

BOOK II

TABLE LISTING SPECIES OF LIPIDS DESCRIBED IN THIS WORK

1 st FAMILY Acid lipids	1 st GENUS	SPECIES
	Which do not evaporate when mixed with boiling water..... <i>Solid</i> in comparison other genera.....	Stearic acid Palmitic acid ^a Oleic acid
	2 nd GENUS	iso-Valeric acid ^b Butyric acid Caproic acid Capric acid Hircic acid ^c
	Which can be distilled with water..... <i>Volatile</i>	
2 nd FAMILY Non-acid lipids	3 rd GENUS	Cholesterol Cetyl alcohol ^d
	Unsaponifiable by alkali and unable to combine with alkali.....	
	4 th GENUS	Spermaceti ^e
	Able to react with alkali to form solid fatty acids and a non-acid, fatty substance.....	
	5 th GENUS	Mutton tallow stearin Human fat stearin Olein
	Able to be converted by alkalis into glycerin (<i>sweet principle</i>) and solid fatty acids.....	
	6 th GENUS	Phocenin ^f Butyrin ^f Hircin ^f
	Able to be converted by alkalis into glycerin, solid fatty acids and volatile fatty acids.....	

- a) 'Acide margarique' has been translated as 'palmitic acid'.
 b) 'iso-Valeric acid' has been used rather than 'Acide phocénique'.
 c) Because there is no equivalent for 'Acide hircique' this name had been anglicized.
 d) "Éthal' is translated as 'cetyl alcohol' in all cases where it occurs.
 e) Similarly, 'Cétine' is translated as 'spermaceti'.
 f) These names have been anglicized to retain some form of system.

CHAPTER 1

STEARIC ACID AND SOME STEARATES

SECTION 1

STEARIC ACID

§ 1. COMPOSITION

28. Combustion of stearic acid hydrate¹ with brown copper oxide gave²:

	BY WEIGHT ³
Oxygen.....	10.1488
Carbon.....	77.4200
Hydrogen.....	12.4312

29. When free stearic acid is exposed to lead oxide⁴ at a temperature just above 100°C, water is released that is not at all acid. By repeatedly carrying out this experiment with 500 mg of free acid mixed with 4.5 g lead oxide, the loss has been found to equal 17 or 18 mg*. I have used the first figure⁵. The loss is the same if 500 mg of free acid is heated with the amount of lead oxide that is needed to neutralize the acid anhydride⁶.

Conclusions

1. The free acid consists of:

Acid anhydride.	483	96.6	100 ⁷
Water.....	17	3.4	3.5, of which 3.129 oxygen ⁸

* The experimental procedure is as follows: Put 500 mg finely ground stearic acid in a glass tube with an internal diameter of 8 mm and 50 to 70 cm long. Add 4.5 g dry lead oxide. Mix these substances with a thick platinum wire that should remain in the tube. Tare the tube with all its contents and put it in a second tube that is heated until no more water is released. This water tends to condense in the upper part of the long tube which must therefore be heated several times. Each time, the contents must first be mixed with the platinum wire. To get constant results, the moisture at the surface of the small tube must be taken into account.

2. Stearic acid anhydride has the following composition:

	BY WEIGHT		BY VOLUME ⁹
Oxygen.....	7.1262	7.377	1.00
Carbon.....	77.4200	80.145	14.19
Hydrogen*	<u>12.0538</u>	12.478	27.15
Total		<u>96.6000</u>	

30. 100 parts of acid anhydride neutralize an amount of base that contains 3 parts of oxygen¹⁰. Consequently, the ratio of the oxygen in the neutral stearates to the oxygen in the base equals 2.5 : 1 or 5 : 2¹¹; therefore, assuming that the acid has the following atomic ratio:

Oxygen.....	1
Carbon.....	14
Hydrogen.....	27

its composition will be:

	AS ATOMS	BY WEIGHT	
Oxygen.....	5	500.0	7.463
Carbon.....	70	5357.1	79.963
Hydrogen.....	135	<u>842.4</u>	<u>12.574</u>
Total		6 699.5	100.000

§ 2. PHYSICAL PROPERTIES OF FREE STEARIC ACID

31. When molten, stearic acid is a clear colorless liquid that crystallizes at 70°C¹² into beautiful, shiny, interlaced flakes and of the purest white.

