting at 58°C analogous to human palmitic acid. The latter was more abundant in lard soap than in beef tallow soap and also more abundant in the latter than in mutton tallow soap.

183. From the above experiments it follows that *I have obtained an acid melting at 70°C and another acid with a melting point of 60°C, which I have not managed to raise*[21]. Let us now add the following result which is part of the memorandum presented to the Academy in 1816: *Having for comparative purposes saponified human fat stearin melting at 49°C and mutton tallow stearin melting at 43°C, the fatty acids in the soap resulting from the first*

stearin melted at 51°C, whereas those in the soap of the second melted at 54 to 53°C[22]*. When these soaps were treated with water they yielded bipalmitates, in which the human derived acid melted at 56.5°C and the mutton derived acid melted at 64.8°C.*

184. Given all this, a clear distinction can be made between the two acids[23] I have been talking about. But after considering: 1. their numerous analogies; 2. how difficult it is to perform an elemental analysis and arrive at a reliable estimate of the proportion of the elements that must constitute margaric acid (*i.e.* palmitic acid) and margarous acid, in which the ratio of the oxygen content of the former to that of the latter is in the proportion of 6 : 5; 3. the possibility that the acid melting at 60°C was actually palmitic acid with a melting point of 70°C combined with a material containing slightly more oxygen and which lowered its melting point, I preferred to call the acid melting at 70°C *stearic acid* and keep the name *palmitic acid* for the acid melting at 55 to 60°C.

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[1] As mentioned in the Foreword and to avoid confusion, the term 'palmitic' will be used instead of the term 'margaric' used by the author.

[2] The MW of palmitic acid is 256 and two molecules of palmitic acid react with lead oxide to form one molecule of water. The ratio of the 'free acid' to water is therefore 512 : 18 or near enough 500 : 17. The molecular weight of the free acid can also be calculated to equal 265.

[3] This value is in accordance with assuming a MW of 18 for water and of 16 for oxygen. However, the molecular formula of water H_2O was at the time not yet clear, as illustrated by the idea that lead oxide reacts with a single molecule of palmitic acid to produce a single molecule of water HO. Assuming a relative atomic mass of 8 for oxygen, the molecular formula of HO is also in accordance with the water content as reported.

[4] In this table, the total of the second column (96.6) equals the dry acid content given in the table above. This total is then divided over O, C and H in accordance with the first table in the chapter by adjusting the oxygen and hydrogen contents for the water that has been removed from the dry acid. So 3.4 parts of water contain 3.0223 parts of oxygen and when these are deducted from the 11.656 parts listed in the first table, we arrive at the figure of 8.6337 (or 8.6334); this is the figure discussed in the table.

In the second column of the table, the figures are normalised to total 100. In the third column, they are converted into atomic ratios by assuming oxygen to be 16.

[5] With the MW of 256 for palmitic acid and 294 for potassium palmitate, 1000 mg would yield (1000 : 294) x 256 = 870.7 mg of palmitic acid and 253.4 mg of potassium chloride containing 160 mg potassium oxide.

[6] As explained before (Endnote 36, previous chapter), dissolving potassium palmitate in water gives a solution comprising potassium ions, palmitate ions, non-dissociated palmitic acid molecules and enough hydroxyl ions to ensure neutrality; because of the alkalinity, the concentration of hydrogen ions will be negligible. On cooling, potassium palmitate and palmitic acid will crystallize, leaving some potassium hydroxide in solution.

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[7] Since the 'bipalmitate' was made by dissolving palmitate in water, dissolving the bipalmitate will hardly alter its composition since this is determined by the solubility of potassium palmitate and palmitic acid.

[8] This remark about the free acids is out of place here and the same has already been mentioned in sub-section (137).

[9] These figures are in full agreement with present theoretical calculations. In fact, when the molecular weight of palmitic acid is calculated on the basis of the acid content of potassium palmitate, a figure of 256 is arrived at and when it is calculated using the yield of sodium chloride, a value of 259 results.

