CHAPTER 3

OLEIC ACID AND SOME OLEATES

SECTION 1

OLEIC ACID

§ 1. COMPOSITION

185. Burning the free oleic acid (from mutton tallow) with brown copper oxide gave:

	BY WEIGHT[1]
Oxygen……………………………………………	10.784
Carbon……………………………………………	77.866
Hydrogen……………………………………...	11.350

186. Heating oleic acid with lead oxide causes water to be released. The average value of several experiments puts the amount at 19 mg water per 500 mg of acid.

Conclusions

1° The free acid is composed of:

Acid anhydride.	481	96.2	100
Water………….	19	3.8	3.95, containing 3.5 oxygen

2° The oleic acid anhydride contains:

	BY WEIGHT	BY VOLUME
Oxygen…………………………..….	7.699	1.00
Carbon………………………………	80.942	13.73
Hydrogen[*]……………………….	11.359	23.69

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[*] Assuming that the water released originates from the oxygen of the lead oxide and the hydrogen of the acid, the portion of this acid that remains bound to the lead will consist of:

	BY WEIGHT		BY VOLUME
Oxygen………..……………………..	10.7840	10.830	1.00
Carbon…………………………………..	77.8660	78.196	9.43
Hydrogen………………………………	10.9280	10.974	16.23
Total……………………….	99.5780		

187. 100 parts of acid anhydride neutralize an amount of base that contains 3 parts of oxygen. Consequently, for the neutral oleates, the ratio of the oxygen in the acid moieties to the oxygen in the base equals 2.5 : 1 or 5 : 2. Accordingly, if the ratio of the elements of the acid anhydride is as follows:

Oxygen	1.0
Carbon	14.0
Hydrogen	23.4

this means that its composition must be:

	ATOMS	BY WEIGHT	
Oxygen	5	500	7.59
Carbon	70	5357	81.32
Hydrogen	117	730	11.09
Total		6587	100.00

§ 2. PHYSICAL PROPERTIES

188. Free oleic acid looks like a colorless oil. At 19°C, its density is 0.898[2] (g/mL). It solidifies a few degrees below zero into a white mass of needles. It has a slight odor and a rancid taste. *In vacuo*, it evaporates without changing.

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

189. It is insoluble in water.

190. It is miscible in all proportions with alcohol with a density of 0.822[3] (g/mL). If water is added to the solution, the acid separates out.

191. It reacts with bases and forms soaps or rather salts that we have called *oleates*. Like palmitic acid, it turns litmus red and decomposes carbonates.

192. It is miscible in all proportions with stearic acid and palmitic acid. When cold alcohol is added to a mixture of these acids, a substantial amount of oleic acid dissolves, but only a little stearic or palmitic acid. If the extraction is repeated at a temperature of 60°C, the mixture is completely dissolved. On cooling, stearic acid or palmitic acid crystals precipitate but the oleic acid stays in solution.

193. At low temperature, oleic acid is able to form a compound with concentrated sulfuric acid without decomposing.

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

Distillation of the acid while in contact with air

194. When oleic acid is distilled from a small retort while in contact with air, it yields an almost colorless oil. Then it starts to boil, discolors, releases a yellow colored oil, then a brown colored oil and carbon dioxide and methane[4] gas. Only a trace of carbon remains in the retort.

195. The liquid products are strongly acidic. When washed with boiling water, the resulting water is acid and yields a little vinegar when distilled and a residue that easily precipitates lead acetate and colors litmus red. Does it derive these properties from sebacic acid[5]? I have not been able to establish this.

196. When heated sufficiently in contact with air, oleic acid burns just like fatty oils.

The effect of sulfuric acid at 60°C while in contact with air

197. When 0.2 g of oleic acid and 2 g of sulfuric acid are placed in a glass tube with an internal diameter of 0.01 m at a temperature of 27°C, the oleic acid dissolves immediately on agitation. There is a small increase in temperature, the solution is slightly colored and a slight odor of sulfur dioxide is given off. Twenty-four hours later, there is no noticeable change except that the color is slightly darker. After a week, the coloration is yet more marked and if the mixture is heated to 100°C for one hour, sulfur dioxide is evolved without bubbles showing. In addition, it seemed to me that a little hydrogen sulfide is also given off without effervescence. At a temperature above 100°C, there is vigorous bubbling and the oleic acid is rapidly carbonized.

Effect of nitric acid

198. An amount of 2 g oleic acid mixed with 200 g nitric acid at 32°C behaves similarly to stearic acid, with the difference that the effect is faster. By proceeding as described in (46), a residue weighing 1.74 g is obtained; it is slightly yellow and contains some crystals that can be split into an aqueous extract (A) and an alcoholic extract (B).

A. Aqueous extract

199. The aqueous extract yields *acid crystals* and a slightly yellow mother liquor which is not astringent and does not form a precipitate with slaked lime.

Acid crystals

200. The acid crystals were compared with those that originate from the effect of nitric acid on stearic acid (48). I have only noticed slight differences:

They are smaller and less transparent.
With potassium they form a *salt* the crystals of which form less pronounced *rosettes.*

201. When evaporated to dryness, the residue weighs 0.049 g. When dissolved in cold alcohol and water is added to the alcoholic solution, two products are obtained: 1. *an oil*; 2. *an aqueous liquid.* *B.* Alcoholic extract

202. The oil resembles the oil obtained from stearic acid since it does not turn a dry litmus paper red, but does turn a wet litmus paper red. It is soluble in potassium hydroxide and it forms insoluble compounds with baryta[6] and lime[7]. 1. Oil

203. The aqueous liquid contains the same compounds as extract A. 2. Aqueous liquid

§ 5. OCCURRENCE

204. It is present in lard, human fat etc.

§ 6. PREPARATION

205. (See Book III, chapter 1)

§ 7. NOMENCLATURE

206. *Oleic* comes from *oleum* (oil). I have given it this name since it looks like an oil and because it is produced in larger quantities from oils or rather from oleins than from fats and stearins in particular.

§ 8. HISTORY

207. When I described oleic acid for the first time I called it *fluid fat* in a Report presented to the Academy on 2 November 1813.