32. When 500 mg of stearic acid is heated under the vacuum created by a barometer, the closed end of which has been bent to form a retort, it starts to boil and evaporates. During this process, the mercury level is lowered by about 6 mm. When the tube has cooled, the volume of gas is

* Assuming that the water being evolved is produced from the oxygen in the lead oxide and the hydrogen of the acid, the portion of the acid that is attached to the lead consists of:

	BY WEIGHT		BY VOLUME
Oxygen.....	10.1488	10.187	1.00
Carbon.....	77.4200	77.713	9.97
Hydrogen.....	<u>12.0538</u>	12.100	19.06
Total.....		<u>99.6226</u>	

barely 1/10th of a milliliter at 760 mmHg pressure and the acid has the same melting point as before being heated. The only sign of change is a slight yellowing, which is most noticeable at the end of the process.

33. Stearic acid has no taste or odor.

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

34. Stearic acid is insoluble in water

35. When it is melted by heating, it becomes totally miscible with alcohol. If you heat 1 part of alcohol having a density of 0.794¹³ (g/mL) with 1 part of stearic acid to 75°C, you obtain a solution with a cloud point of 50°C where it starts to form glossy flakes. At 45°C, the solution completely solidifies.

36. When slowly recrystallized from alcohol, stearic acid separates out in the form of large white, glossy flakes.

37. If you heat 1 part of stearic acid with 1 part ether having a density of 0.727¹⁴ (g/mL), in a test tube that you close off with your finger, it dissolves, but when the last of the acid disappears, a lot of ether evaporates. In the experiment that I have carried out, the solution was clear at 60°C; at 57°C, it solidified into glistening lamellae.

38. Stearic acid can dissolve in concentrated sulfuric acid without changing.

39. When added to bases that can form salts, stearic acid forms true salts. The interaction between these entities can be demonstrated: 1. by the strength with which the acid colors litmus (75)¹⁵; 2. by the decomposition of the carbonates¹⁶ of potassium and sodium that the acid induces at a temperature of 100°C.

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

40. An amount of 1 g of stearic acid was introduced into a retort of 29 mL the spout of which was positioned under a bell jar filled with mercury. Shortly after the application of heat, the acid melted and some air was expelled into the jar. Gradually, the acid started to boil, it became reddish brown and vapor started to condense in the neck of the retort,

Distillation of
the acid while
in contact
with air

first as a liquid and later as a reddish white solid. Finally, it turned into a thick brown liquid and only a trace of carbon was left.

The gas that was collected in the bell jar occupied 13.5 mL; it had a slight odor. It contained only 0.01 mL carbon dioxide and just traces of flammable gas.

a. gaseous product

The volume of the gas in the retort was 16.4 mL. When treated with an aqueous solution of caustic potash, 1.5 mL carbon dioxide was absorbed and the residue contained enough flammable gas to burn with a sluggish blue flame when brought into contact with a burning candle.

It weighed 0.96 g and was odorous and reddish brown. It was evidently impregnated with an aqueous liquid into which a volatile acid was dissolved because when a piece of litmus paper was inserted into the neck of the retort where it had collected, this paper turned red in spite of the fact that it was not in direct contact with the solid product and that the retort had first been filled with mercury and emptied again.

b. solid product

The product melted half a degree lower than stearic acid. On treatment with caustic potash, everything dissolved except for a few molten droplets of oily appearance, the amount of which was too small to be collected. When left undisturbed, the solution turned into a mucilage with a pearly sheen, just as a concentrated potassium stearate solution.

41. When stearic acid is heated sufficiently in contact with air, it will burn like wax.

42. When 0.2 g of very finely dispersed stearic acid is heated to a temperature of 27°C in a glass bell jar with an interior diameter of 10 mm and 2 g of sulfuric acid are then added, the stearic acid immediately soaks up the latter. There is no discoloration, or extremely little. On agitation, part of the stearic acid dissolves and the remainder comes to the surface of the liquid. Half an hour after the components have been mixed, small, pearly, white needles are deposited on the walls of the tube from top to bottom, combining to form stars. After two hours, these needles retain the entire liquid between them. After twenty-four hours, things look very much the same and during all this time no evolution of sulfur dioxide can be smelled. Nevertheless, a litmus paper introduced into the tube turns slightly red. Finally, after a week the portion of the stearic acid that had not dissolved during the first twenty-four hours is also converted into fine, radiate needles, similar to those mentioned above. Some parts of the material that are in contact with the air in the tube have a slight lilac color. Taking an aliquot of the material and mixing it with water liberates an odor of hydrogen¹⁷ and causes white flakes to be formed that after melting, solidification and washing exhibit the properties of stearic acid with the difference that they have a slight odor and are slightly colored and that they melt at about 1°C lower; as far as I can see, these flakes do not retain any sulfuric acid.