[10] These 3 days may also mean 2 days, just as 8 days usually mean a week especially when followed by 15 days which then clearly means two weeks.

[11] The opodelpoc ointment was invented by Paracelsus, or at least, he concocted the name. It consists of a mixture of soap and alcohol, to which camphor and sometimes a number of herbal essences, most notably wormwood, were added. The US Pharmacopoeia gives the following recipe: Powdered soap, 60 g; Camphor, 45 g; Oil of rosemary, 10 mL; Alcohol, 700 mL; water, enough to make 1000mL.

[12] The color change of litmus requires hydroxyl ions, which are absent in alcohol. Adding water allows these anions to be formed and cause the litmus to turn blue.

[13] Using a value of 647 for the MW of barium palmitate, $Ba(C_{15}H_{31}COO)_2$, and of 233 for $BaSO_4$, the amount of sulfate in 100 mg of barium palmitate is calculated as 36 mg. Using both the weights reported, a relative molecular mass of 275 results for palmitic acid, slightly more than the actual value of 256.

[14] Similarly, the amount of strontium sulfate can be calculated as 30.7 mg and the relative molecular mass of palmitic acid as 273.

[15] The relative molecular masses of 550 and 136 for calcium palmitate and calcium sulfate respectively give: (100 : 550) x 136 = 24.7 as against 24 as measured. This corresponds to a relative molecular mass of 264 for palmitic acid.

[16] Yes indeed: {41.74 : (207 + 16)} x 16 = 2.9948. In addition, the data permit the relative molecular mass of palmitic acid to be calculated as 276.

[17] Lead subpalmitate is also called basic lead palmitate, $Pb(OH)(C_{15}H_{31}COO)$, having a molecular weight of 207 + 17 + 255 = 479. Accordingly, 1.7 g subpalmitate gives an amount of (1700 : 479) x (207 + 16) = 791.4 mg lead oxide. The subpalmitate can therefore be considered as a true compound.

[18] "The Institute" is a colloquial expression for the Academy of Science.

[19] In fact, and as mentioned before, the author called it *margaric acid*. In the literature (Aaron J. Ihde, *The Development of Modern Chemistry,* Dover Publications Inc., New York, 1984 p. 169) it is mentioned that this margaric acid was later shown to be an equimolar mixture of stearic acid and palmitic acid but given the melting point of 60°C, it looks as if the margaric acid was indeed just palmitic acid.

[20] Phosphor**ous** acid (H_3PO_s) contains less oxygen than phosphor**ic** acid (H_3PO_4). It is therefore perfectly logical to give the name *margarous acid* to an acid that contains less oxygen than *margaric acid*.

[21] The determination of the melting point serves two purposes. A sharp melting point indicates that a compound is pure and its actual value helps to identify the compound and distinguishes it from other compounds with different melting points.

[22] For animal fats, the determination of their 'titer', *i.e.* the melting point of the fatty acids obtained by saponification became and has long been a way to characterize the material. There are standard methods for its determination such as Method Cc 12 (97) of the American Oil Chemists' Society, and method C-IV 3 (81) of the Deutsche Gesellschaft für Fettchemie and others.

[23] Although the author did not calculate the relative molecular masses of free stearic acid and free palmitic acid himself, he provides the data from which they can be calculated; this has been done in previous endnotes. The table below summarizes the outcome of these calculations:

Metal in soap	Stearic acid		Palmitic acid	
	sub-section	MW	sub-section	MW
Potassium	58	270	141	273
Sodium	101	261	155	259
Barium	115	275	166	275
Strontium	118	275	168	273
Calcium	121	262	170	264
Lead	124	276	172	276
Literature value		284		256

According to this summary, the values found for stearic acid are in general on the low side, which may have been caused by the presence of some palmitic acid as suggested in the literature (Costa). The values for palmitic acid tend to be on the high side, presumably because of the presence of some stearic acid and/or oleic acid.