208[8]. MELTING POINTS OF MIXTURES OF OLEIC ACID AND PALMITIC ACID

ACID		Melting point		ACID		Melting point
Oleic[1]	Palmitic[2]			Oleic[1]	Palmitic[2]	
99	1	Cloud point of 2°	solidifies at 0°	49	51	44.25
98	2	7	2	48	52	44.50
97	3	7	3	47	53	45
96	4	7.5	5	46	54	45
95	5	9.5	7	45	55	45.75
94	6	11	8	44	56	46
93	7	15	9	43	57	46.25
92	8	16	10	42	58	46.50
91	9	16	14	41	59	46.50
90	10	21	17	40	60	46.75
89	11	25.5	18	39	61	47
88	12	26	21	38	62	47.75
87	13	27	24	37	63	47.75
86	14	28	25.5	36	64	47.75
85	15	30	melts at 26.5	35	65	48
84	16	30	27.5	34	66	48
83	17	32	28.5	33	67	48
82	18	32	29.5	32	68	48.25
81	19	32.5	30.5	31	69	48.25
80	20	35	31.5	30	70	48.50
79	21	35	32	29	71	48.50
78	22	36	33	28	72	48.50
77	23	36	34	27	73	48.75
76	24	36.5	34.5	26	74	49.25
75	25	37	35.5	25	75	49.50
74	26	37	35.5	24	76	49.50
73	27		36	23	77	49.75
72	28		36.5	22	78	50
71	29		37	21	79	50
70	30		37.5	20	80	50.25
69	31		38	19	81	50.25
68	32		38.5	18	82	50.75
67	33		38.75	17	83	51
66	34		39	16	84	51.50
65	35		39.5	15	85	51.75
64	36		39.75	14	86	52
63	37		40	13	87	52
62	38		40.25	12	88	52.50
61	39		41	11	89	52.50
60	40		41	10	90	53
59	41		41.75	9	91	53
58	42		42	8	92	53.25
57	43		42	7	93	54
56	44		42.25	6	94	54
55	45		42.50	5	95	54
54	46		43	4	96	54.5
53	47		43.5	3	97	54.5
52	48		43.75	2	98	55
51	49		44	1	99	55
50	50		44			

[1] This oleic acid originates from human fat; when kept for several days at a temperature of zero degrees centigrade, a small amount of palmitic acid was deposited.

[2] This palmitic acid originates from human fat. It melted at 55°C.

SECTION 2

OLEATES

ARTICLE 1

POTASSIUM OLEATE

209

Composition of potassium oleate

Oleic acid anhydride. 100[9]
Potassium oxide…… 17.91 of which 3.036 is oxygen

When determining experimentally the composition of this salt by the amount of acid that dissolves in a potassium hydroxide solution of known alkalinity, we found that 100 parts of the free acid require 16.55[10] parts of potassium oxide, from which it follows that the potassium hydroxide solution can dissolve a little more oleic acid than the amount required to neutralize it[11].

Preparation of potassium oleate

210. Place 1 part of oleic acid and 1 part of pure potassium hydroxide[12] diluted with 5 parts of water in a dish and heat while stirring. The reaction between the acid and the alkali, which started when the mixture was cold, is then completed. The oleate is soft. It does not dissolve in the water, which contains the stoichiometric excess of alkali, nor does it absorb this liquid to form a gel. After cooling it loses some of its softness. It is separated from the alkaline mother liquor and pressed between filter paper. Subsequently, it is dissolved in 10 to 15 times its weight of boiling alcohol with a density of 0.821[13](g/mL) in order to remove a slight excess of alkali present as potassium carbonate[14]. The oleate is obtained by evaporating the alcohol. If it still contains an excess of alkali, it must be dissolved again in some water, exposed to air so that the excess of caustic potash absorbs carbon dioxide, then dried and redissolved in concentrated alcohol.

Observation

211. Oleic acid reacts when cold with moistened potassium hydroxide while generating perceptible heat. At an elevated temperature, 2 parts of oleic acid and 1 part of potassium hydroxide and 8 parts of water react in such a manner that the potassium oleate absorbs all the water present that contains the excess of alkali and forms a viscous gel that is semi-transparent and retains its physical properties when cooled to 13°C. If an amount of ½ part of potassium hydroxide dissolved in 4 parts of water is added to this gel and the mixture is heated, subsequent cooling causes

the oleate to separate as a gel from the excess of potassium hydroxide that remains dissolved in a small amount of water. This gel retains its transparency. If the oleate is pressed between papers until it no longer moistens them and is subsequently dissolved in boiling alcohol that is allowed to evaporate from the solution, the residue is a gelatinous and transparent oleate that still has the same properties after having been exposed to the air for six months.

Properties

212. The potassium oleate is a colorless powder with little or no odor; it has a bitter and soapy taste.

213. If 1 part of dry oleate is mixed with 2 parts of cold water, a transparent gel is formed. On adding a further 2 parts of water, the gel turns into a syrupy, ropy liquid.

214. When potassium oleate is dissolved in a large amount of water, it appeared to me that it eventually separated into potassium hydroxide, which remains in solution, and a gelatinous peroleate[15] that settles out.

215. When 1 part of potassium oleate is mixed with 1 part of alcohol having a density of 0.821 (g/mL) at a temperature of 13°C, it does not fully dissolve. If the temperature is raised to 50°C, the dissolution becomes complete; at 40.5°C the solution becomes cloudy and at 31°C it becomes a soft mass; at 12°C, this mass has become solid. Adding 1 part of alcohol and heating leads to complete dissolution and the resulting liquid can be cooled to 12°C without becoming cloudy. When left at 10°C for several hours, a deposit of neutral oleate crystals is formed. The mother liquor contains:

Alcohol……………………………………………..	100
Oleate………………………………………………	46.4

216. 100 parts of boiling ether can dissolve at least 3.43 parts of oleate. The solution remains clear at a temperature of 12 degrees centigrade.

217. Potassium oleate does not dissolve in a concentrated solution of potassium carbonate or in a saturated solution of potassium chloride.

218. An aqueous solution of potassium oleate is decomposed by lime-water and solutions of strontium and barium hydroxide: insoluble oleates are formed. This also holds for all salts derived from bases that form insoluble oleates.