The action of sulfuric acid at 66°C in contact with air

43. Taking another aliquot of the material and heating it in a bath with boiling water results in a pale yellow liquid that separates into two layers. The less dense and thinner layer contains the most stearic acid; it solidifies when cooled to 45 to 44 degrees centigrade into a material that is still soft at 25°C. The bottom layer does not solidify after exposure to a temperature of 12°C for two hours but after twenty-four hours, it has thrown a deposit of small, needle-shaped crystals arranged in globules. Otherwise, this bottom layer hardly contains anything in solution that can at least be partially precipitated by water. I do not know if the sulfuric acid concentration in the two layers is the same.

44. Maintaining sulfuric acid in contact with stearic acid at 100°C for several hours causes the latter to blacken and sulfur dioxide is evolved. Finally, at a temperature of over 100°C, it is carbonized.

Action of
nitric acid

45. When 2 g of stearic acid are soaked in 200 g of nitric acid for three days at 32°C, nothing much happens.

46. When heat is applied, nitrous vapors evolve. If you take a retort and a recipient and redistill the product several times, all the stearic acid will finally be dissolved. You should stop when the product forms a perfectly transparent solution with the residue, transfer the solution to a dish and evaporate to dryness on a water bath. The residue weighs 1.854 g. It is viscous, partially crystallized, slightly yellow and acid. Mix this residue with 52 g of water and after leaving it to soak for twenty-four hours, filter it and wash the filter cake with 8 g of water. Now treat the cake with boiling alcohol. In this way, the following are obtained: A, *an aqueous extract*; B, *an alcoholic extract*.

A. Aqueous
extract

47. The aqueous extract gives *acid crystals* and a mother liquor that is slightly yellow; it does not taste astringent and does not form a precipitate with lime water.

Acid crystals

48. The *acid crystals* have a distinctive and quite sour flavor and taste of roasted amber¹⁸. They are quite small and do not have a clear shape. They are stuck together in thin flakes. When heated, they melt and stain paper like an oil and then they sublime while leaving a small trace of carbon.

At 20°C, 1 part of the crystals does not dissolve in 20 parts of water but when you add a further 5 parts of water, dissolution is almost complete. It becomes complete on heating and, no deposit is thrown on cooling.

The solution is very acid. It does not form precipitates with manganese chloride, ferric oxide, silver or copper nitrate, or lime water.

Some flakes are formed with barium and strontium hydroxide but these seem to originate from some impurities in the acid rather than from the acid itself.

The solution forms a slight precipitate with lead acetate and a more abundant precipitate with lead vinegar¹⁹.

It decomposes carbonates, producing effervescence.

The *acid crystals* form a salt with potash that crystallizes in extremely fine rosettes This salt makes litmus paper turn red when wet; the salt also has a fresh, somewhat sharp flavor and a distinctive taste.

Its solution does not form a precipitate with calcium chloride, not even when some limewater is added.

It does not form a precipitate with strontium nitrate, even when strontium hydroxide is added.

It becomes slightly cloudy with barium nitrate.

With lead acetate the solution forms a precipitate that disappears when an excess of the solution or the acetate are added.

Silver nitrate produces a slight cloudiness that clears after the addition of water.

With copper sulfate it forms a precipitate that dissolves in water.

In a concentrated solution, the sulfates of zinc and of manganese oxide²⁰ form a slight precipitate that disappears entirely or almost entirely on dilution with water.

Strongly diluted sulfuric acid acts like these sulfates.

49. The acid discussed above is the same as the acid obtained by Vogel and Braconnot by treating tallow with nitric acid. Vogel took this to be 'sacholactic acid'²¹ but Braconnot rightly noted that it was different. I, too, think this is a different acid.

50. When the alcoholic extract is evaporated to dryness, it weighs 0.1 g. If it is dissolved again in alcohol and water is added to the alcoholic solution, the following are obtained: 1. *an oil*; 2. *an aqueous liquid*.

B. Alcoholic
extract

51. The oil is still liquid at 0°C. It wets dry litmus paper without causing it to turn red, just as olive oil would, but if the paper is wetted, it turns red immediately and smells like roasted amber²². When dissolved in alcohol, it is precipitated by water but nevertheless, it appears to dissolve in a large amount of boiling water. It dissolves in a potassium hydroxide solution but with barium and strontium hydroxide solutions it forms insoluble compounds similar to oleates.

1. Oil

52. The aqueous liquid contains the same materials as *extract A*.

2. Aqueous
liquid

§ 5. OCCURRENCE

53. Stearic acid occurs in the soaps of mutton, beef and pork fats.

§ 6. PREPARATION

54. See Book III, Chapter 1.

§ 7. NOMENCLATURE

55. The name *stearic* comes from $\sigma\tau\acute{\epsilon}\alpha\rho$, meaning 'tallow' or 'solidified fat'. I have chosen this name because this acid is the characteristic product of the saponification of beef tallow.