219. Sulfuric acid, sulfurous acid, phosphoric acid, phosphorous acid, boric acid, in short all acids that are soluble in water, decompose potassium oleate. They split the oleic acid from the base and form free oleic

acid. It should be noted that passing carbon dioxide gas through an aqueous solution of potassium oleate at 5°C leads to the same effect, which is remarkable, since it is known that heating oleic acid and potassium carbonate in water causes it to release its carbon dioxide.

Potassium oleate is decomposed on electrolysis[16]: the acid moves to the positive pole and the potassium to the negative one.

ARTICLE 2

POTASSIUM PEROLEATE[17]

220. When 103.5 parts of free oleic acid are put into 400 parts of water containing 9.21 parts of potassium[18] and the mixture is allowed to digest while being gently heated, a gelatinous mass is obtained that can be diluted with 1 000 parts of water without it dissolving or causing oleic acid to separate out. The water in which the peroleate is suspended is very difficult to filter: it always retains some potassium and probably also a certain amount of acid.

221. The potassium peroleate is soluble in boiling alcohol and in cold alcohol. The solution colors a litmus solution bright red. If water is added to the mixture of the liquids, the color changes to blue because the alkali of the litmus that was originally attached to the peroleate, recombines with the dye[19]. However, since the peroleate only forms a deposit very slowly, it follows that the alkali of the litmus still exerts some effect on the peroleate; in fact, the alcohol present in the liquid may be partially responsible for slowing down the precipitation[20].

ARTICLE 3

SODIUM OLEATE

Composition

Oleic acid anhydride………………………………….	100[21]
Sodium oxide..………………………………………	11.87

222. When trying to determine the composition of this salt by measuring the amount of acid that can be dissolved in aqueous caustic soda of known strength, it was found that 100 parts of acid require 10.46 parts of sodium oxide. This means that like potassium carbonate, sodium carbonate can dissolve slightly more acid than required for its neutralization[22].

Preparation of sodium oleate

223. Place 1 part of oleic acid and 0.66 parts of caustic soda[23] diluted with 5 parts of water in a dish and heat while agitating. The oleate is

formed as a soft gelatinous mass that does not dissolve in water containing an amount of alkali that is in stoichiometric excess. On cooling, the oleate separates as a single mass that is much firmer and more resilient than potassium oleate. After having been separated from the alkaline solution, the sodium oleate can be ground to a powder and pressed between filter paper until no more moisture can be expelled and subsequently treated with 10 to 15 times its weight of boiling alcohol with a density of 0.821 (g/mL), in the same way as we treated potassium oleate.

Observations

224. When cold, oleic acid reacts with moistened sodium hydroxide while giving off heat. When heated, 2 parts of oleic acid, 1 part of sodium hydroxide and 8 parts of water react to form sodium oleate in the form of gelatinous, semi-transparent lumps but on cooling, these lumps become opaque. By adding 4 parts of water and heating the mixture, the sodium oleate forms a transparent gel that also becomes opaque on cooling and separates from the water containing the excess of alkali. Drying that oleate, treating it with boiling alcohol and allowing the solution to evaporate to dryness in a glass recipient leads to the formation of the oleate as a solid, brittle, semi-transparent mass that looks perfectly dry and that easily detaches itself from sides of the glass in the form of flakes.

Properties

225. Sodium oleate is colorless with little or no odor; it has a bitter, alkaline taste.

226. It attracts moisture from the air but unlike potassium oleate, it does not tend to liquefy when exposed to air that is saturated with water.

227. At 12°C, 1 part of sodium oleate easily dissolves in 10 parts of water. It is likely that a very dilute solution will eventually split into sodium hydroxide and sodium peroleate, which will precipitate.

228. When 1 part of sodium oleate is added to 5 parts of alcohol with a density of 0.821 (g/mL), it does not dissolve, even after heating, but when the amount of alcohol is doubled, dissolution takes place. It only started to become cloudy at 31.5°C. This means that at 32 degrees centigrade, 100 parts of alcohol can dissolve 10 parts of sodium oleate. On the other hand, we have also seen that at 13 degrees centigrade, the same amount of alcohol can dissolve only 4.84 parts of oleate.

229. Ether has little affect on sodium oleate because at its boiling point, 100 parts of ether do not completely dissolve 2 parts of oleate. On cooling, the solution throws a deposit. By evaporating the solution after it has been cooled and the deposit removed, we found that 100 parts of ether had dissolved 1.14 parts of an oleate that contained a striking excess of oleic acid. This material is not completely soluble in water either and the alcoholic solution colors litmus a fairly bright red.

230. Reagents that decompose potassium oleate by combining with the base exert the same effect on sodium oleate.

231. Sodium peroleate also exists but I have not studied it.

ARTICLE 4

BARIUM OLEATE

Preparation

232. This compound can be prepared by boiling baryta water with oleic acid in the same way as the stearate of this base (114) is prepared, or by mixing oleic acid with a little water and barium carbonate, boiling the mixture, treating the residue with boiling alcohol and filtering the liquid while still hot. On cooling, the liquid deposits pure barium oleate.

233. It has no color, odor or taste. It is insoluble in water and only slightly soluble in boiling alcohol.

234. Slightly warm oleic acid dissolves substantial amounts of barium oleate. When these compounds are mixed in certain proportions, the resulting mixtures can be dissolved in their entirety in an amount of hot alcohol that seems to me to be determined by these proportions. In other proportions, the alcohol tends to dissolve a little oleate with a large excess of oleic acid, leaving a residue of barium oleate that retains only very little free acid.

235. When barium peroleate is dissolved in alcohol it turns litmus red. When dry, it has no effect on dry litmus paper but when both these materials are in contact with humidity, the litmus paper immediately turns red. Furthermore, dry oleic acid behaves in the same way.

Composition

236. 1 gram of this oleate yields 350 mg of barium sulfate[24], which corresponds to 229.7 mg of base. Accordingly, the composition of the salt is:

Oleic acid anhydride….	77.03	100
Barium oxide…………..	22.97	29.8 containing 3 oxygen

The calculated composition gives:

Acid anhydride……….	100
Barium oxide…………..	29.5 containing 3.036 oxygen

ARTICLE 5

STRONTIUM OLEATE

237. This soap has similar properties to the previous one. It can be prepared in the same manner.

Composition

238. On calcination, 400 mg[*] leave an ash that yields 113 mg of strontium sulfate which corresponds to 63.7 mg of the base; thus:

Oleic acid anhydride[25].	3363	84.075	100
Strontium oxide………	637	15.925	18.94, containing 2.93 oxygen

The calculated composition gives:

Acid anhydride…….……………………………….	100
Strontium oxide……….…………………………….	19.64

ARTICLE 6

CALCIUM OLEATE

Preparation

239. Calcium oleate is obtained by mixing warm aqueous solutions of calcium chloride and potassium oleate. The calcium oleate precipitates.

240. It is white and powdery when dry. It melts when heated gently.

241. When 1 g of this soap is burned, it yields an amount of lime that corresponds to 212 mg of calcium sulfate *i.e.* 88.04 mg of calcium oxide. Thus:

Acid anhydride..	91.2	100[26]
Lime…………….	8.8	9.65, containing 2.71 oxygen

The calculated composition gives:

Acid anhydride……………………………………..….	100
Lime………………………………………………….	10.8

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[*] When the oleate sample analysed was treated with boiling alcohol, it did not release any oleic acid.

ARTICLE 7

MAGNESIUM OLEATE

242. It is prepared by mixing a warm aqueous solution of potassium oleate with a solution of magnesium sulfate; the oleate precipitates. Preparation

243 It is white and forms lumps that are slightly translucent. It softens between the fingers.

244. If 1 g is incinerated it yields 70 mg of magnesium oxide; thus: Composition

Acid anhydride	93	100[27]
Magnesium oxide	7	7.53, containing 2.915 oxygen

The calculated composition gives:

Acid anhydride	100
Magnesium oxide	7.84

ARTICLE 8

ZINC OLEATE

245. It is prepared by mixing warm solutions of potassium oleate and zinc sulfate. Preparation

246. It is white and melts below 100 degrees centigrade.

247. An amount of 0.929 g of dry soap is carefully carbonized and then reduced to ash that is subsequently taken up by nitric acid. 120 mg of oxide are obtained. Thus: Composition

Oleic acid anhydride	100[28]
Zinc oxide	14.83, containing 2.947 oxygen

The composition is calculated as:

Acid amhydride	100
Oxide	15.27

ARTICLE 9

COPPER OLEATE

Preparation

248. It is prepared by mixing warm solutions of potassium oleate and copper sulfate.

249. It is green and when exposed to the sun it liquefies. At 100°C it is liquid.

250. An amount of 0.94 g of copper oleate that has been dried as well as possible liberates water when gradually heated to a red glow. A pellet of cuprous oxide or rather copper appears in the mass; it first turns bottle green then a yellowish brown and is reduced to carbon. When the residue is treated with nitric acid, it leaves 115 mg of cupric oxide.

Oleic acid anhydride..	100[29]
Cupric oxide…………	13.94, containing 2.812 oxygen

The composition is calculated as:

Acid anhydride……………………………	100
Oxide………………………………………..	15.05

ARTICLE 10

COBALT OLEATE

251. It was prepared by mixing warm potassium oleate with cobalt sulfate. The soap took a long time to separate from the liquid in which it had formed. Finally, when the particles had agglomerated, it was a greenish blue color that subsequently changed to green. Since the oleic acid from which the cobalt oleate was prepared was rather yellow, I am inclined to think that the true color of this soap is blue.

ARTICLE 11

NICKEL OLEATE

252. It is prepared by mixing warm solutions of potassium oleate and nickel sulfate. It takes a long time to separate from the liquor in which it is formed. Its color is a very pleasant yellowish green.

ARTICLE 12

CHROMIUM OLEATE

253. It is prepared from potassium oleate and chromium chloride. It is violet. For several days it remains soft but eventually, it becomes completely hard through exposure to dry air.

ARTICLE 13

BASIC LEAD OLEATE

Preparation

254. It is prepared by boiling an excess of basic lead acetate with oleic acid.

Properties

255. This salt is almost liquid at 100 degrees centigrade and it is transparent when molten. At a temperature of 20°C, it is soft.

Composition

256. During the first test, I arrived at an acid to base ratio of 100 : 103.5. But tests carried out subsequently to compare oleic acids from different fats all showed:

Acid anhydride…..….…	100[30]
Lead oxide……………….	82.4, containing 5.909 oxygen

Finally, recent experiments have given:

Acid anhydride…………..	100
Lead oxide…………….. …	85, containing 6.0953 oxygen

When assuming that the basic oleate contains twice as much base as oleate, the calculation gives:

Acid anhydride…………..…………………………..	100
Lead oxide……………………………………...…..	84.67

ARTICLE 14

AMMONIUM OLEATE

257. When oleic acid is brought into contact with liquid ammonia, they immediately combine under liberation of heat. Depending on the concentration of the ammonia, a material is formed that is more or less gelatinous and totally soluble in a sufficient amount of water of 15°C.

258. When boiled, the solution gets cloudy and loses ammonia.

259. I think that ammonium oleate could be used in medicine.

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[1] Given the molecular formula of $C_{18}H_{34}O_2$, the oxygen content would be 11.35%, carbon 76.60% and hydrogen 12.06%. As before, the oxygen content is underestimated.

[2] The author never mentions units when reporting a density; his units are g/mL.

[3] At 15°C, a density of 0.822 (g/mL) corresponds to 90.3 % by weight or 93.5 % by volume.

[4] Looking up "hydrogène carburé" in Google France reveals that it can be used in lamps and in balloons. So it must be lighter than air. It was also found in the intestine of a dead cow. All these properties point to methane.

[5] Sebacic acid is decanedioic acid: $HOOC(CH_2)_8COOH$.

[6] Baryta is an old name for barium hydroxide $Ba(OH)_2$.

[7] The text says "chaux" which is lime (CaO) but in accordance with the 'baryta' it should be "chaux éteinte", slaked lime, $Ca(OH)_2$.

[8] This table also appears in Berzelius, *Traité de Chimie Minérale, Végétale et Animale*, (Firmin Didot Frères, Paris, 1850). Berzelius wrote in Swedish and his *Lehrbuch der Chemie* became well-known thanks to the translation by Friedrich Wöhler (1800-1882). Berzelius remarks that the oleic acid used by Chevreul was impure because of oxidation.