§ 8. HISTORY

56. I described it in 1816 and I gave it the name *margarous acid* in 1820 after I had analyzed it. (See observations at the end of the chapter on palmitic acid).

SECTION 2

STEARATES

ARTICLE 1

POTASSIUM STEARATE

57. Heat 2 parts of stearic acid in a dish with 2 parts of potassium hydroxide²³ that has been dissolved in 20 parts of water²⁴. Remove the dish from the fire after the reaction is complete. As it cools, the stearate separates in the form of lumps from the mother liquor, which contains only water and the excess of caustic potash²⁵. The stearate is pressed after having been wrapped in filter paper and then it is dissolved in 15 to 20 times its weight in alcohol with a density of 0.821²⁶(g/mL). On cooling, a crystalline salt is obtained²⁷ which is put on a filter from which the calcium carbonate has been removed by washing with hydrochloric acid, and the salt is washed with cold alcohol. If you suspect that it still contains an excess of alkali, it must be dissolved in alcohol once again.

Preparation

58. Treating 1 g with hydrochloric acid gives 0.86 g of free acid that corresponds to 0.8308 dry acid²⁸, and 0.237 g²⁹ of potassium chloride which corresponds to 0.1499 g³⁰ potassium. Thus:

Composition

Acid anhydride³¹.... 100
Potassium oxide..... 18, which contain 3.051 g of oxygen

59. The potassium stearate is in the form of small specks or large flakes that are very shiny and absolutely colorless. It is soft to the touch and has a slightly alkaline flavor.

Properties

60. If it is dissolved in boiling alcohol with a density of 0.794³² (g/mL), and the solution is concentrated by boiling until it starts to deposit a salt, this solution will be found to contain 15 parts of salt for 100 parts of alcohol. (See footnote on page 27 for the experimental procedure).

Action of alcohol

61. 1 part of potassium stearate is dissolved in 10 parts of alcohol with a density of 0.821 (g/mL) at a temperature of 66°C. The solution has a cloud point of 55°C and solidifies at 38°C.

62. 100 parts of alcohol of 10 degrees can dissolve 0.432 parts of stearate³³.

Action of diethyl ether with a density of 0.728 (g/mL)

63. When 100 parts of this ether are heated to its boiling point with 1 part of stearate, only a few flakes precipitate on cooling. For 100 parts of ether, the cold mother liquor contains 0.16 parts of stearic acid comprising one atom³⁴ of potassium bistearate, from which it can be concluded that the ether has split 1 part of potassium stearate.

Action of water

64. When 0.20 g of potassium stearate is placed in an atmosphere that is fully saturated with water at 12°C, it was found to have absorbed 0.02 g after six days. When the salt is exposed once more to the same atmosphere for a further twenty-four hours, it does not increase noticeably in weight.

65. At room temperature, 1 part of potassium stearate and 10 parts of water form an opaque mucilage that liquefies at 99°C. On cooling, a mucilage with a pearly sheen results.

66. If 1 part of potassium stearate is heated in 25 parts of water, it dissolves completely. The solution is completely clear at 100°C and at 92°C, this is still the case. It can be filtered. On cooling it sets to a viscous, pearly mass. The stearate can still be dissolved by an even larger volume of water.

67. If 1 part of potassium stearate is dissolved in 100 parts of boiling water, a solid material results on cooling. It consists of potassium stearate and bistearate and the water still contains slightly more than a quarter of the potassium stearate used in the experiment.

68. When 1 part of potassium stearate is dissolved in 20 parts boiling water and if then the solution is mixed with 1 000 parts of boiling water, a deposit will form on cooling that looks pearly while suspended in the liquid but loses this appearance when collected on a filter. The mother liquor from which the deposit has been formed contains some potassium and an almost undetectable trace of stearic acid. The deposit melts at a temperature well above 100°C. It consists of 100 parts of acid and 9.2 parts of potassium oxide^{*}.

69. When a solution of 1 part of potassium stearate in 20 parts of boiling water is mixed with 5 000 parts of cold water, a pearly deposit is formed with approximately the same composition as the previous one[†].

^{*} In the experiment concerned, 500 mg of this deposit yielded 462 mg of free acid and 65 mg of potassium chloride, which corresponds to 41.1 mg of potassium oxide

[†] Because 500 mg of this deposit yielded 463 mg free acid and 65 mg potassium chloride.

70. When an alcoholic solution of 1 part of potassium stearate is mixed with 5 000 parts of cold water, a deposit is formed that has a pearly sheen while suspended in the mother liquor but loses this shine when collected on a filter. This deposit has a somewhat higher potassium content than the previous one: for 100 parts of acid it contains 9.63 parts of potassium expressed as potassium oxide*.