[9] Using a relative molecular mass of 94 for potassium oxide, the relative molecular mass of the anhydride can be calculated as: 100 x 94 : 17.91 = 525. This compares very well with the mass of two molecules of acid minus water: 2 x 282.4 – 18 = 547. Given the raw materials from which the oleic acid was isolated and the method of isolation, it is likely to have contained some linoleic acid. Fortunately, this has almost the same relative molecular mass as oleic acid.

[10] Using a relative molecular mass of 282 for oleic acid, the relative molecular mass of the potassium compound equals 16.68 x 282.4 : 100 = 46.7. This is very close to the sum of the relative atomic masses of potassium (39.1) and half an oxygen (16 ; 2 = 8). Accordingly, the "potasse", which normally means 'potassium hydroxide has in this instance been translated as "potassium oxide".

[11] The notion that salts of weak acids such as oleic acid and strong bases such as potassium hydroxide are alkaline was apparently not yet common knowledge. Hence the remark that more acid is required to get a neutral solution.

[12] This is the 'potasse à l'alcool' mentioned in my foreword and in endnote 23 (Book I, Chapter 1, page 37).

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

[14]The French is 'sous-carbonate', a carbonate with a reduced amount of carbon dioxide. Since potassium carbonate (K_2CO_3) has half a CO_2 per potassium atom and potassium

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hydrogen carbonate or potassium bicarbonate ($KHCO_3$) has one CO_2 per potassium atom, the former, having less, is the 'sous-carbonate'.

[15] The name "suroléate" was coined by the author. As explained in more detail in subsection (220), it probably refers to a combination of potassium oleate and oleic acid. A Google search reveals that the term has subsequently been copied by several authors including F. Cuvier in 1827, J.-B. Dumas in 1835 and J.J. Berzelius in 1850 but according to Google, it may not have not been used since. It is interesting to note that Berzelius also copies a whole number of observations reported by Chevreul without acknowledging their source.

[16] The original says 'decomposé par la pile', decomposed by a pile. This refers to the voltaic pile or alternating stack of metals of differing nobility that generates an electric current. In modern French, a battery is still referred to as a 'pile'.

[17] Just as the 'surstéarate' has been translated into 'perstearate', the oleic acid equivalent has been translated into 'peroleate'. See also endnote 41 on page 39.

[18] Here the author mentions "potasse réelle" which presumably refers to the element.

[19] If potassium oleate present in the potassium peroleate is hardly dissociated when dissolved in alcohol and the oleic acid present therein is somewhat dissociated, the solution will react acid to litmus. If adding water to the alcoholic solution causes the potassium oleate to start to dissociate, the resulting oleate anions will react with the few hydrogen cations present so that the pH will rise and react basic to litmus.

[20] At the time of writing, acidity was not yet ascribed to an excess of hydrogen cations over hydroxyl anions.

[21] The sodium oxide content allows the relative molecular mass of the anhydride to be calculated as: $100 \times (2 \times 23 + 16) : 11.87 = 522$, which is very close to the value of 525 that resulted from the potassium oxide content of potassium oleate.

[22] See endnote 11.

[23] The French text refers to "soude à l'alcool". According to G. Eugène Lormé in the *Nouvel Manuel Complet du Fabricant de Produits Chimiques* (1861) less impure sodium hydroxide was made by adding alcohol to a concentrated solution of sodium hydroxide as obtained by the causticization of soda ash ("Soude à la chaux"). Just as in the case of caustic potash, this addition led to the formation of two layers and reasonably pure sodium hydroxide was recovered from the alcohol layer. The book mentions that the product is only used in the laboratory. Soap works use the less expensive, crude caustic.

[24] The relative molecular mass of barium oleate, $Ba(oleate)_2$ equals 700 and that of BaO equals 153.4. Accordingly, 1 g of barium oleate should contain 0.2191 g of barium oxide rather than the 0.2297 mentioned. The difference does not stem from the sulfate since according to current relative atomic masses, 0.35 g of barium sulfate does indeed correspond to 0.2300 g of barium oxide, which is near enough to the 0.2297 in the text.

[25] This table is very illustrative of the way the calculations are made. The primary data are that 400 mg strontium oleate yields 113 mg strontium sulfate. Given the relative molecular masses of strontium sulfate and oxide of 183.6 and 103.6 respectively, it follows that this 113 mg of sulfate corresponds to 63.7 mg of strontium oxide. This is the amount listed in the second column of the table and to arrive at a total of 400, the acid is

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then equated to 400 – 63.7 = 336.3. Accordingly, what is listed is not the free acid but the acid minus water.

The next column expresses the data in percentages and the last column normalizes the same data to 100 parts of 'oleic acid' and mentions the oxygen content of 18.94 parts of strontium oxide as 2.93 parts, which is near enough correct. This figure of 18.94 can be used to calculate the relative molecular mass of oleic acid anhydride according to: 100 x 103 : 18.94 = 544. As mentioned in endnote 9 above, the actual value is 547, which is very close indeed.

[26] So the relative molecular mass of the anhydride is: 100 x (40 + 16) : 9.65 = 580, which is considerably higher than the actual value of 547. The next table quoting a lime content of 10.8 parts per 100 parts anhydride does not help either since this leads to a molecular mass of 518, which is equally off the mark. Besides, it is not clear what the author means when providing calculated compositions.

[27] With a relative atomic mass of 24.3 for Mg and a relative molecular mass of 40.3 for MgO, the relative molecular mass of the anhydride can be calculated as:

100 x 40.3 : 7.53 = 535.

[28] Given the relative molecular mass of 81.4 for ZnO, the relative molecular mass of the oleic acid anhydride becomes: 100 x 81.4 : 14.83 = 549.

[29] With copper at 63.5 and thus CuO at 79.5, the relative molecular mass of the oleic acid anhydride can be calculated as: 100 x 79.5 : 13.94 = 570.

[30] Basic lead oleate ($Pb(OH)C_{17}H_{33}COO$) contains only a single oleic acid moiety, as shown by the calculation of the relative molecular mass of what is there besides the lead oxide: 100 x (207 + 16) : 82.4 = 271. This value should be compared with the value of 282.4, which is the relative molecular mass of oleic acid.

COMPARATIVE EXAMINATION OF SODIUM STEARATE FROM MUTTON TALLOW, SODIUM PALMITATE FROM HUMAN FAT AND SODIUM OLEATE FROM HUMAN FAT

SODIUM STEARATE FROM MUTTON TALLOW *(acid melting at 70°C)*

(A) We heated 2 g of stearic acid made from mutton tallow stearin and 1.32 g of sodium hydroxide together with 10 g of water. The acid reacted immediately with the alkali. The stearate appeared in small lumps. After cooling, all alkaline liquid had been absorbed.

(B) After the addition of 20 g of water, we heated the mixture to boiling point. The lumps softened and lost their opacity without dissolving. After cooling, the lumps formed a mass that separated out from a transparent alkaline liquid.

(B′) After the addition of 10 g of water and heating, the lumps softened and lost their opacity but they did not dissolve. We had to add 40 g of water to obtain a partially gelatinous mass and finally, a further 10 g to obtain a totally gelatinous mass. So a total of 90 g water was used.

(C) On cooling, a pearly mass was obtained that retained almost all the alkaline liquid between its particles. By pressing the stearate between paper, this liquid could be easily removed. The alkaline liquid did not retain any acid. All the stearate was dissolved by 10 g of boiling alcohol with a density of 0.837 (g/mL). After filtration and cooling, the stearate formed a gel-like deposit. The alcohol was allowed to evaporate from the gel and the residue was dried at 100°C.

(D) *Effect of alcohol with a density of 0.821 (g/mL)* – 1 g of stearate that had been dried at 100°C was heated to 79°C with 10 g alcohol; dissolution was incomplete. After the addition of 10 g, only a tiny residue was left. When removed from the heat, the solution started to gel at 71°C; at 67°C it started to lose its transparency and at 69°C, it was completely transformed into a transparent gel. The reading of the thermometer, which was well immersed in the material, dropped to 66°C and then rose to 68.5°C. After 24 hours, the gel had contracted and seemed to have converted into a multitude of small, brilliant crystals that were dispersed in wavy zones like watered silk fabric. After agitation, they settled at the bottom of the liquid. The crystals were extremely shiny.

(E) 10 g of an alcoholic solution that was saturated at 10°C were evaporated and left a residue of 20 mg dry stearate; thus:

Alcohol	99.8	100
Stearate	0.2	0.2004

(F) *Effect of water* – 350 mg of sodium stearate and 3.5 g of water had not visibly reacted after 6 hours. When this mixture was heated to 90°C, a thick liquid was obtained that was almost transparent. At 83°C, the liquid was semi-transparent; at 64°C, it was a semi-transparent mucilage; at 62°C, it was a white, opaque mass that was completely solid, with all the liquid absorbed. As the mass continued to cool, the stearate contracted and liquid leaked from the mass. On pressure, the mass broke up easily.

(G) Adding an amount of 31.5 g of water to the above mass and heating the mixture caused everything to dissolve. After 24 hours the stearate converted into a white mass that exuded a transparent *aqueous liquid*.

The *dried stearate* glistened and obviously consisted of small needle-shaped particles. When dissolved in alcohol, the solution did not turn litmus noticeably red; nevertheless, the stearate had lost some of its sodium because it was not completely soluble in boiling water and a small amount remained in the form of shiny crystals

The *aqueous liquid* that oozed from the 35 g of the stearate mixture contained 9 mg of sodium hydroxide (100%) and only a trace of acid that was hardly noticeable. The amount of stearate used in the experiment contained 37.5 mg of sodium hydroxide; thus the water had removed just less than a quarter.

(H) 200 mg were put in a dish at 12°C, and exposed to air that is saturated with water; there was no noticeable change after six days. The gain in weight was 12 mg. No further changes were noted after a further exposure of 24 hours.

(I) E*ffect of ether with a density 0f 0.728 (g/mL)* – 200 mg were boiled with 20 g ether. The amount of stearate did not seem to diminish. Nevertheless, on cooling several flakes were deposited. When 13.15 g of the solution were cooled to 12°C, a residue of 20 mg was left consisting of stearic acid containing a trace of alkali; thus:

Ether	13.13	100
Stearic acid	0.02	0.15

SODIUM PALMITATE FROM HUMAN FAT *(acid melting at 60 degrees centigrade)*

(A) *Idem* but with the difference that water seemed to be a more effective solvent.

(B) *Idem* but with the difference that the cooled palmitate formed a more homogeneous mass than the previous sample.

(B′) We added 10 g of water and heated the mixture: not only did the lumps disappear but the water was absorbed and a viscous mass was obtained that became transparent on the addition of a further 10 g of water. The total amount of water used was therefore 50 g.

(C) *Idem* but with the following differences: 1. all the alkaline liquid was retained within the palmitate particles; 2. the alcoholic solution gelled at a lower temperature; 3. the cold gel was less opaque.

(D) *Effect of alcohol with a density of 0.821 (g/mL)* – An amount of 1 g palmitate that has been dried at 100°C did not completely dissolve in 10 g of alcohol at 79°C. After the addition of 10 g of alcohol it dissolved completely. After having been boiled at 80°C, the liquid immediately lost its transparency; at 72°C, some flakes appeared and the liquid became semi-transparent; at 62°C, it started to gel and at 58°C, gelling was complete. After 24 hours this gel retained all the alcohol within its particles; it was opalescent and contained no crystals. After having added 10 g of alcohol (density 0.821) and heating, we observed that cooling did not generate any crystals but instead, a bluish, semi-transparent gel resulted.

(E) An amount of 10 g of an alcoholic solution that is saturated at 10°C left a residue of dry palmitate of 38 mg; thus:

Alcohol	99.62	100
Palmitate	0.38	0.381

(F) *Effect of water* – After 6 hours, 0.35 g of palmitate and 3.5 g of water had not noticeably reacted. When heated to 80°C, the mixture became a perfectly transparent liquid; at 70°C, it was still almost transparent and hardly viscous; at 57°C, streaks with a satin luster appeared; at 54°C, it was a white gel; at 53°C, the entire material was an opaque solid that could be broken up by applying pressure but less easily than the preceding sample since it was less ductile.

(G) When a further 31.5 g were added, the same phenomena were observed as with the previous sample except that the cooled palmitate appeared to be less opaque and homogeneous to look at. It consisted of small needles and it behaved like the previous sample when the reagents were added.