71. When 1 part of crystallized and very finely dispersed potassium stearate is mixed with 5000 parts of water, it does not swell. It releases half of its alkali into the liquid. In an experiment carried out for comparison with the two previous ones, where the stearate was left for ten days in contact with the water, the deposit was noticeably pearly. For 100 parts of acid, it contained 9.7 parts of potassium oxide†. Without doubt a prolonged contact would have caused the stearate to lose at least half of its alkali.

72. From the above it is clear that: 1. alcohol, which can dissolve both potassium hydroxide and stearic acid, dissolves potassium stearate without noticeably altering this salt; 2. ether, that is a better solvent for stearic acid than for potassium hydroxide, changes the composition of potassium stearate by dissolving relatively more acid than base; 3. water, in which stearic acid is insoluble, can only dissolve the potassium stearate if the temperature is raised but if there is only a small quantity of water and it is cold, it forms a thick mucilage with this salt. If the proportion of water is sufficient, it splits the salt into potassium hydroxide that dissolves and a bistearate that does not dissolve and, most remarkably, under the latter circumstances, it does not form a mucilage.

73. An amount of 500 mg of potassium stearate is placed in a bell jar with 2.5 mL alcohol having a density of 0.821³⁵ (g/mL). Then the jar is filled with mercury and put upside down in a mercury bath. Finally, 4 mL oxygen are added. The apparatus was heated by two furnaces that were lit for five hours each day. The mercury reached a temperature of 55 to 65°C. After a month, the oxygen absorption was nil, the oxygen gas was as pure as before the experiment and the melting point and physical properties of the stearic acid had not changed.

Action of
oxygen gas on
potassium
stearate

74. In a similar experiment, 0.5 g of stearic acid and 2 mL of water were exposed to 4 mL of oxygen under exactly the same circumstances as above and yielded the same results. Nevertheless, we seemed to observe the absorption of a small amount *viz.* 0.1 mL.

75. Stearic acid decomposes potassium carbonate when heated. To demonstrate the decomposition, 1 part of stearic acid and 8 to 10 parts of

Effect of stearic
acid on
potassium
carbonate

* Because 500 mg deposit yielded 462 mg free acid and 68 mg of potassium chloride.

† Because 500 mg of this deposit yielded 464 mg free acid and 70 mg chloride.

water containing $\frac{1}{2}$ part of potassium carbonate are allowed to rise in a tube filled with mercury. The reagents are heated to equilibrium with a red-hot poker. After cooling, there is a gaseous residue, which is pure carbon dioxide. If you repeat the experiment in a small flask fitted with a gas tube, you will notice that the stearic acid dissolves before any carbon dioxide gas is liberated and that this liberation only commences when the liquid is boiling. First the stearate is formed and probably also the neutral carbonate, which then decomposes to give carbon dioxide at higher temperatures³⁶. The product of the reaction between stearic acid and the potassium carbonate is the neutral stearate. When water is added to the product and it is heated, a perfectly clear solution is obtained. When this solution is mixed with water and then cooled, it yields a bistearate comprising 100 parts of acid³⁷ and 8.22 parts of potassium[†]. After it has been filtered several times, the solution from which it has precipitated contains only traces of stearic acid.

ARTICLE 2

POTASSIUM BISTEARATE

Preparation

76. Dissolve 1 part of potassium stearate in a sufficient amount of boiling water and add this solution to 1000 parts of cold water. A deposit of potassium bistearate will be formed³⁸; collect this on a filter and let it dry in the air. Then dissolve it in boiling alcohol and cool to obtain crystalline potassium bistearate³⁹.

77. An amount of 400 mg of potassium bistearate gives 373 mg free acid, corresponding to 360.3 mg acid anhydride, and 51 mg potassium chloride, corresponding to 32.3 mg of potassium oxide.

Acid anhydride..	3603	100
Potassium oxide.	323	8.97, which contains 1.52 oxygen

78. When the potassium bistearate is heated with lead oxide, some water is obtained⁴⁰. When the neutral stearate is heated under the same circumstances, no water is released.

79. Potassium bistearate is made up of small flakes with a silvery sheen, odorless and soft to the touch.

[†] It is also possible that first of all a ternary compound is formed between the two acids and the potassium that loses its carbon dioxide at a temperature of just over 100°C.

[†] An amount of 500 mg of this bistearate yields 470 mg of free acid and 59 mg potassium chloride, which corresponds to 37.3 mg potassium oxide.