The *aqueous liquid* contained the same amount of caustic soda as the previous sample.

(H) An amount of 200 mg was exposed to air that is saturated with water at 12°C; after six days there was no noticeable change. The gain in weight was 28 mg. This did not change after a further exposure for 24 hours.

(I) *Effect of ether with a density of 7.28 (g/mL)* – *Idem* except that no flakes were deposited on cooling. When 17.27 g of solution was cooled to 12°C, it left 30 mg of palmitic acid that contained a trace of alkali; thus;

Ether	17.24	100
Palmitic acid	0.03	0.17

SODIUM OLEATE FROM HUMAN FAT

(A) 2 g of free oleic acid from human fat, 1.32 g of sodium hydroxide and 10 g water were brought into contact; they reacted while cold. On heating, the oleate became gelatinous and very soft but it did not dissolve and absorb all the alkaline liquid to form a gel. On cooling, the oleate separated out as a single mass that was much harder and more resilient than potassium oleate.

(B) The alkaline liquid that separated from the oleate contained no oleic acid.

(C) After being pressed between filter paper, the oleate emerged as small, dry crumbly lumps that were not as hard as the palmitate. It was dissolved in 10 g of alcohol with a density of 0.837 (g/mL) at a slightly elevated temperature. After filtration, the solution did not gel on cooling. Only when heated in an evaporation dish, where it lost all its alcohol and some of the water, did it form a gel; it was heated at 100°C until no more water was given off. The parts that had been most directly exposed to the heat melted and became transparent. This oleate was then placed in a dish and heated until no more water was given off; it was then semi-transparent and completely molten.

(D) E*ffect of alcohol with a density of 0.821(g/mL)* – When 1 g of oleate was added to 5 g of alcohol, a significant proportion dissolved while it was still cold. After heating, it was still not completely dissolved. Complete dissolution was attained after the addition of 5 g of alcohol. The solution started to become noticeably cloudy when it cooled to31.5°C and at 25°C, it had thrown an abundant, apparently membranous deposit.

(E) 10 g of an alcoholic solution that is saturated at 13°C left a dry residue of 461 mg after evaporation; thus:

Alcohol	95.39	100
Oleate	4.61	4.84

(F and G) *Effect of water* – 350 mg sodium oleate dissolved in 3.5 g of water at 12°C.

(H) 200 mg are placed in a dish and exposed to an environment that is saturated with water vapor. After an hour, the oleate did not appear to have changed; after 24 hours, it appeared to have absorbed some water but it was not at all liquid. Six days later, it was thick and opaque and it had absorbed 195 mg of water. After a further 24 hours, it had not absorbed any more water.

(I) *Effect of ether with a density of 0.7.28 (g/mL)* – 0.2 g of sodium oleate were added to 10 g of ether. Dissolution began at 12°C. It was then boiled but a substantial amount failed to dissolve. When the liquid was cooled to 12°C, it produced a deposit of oleate in the form of a membrane. 6.17 g of this solution was evaporated and left a dry residue of 70 mg, a large part of which was soluble in alcohol. The solution turned litmus bright red. It was a mixture of sodium oleate and oleic acid.

Ether	6.10	100
Peroleate	0.07	1.14

COMPARATIVE EXAMINATION OF POTASSIUM STEARATE FROM MUTTON TALLOW, POTASSIUM PALMITATE FROM HUMAN FAT AND POTASSIUM OLEATE FROM HUMAN FAT

POTASSIUM STEARATE FROM MUTTON TALLOW *(acid melting at 70°C)*

(A) 2 g of free stearic acid from mutton tallow, 2 g potassium hydroxide and 10 g of water were heated. The acid combined with the alkali. After cooling the materials showed an alkaline liquid and a lumpy material.

(B) 10 g of water were added to the materials and the mixture was heated. The stearate softened apparently without absorbing the alkaline liquid and after cooling, lumps were formed. 5 g of water was added and the mixture was heated. The stearate seemed to absorb the liquid but without forming a transparent gel. Finally, 10 g of water were added. The stearate formed a transparent gel that on cooling separated into a clear, alkaline liquid that did not retain any acid.

(C) After the stearate had been separated from the alkaline liquid by pressing between filter paper, it was dissolved in 10 g of boiling alcohol with a density of 0.837 (g/mL). The solution was filtered, the filtrate was evaporated to dryness and the residue was dried at 100°C.

(D) *Effect of alcohol with a density of 0.821 (g/mL)*. When 1 g of stearate that had been dried at 100°C was left in contact with 10 g of alcohol with a density of 0.821 (g/mL) at a temperature of 12°C for 12 hours, it – or most of it – did not dissolve. It was heated in a water bath and at 66°C, the dissolution was complete. It was taken off the heat. At 55°C, flakes of stearate, probably made up of very fine needles, appeared. At 50°C, they were so abundant that the liquid was no longer transparent. At 38°C, there were so many that they appeared to have absorbed all the alcohol. Nevertheless, the stearate was not in a gelatinous form.

(E) 10 g of a solution that was saturated at 10°C left a residue of 43 mg stearate. Hence:

Alcohol…………………………………………	99.57	100
Stearate………………………………………..	0.43	0.432

(F) *Effect of water*. 350 mg of stearate that had been dried at 100°C was mixed at 12°C with 3.5 g of water; an opaque mucilage resulted. It was heated and at 99°C, the palmitate *(This should really be 'stearate', AJD)* produced a thick solution that was not perfectly transparent. At 66°C, the liquor was semi-transparent and not very fluid. At 40°C, it was opaque and thick, with a lot of satiny streaks. At 33°C, it was a thick, white, satiny mucilage and finally, at 15°C, the opacity, the sheen and the consistency were much increased.

(G) An amount of 31.5 g of water was added. Twenty-four hours later, the liquid was thick and milky in appearance. After 48 hours, it had deposited much *pearly material* that was separated by filtration from the *aqueous supernatant.*

Pearly material. When dissolved in alcohol, the alcoholic solution turned litmus noticeably red. When boiled in water, the material formed a milky liquor without pearly flakes which became more opaque on cooling.