80. It does not melt when heated to 100°C.
81. If 1 part of potassium bistearate is mixed with 1 000 parts of cold water, nothing much seems to happen. However, if you analyze the water after a month of contact, you will find a little potassium and nearly undetectable traces of stearic acid.
82. Warm water has a marked effect on this salt. When you heat 1 000 parts of water with 1 part of potassium bistearate to boiling point and remove the liquid from the fire after it has boiled for a few minutes, the liquid is milky and mucilaginous. It has become impossible to read letters 7 mm high through a 3 mm layer of the liquid. The liquid will lose its opacity when cooled to a temperature of 75 to 72°C and thereafter it becomes almost semi-transparent and you can read through it. It has also lost its viscosity. At 67°C it deposits some flakes and at 59°C it starts to deposit pearly material that increases in volume until 26°C. The liquid will then be cloudy, but not to the same extent as at 100°C.
83. When the liquid is at its most opaque, that is to say when it is boiling, it contains stearic acid in two forms: 1. a portion is dissolved as a neutral stearate; 2. another portion is simply held in suspension by the water and its neutral stearate. When the boiling liquid is passed through a double paper filter, it yields: 1. a solution of neutral stearate which on cooling throws a deposit of bistearate; 2. a 'perstearate'^{41'} which contains more acid than the bistearate used in the experiment. It is clear that if filtration is delayed until the liquor is completely cold, or rather until the stearate it holds in solution has broken down into potassium hydroxide and bistearate, a deposit will be formed that consists of: 1. this bistearate; 2. a perstearate that is more acid than the materials used in the experiment.
84. A *deposit* that is similar to the previous one (which was obtained with 3 g of potassium bistearate[†] in 3 L boiling water and collected after cooling on a filter from which calcium carbonate had been removed) was completely liquid at 100°C and set at 75 to 71°C. It consisted of 100 parts of acid and 6.18 parts potassium oxide[‡]. Assuming that: 1. 1 part of po-

^{*} The bistearate used in the previous experiments had been prepared by adding a solution of 5 g of potassium stearate in 20 g boiling water to 15 L of cold water; it had not been recrystallized in alcohol.

[†] See previous footnote.

[‡] An amount of 400 mg yielded 382 mg free acid, which corresponds to 369 mg of acid anhydride and 36 mg of potassium chloride corresponding to 22.8 mg of potassium oxide.

tassium bistearate is formed from 1 part of potassium oxide and 2 parts of stearic acid; 2. the boiling water dissolves $\frac{1}{2}$ a part of potassium oxide and $\frac{1}{2}$ a part of acid, while the residue contains $\frac{1}{2}$ a part of potassium oxide and $1\frac{1}{2}$ part of acid, it follows that when the mother liquor has been completely cooled and then filtered, only $\frac{1}{4}$ of the potassium oxide will remain in solution because the other $\frac{1}{4}$ is linked to $\frac{1}{2}$ a part of the acid and deposited as bistearate.⁴² Accordingly, the deposit must have been formed from 2 parts of stearic acid and $\frac{3}{4}$ parts of potassium oxide which is a proportion of 6.76 parts of potassium oxide per 100 parts of acid instead of the 6.18 found in the experiment.

85. Boiling the *deposit* (84) in 1 000 times its weight in water caused it to melt and adopt an *oily aspect*. On cooling, this material became firm and gradually became white and swollen as it absorbed water. The liquor became quite turbid because the large number of small globules of the same material that were dispersed in it also absorbed water. The filtrate contained a significant amount of potassium. In addition, the deposit with the oily aspect was analyzed to contain less potassium than the 'perstearate' that had been subjected to a single treatment with boiling water. Since the material with the oily aspect contains 4.47 parts of potassium oxide for 100 parts acid, it constitutes approximately $\frac{1}{4}$ of the amount present in the neutral stearate. Consequently, the material with the oily aspect can be regarded as potassium quadrostearate⁴³.

86. Boiling the deposit (84) in alcohol caused it to dissolve and on cooling, the solution deposited a true potassium bistearate comprising 9.3 parts of potassium oxide[†] for 100 parts of acid. The salt came in the form of small flakes with a very bright silvery sheen. After cooling, the alcohol contained some dissolved stearic acid and a little potassium bistearate. After having concentrated the solution once again, I obtained a deposit of bistearate and a mother liquor, which after having been filtered, mixed with water and heated, left a stearic acid behind that contained hardly any potassium. When a residue of 200 mg was treated with hydrochloric acid, it did not lose any weight and after evaporating the acid, such a small trace was left that a balance with a sensitivity of 1 mg did not register it. Although it contained so little potassium, I believe I had observed that the potassium gave it its ability to absorb water.

87. We therefore see that when boiling water reacts with potassium bistearate, it removes a portion of alkali and that the non-dissolved

* An amount of 210 mg gave 205 mg free acid, which corresponds to 198 mg acid anhydride, and only 14 mg of potassium chloride, which corresponds to 8.86 mg potassium oxide.

† An amount of 300 mg gave 280 mg of the free acid, which corresponds to 270 mg of the acid anhydride, and 40 mg potassium chloride, which corresponds to 25.3 mg potassium oxide.

residue forms a solution in boiling alcohol that on cooling, splits up into potassium bistearate which crystallizes and stearic acid which remains in the alcohol with some potassium bistearate. The forces acting in this case are the crystalline force⁴⁴ of the bistearate on the one hand and the affinity between the alcohol and the stearic acid on the other.

88. 100 parts of boiling alcohol with a density of 0.794⁴⁵ (g/mL) dissolve 27 parts of potassium bistearate*.

Effect of alcohol

100 parts of alcohol with a density of 0.794 (g/mL) that had been heated over some bistearate, still contain 0.36 parts in solution at a temperature of 24°C. I have the impression that the material that stays in solution has a stearic acid content that is slightly higher than that of the precipitate. And if I am not mistaken, the alcohol has a tendency similar to that of ether to separate stearic acid from the bistearate, but this tendency is much weaker.

89. The alcoholic solution of potassium bistearate does not react with hematin⁴⁶. This demonstrates that potassium is more strongly attracted by stearic acid than by this coloring compound.

90. When you mix an alcoholic solution of potassium bistearate with water, you obtain an abundant, pearly precipitate which contains less potassium than the starting material and in the water, you will detect some potassium and a very small amount of stearic acid. This explains why the hematoxylin, which had no noticeable effect when it was mixed with an alcoholic solution of bistearate, turns purple as soon as some water is added to the solution. - In one of my experiments, 1 part of bistearate was dissolved in boiling alcohol and the resulting solution was diluted with 1754 parts of water. This gave a precipitate comprising 100 parts of stearic acid for every 6.9 part of potassium oxide, which means that it was similar to the deposit (84). By treating it with boiling alcohol, potassium bistearate was obtained on cooling.

91. In the mixture of an alcoholic solution of potassium bistearate and water, this water has an affinity for the alcohol and the potassium. On the other hand, stearic acid is almost insoluble in highly diluted alcohol. Accordingly, these phenomena cause the bistearate to be split in the same way as in boiling water.

* This solubility was determined as follows: 27 parts of bistearate were introduced into a pear-shaped flask. Alcohol was added and the mixture was brought to the boil. Everything dissolved. Boiling was continued until the bistearate started to precipitate. At this point, the flask was put in a balance. When this had been equilibrated, the flask was removed, emptied and dried. To re-establish the equilibrium, 127 parts had to be added on the side of the flask. The solubility of potassium bistearate in alcohol with a density of 0.794 (g/mL) was determined in the same way. It was observed that although the bistearate was less soluble than in boiling alcohol, it dissolved more readily.

Effect of diethyl
ether

92. Boiling diethyl ether removes a significant amount of stearic acid from potassium bistearate. This is bound to be so since it removes stearic acid from neutral stearate, as shown above⁴⁷.

93. Heating 700 mg of bistearate in 20 g of ether to its boiling point does not cause all the salt to dissolve. After the liquor has been left to stand for twenty-four hours, it will contain an amount of 88 mg stearic acid for every 20 g of ether which on incineration, will not even leave 1 mg of potassium carbonate.

94. The following experiment has convinced me that ether can convert potassium bistearate into stearic acid and a stearate that is soluble in boiling water.

An amount of 100 mg of bistearate was treated with:

1. 52 mL of perfectly neutral boiling ether;
2. 32 mL of the same;
3. 52 mL of the same;
4. 42 mL of the same.

Each washing liquor was left for twelve hours after it had been taken from the fire before being filtered.

The first three were combined and after evaporation to dryness yielded a residue weighing 52 mg and having the same melting point as stearic acid. When 40 mg of this residue were burnt, they left a trace of alkaline, yellowish ash that was so little that it could not be measured by an assay balance sensitive to 1 mg.

The fourth washing liquor left hardly 1 mg on evaporation to dryness.

The matter that was not dissolved by cold ether was pearly and totally soluble in boiling water. It was therefore a *neutral stearate* or rather an *alkaline stearate* since we know that ether removes the acid from the neutral stearate.