Aqueous supernatant. 35 g contained 15.5 mg *(The text says 10*^{g} *0155 but this must also be a typesetting error, AJD)* of pure potassium hydroxide with an almost imperceptible trace of acid. The amount of stearate used in the experiment contained 63.7 mg of potassium hydroxide; therefore, the water extracted just over a quarter.

(H) An amount of 200 mg was placed in an atmosphere saturated with water vapor at 12°C. After six days, there was no significant change. The increase in weight was 20 mg and it remained constant after further exposure for 24 hours.

(I) *Effect of ether with a density of 0.728 (g/mL)*. 200 mg were boiled in 20 g of ether. The stearate did not diminish significantly. Nevertheless some flakes were deposited on cooling. An amount of 18.32 g of solution cooled to 12°C yielded 30 mg of stearic acid that contained a trace of alkali, thus:

Ether………………………………………………	18.29	100
Stearic acid………………………………………..	0.03	0.16

POTASSIUM PALMITATE FROM HUMAN FAT *(acid melting at 60°C)*

(A) 2 g of free palmitic acid from human fat, 2 g of potassium hydroxide and 10 g of water were heated together. The acid reacted with the alkali. On cooling the materials had turned into an alkaline liquid and a lumpy material that seemed less hard than in the previous experiment.

(B) 10 g of water was added to the material; it was heated. The palmitate softened. It had absorbed all the alkaline liquid and formed a perfectly transparent gel. On cooling, the palmitate separated from a clear alkaline liquid that did not contain significant amounts of acid.

(C) *Idem.* except that the palmitate from human fat is more soluble in alcohol than the stearate in the previous experiment.

(D) *Effect of alcohol with a density of 0.821 (g/mL).* 1 g of palmitate did not seem to be more soluble in 10 g of cold alcohol with a density of 0.821 (g/mL) than the previous material. When heated, it dissolved. It was taken off the heat. At 43°C, the liquor became cloudy, but the deposit, instead of being completely flaky like the previous material, was only partially so. The other part was gelatinous and at 40°C the latter was so solid that the flask could be inverted without the liquid running out. At 38°C, the gel was totally opaque.

(E) 10 g of a solution that is saturated at 10°C left a residue of 120 mg dry palmitate. Thus:

Alcohol	98.8	100
Palmitate	1.2	1.21

(F) *Effect of water*. 350 mg of palmitate that had been dried at 100°C were mixed at 12°C with 3.5 g of water. A semi-transparent mucilage resulted. On heating to 70°C, the liquor became perfectly transparent. At 60°C, some pearly streaks appeared and the liquid was very fluid. At 40°C, the streaks had increased but the liquor was still very fluid and semi-transparent. It was only at 36°C that its consistency increased markedly and that it became opaque. However, it did not look like a mucilage, not even at 15°C.

(G) 31.5 g of water were added. 24 hours later, the liquid was thick and milky in appearance but less opaque than in the previous experiment. After 48 hours it still looked the same. The entire amount was filtered but the liquid passed more slowly through the paper.

Pearly material. It was less pearly than the previous material. In solution with alcohol, it turned litmus significantly red. When mixed with water, the material behaved similarly to the previous material.

Aqueous filtrate. 35 g of the filtrate contained 17.7 mg potassium. Accordingly, the water had removed 1/3.6 of potassium hydroxide from the palmitate.

(H) 200 mg were kept in an environment that was saturated with water vapor at 12°C. At the end of seven days, there were some drops of liquid. The increase in weight was 110 mg. There was no change after a further exposure of 24 hours.

(I) *Effect of ether with a density of 0.728 (g/mL). Idem,* except fact that no flakes were deposited on cooling.

16.700 g of the solution cooled to 12°C contained 25 mg palmitic acid which retained a trace of alkali. Thus:

Ether	16.675	100
Acid	0.025	0.25

POTASSIUM OLEATE FROM HUMAN FAT

(A) 2 g of free oleic acid from human fat, 2 g of potash and 10 g of water were mixed. The reaction took place without heating. On heating, the oleate became very soft and did not dissolve in the alkaline liquid and absorb the latter to form a gel. On cooling, the oleate lost some of its softness.

(B) The alkaline liquid that was separated from the oleate did not contain any acid.

(C) After the oleate had been pressed between filter paper it was very soft, unlike the palmitate, which was hard. It was dissolved by 10 g alcohol with a density of 0.837 (g/mL) at an only slightly elevated temperature. The liquor did not become cloudy on cooling, as was the case for the previous products. It was only after having been heated, whereby it lost all its alcohol and part of its water, that it set as a transparent gel. When the surface of this gel started to become opaque, it was put on a dish where it was allowed to dry over a hot sand bath that had been removed from the fire. It was placed in a glass tube.

(D) *Effect of alcohol with a density of 0.821 (g/mL).* 1 g of oleate was mixed with 1 g of alcohol. Dissolution was incomplete while cold but became complete on heating. The solution started to become cloudy at 40.5°C. It formed a soft mass at 31°C and a solid mass at 12°C. A further 1 g of alcohol was added and on heating the dissolution became complete. When cooled to 12°C, it was not cloudy. But when the temperature had been lowered to 10°C and the liquor had been exposed to this temperature for several hours, oleate crystals were formed.

(E) 100 parts of alcohol with a density of 0.821 (g/mL) dissolved 46.4 parts of potassium oleate at 10°C.

(F and G) *Effect of water*. 250 mg were mixed with 500 mg water. The latter was absorbed without heating and formed a transparent gel. A further 500 mg of water were added. When the gel was pressed with a glass rod, everything dissolved and the liquid became thick and syrupy.

(H) 200 mg were placed in a dish in an environment that was saturated with water vapor. After an hour, parts were already liquefied. After 24 hours the oleate was entirely agglutinated into a material that was perfectly transparent and probably gelatinous. When the material was weighed after six days exposure, it had absorbed 315 mg of water. After seven days it was 325 mg but there was no further increase after a further exposure of 24 hours.

(I) *Effect of ether with a density of 0.728 (g/mL).* 200 mg of potassium oleate did not dissolve completely in 2.913 g of ether at 12°C nor did it do so at boiling point. After adding 2.913 g of ether the mixture was boiled. The dissolution was complete and it did not get cloudy on cooling. It follows that at 12°C, 100 parts of ether can dissolve at least 3.43 parts of potassium oleate.