Effect of stearic
acid on litmus

95. When stearic acid is mixed with a concentrated aqueous litmus tincture, nothing happens when it is cold. After heating, the acid combines with the alkali of the tincture and its blue color changes to red. If the concentrated tincture is in excess, and the acid can therefore absorb all the alkali it is capable of absorbing under these conditions, an insoluble material is formed, leaving an aqueous blue colored solution. When you separate this material, dry it between filter papers, let it dry further, then dissolve it in boiling alcohol with a density of 0.800⁴⁸ (g/mL) and filter the solution while still warm, a small amount of blue extract is retained by the paper. When the solution is allowed to cool, it generates a deposit of *neutral potassium stearate in crystal form*. Accordingly, the stearic acid has enough energy to remove all alkali necessary for its neutralization⁴⁹ from concentrated aqueous litmus tincture.

96. If a very dilute extract is used instead of the concentrated colored tincture, this will also turn red. However, on cooling *no neutral stearate is obtained but only bistearate*, since stearate, which is quite soluble as such in a large amount of boiling water, will be split into potassium hydroxide and bistearate at ambient temperature.

97. The following experiments are eminently suitable to demonstrate: 1. the effect of stearic acid on litmus; 2. the effect of cold water in splitting neutral potassium stearate into the insoluble bistearate and potassium hydroxide which remains in solution. When you add a solution of potassium bistearate in diluted alcohol drop by drop to an aqueous litmus extract, this turns red because it releases its alkali to the bistearate, which then becomes neutral stearate. When water is added to the red solution, it becomes blue again and small flakes of potassium bistearate are deposited.

98. For the alcoholic solution of bistearate to turn the litmus red, the alcohol that is used as a solvent must be quite weak. If it is concentrated, the litmus does not change color. This is proved as follows:

When you heat 20 mg of potassium bistearate in 5 g of alcohol with a density of 0.792 (g/mL), you get a solution that does not change the color of 0.2 g of an aqueous litmus extract* to red when you add the latter drop by drop, or even when you when you bring the solution to the boil. If you add 5 g of water to the solution, no precipitate is formed but the litmus turns red. To make the experiment more striking, it is a good idea to color the water blue with litmus to eliminate the notion that the effect obtained might stem from acid contained in the water. If you then add 10 g of water to the red solution, a precipitate of potassium bistearate is formed and the litmus turns blue again. These observations allow us to conclude that *in a concentrated alcoholic solution, the stearic acid in the potassium bistearate that is in excess of the neutralization equivalent, is more strongly attracted by the potassium stearate than by the potassium in the litmus. If the bistearate is dissolved in weak alcohol, for instance with a density of 0.914⁵⁰ (g/mL), the opposite takes place.*

99. The causes of the effects I have just described are: 1. *the strength of the solid litmus tincture or rather its insolubility in absolute alcohol*[†]. This

* The extract I used contained:

Water.....	1.85	92.5
Dry matter.....	0.15	7.5

[†] This insolubility was demonstrated by the following experiment: if you add a small amount of aqueous litmus tincture to a solution of potassium bistearate in absolute alcohol, a blue precipitate is formed and if you filter the suspension, the filtrate is colorless. Even when the liquids are warm, the same results are obtained.

strength, which increases the stability of the combination of the color compound with the alkali, is evidently opposed to the effect the second portion of the acid within the bistearate exerts on the alkali of the litmus; 2. *the affinity of the second portion of the stearic acid for the potassium stearate with which it is combined within the bistearate*; since for the litmus to turn red, this portion must leave the neutral stearate and attach itself to the alkali of the color compound. The proof that this affinity has an influence is provided by the observation that the drop-by-drop addition of 20 mg of litmus tincture to a solution of 20 mg stearic acid in 5 g of alcohol with a density of 0.792 (g/mL) causes an immediate color change to purplish red. If you then filter the liquid after having brought it to the boil, the filtrate is red and dark red flakes are retained on the paper.

ARTICLE 3

SODIUM STEARATE

Preparation

100. Heat in a porcelain dish 20 parts of stearic acid and 300 parts of water in which 13 parts of soda ash⁵¹ have been dissolved. The acid unites with the alkali and the reaction product separates in the form of a lumpy mass from the alkaline liquid that no longer contains any stearic acid.

Separate the stearate from the mother liquor, let it drain and press it between filter paper. Let it dry in the sun and dissolve it in 25 times its weight of boiling alcohol to separate it from the small amount of sodium carbonate. On cooling, the filtered liquid sets as a solid mass but the stearate gradually changes from a gelatinous state to small, glittering crystals. Collect them on a filter, wash with cold alcohol and allow to dry.

Composition

101. When an amount of 0.500 g was decomposed by hydrochloric acid, 461 mg of free stearic acid and 103 mg of sodium chloride were obtained; the latter corresponds to 54 mg sodium oxide⁵². Accordingly:

Acid anhydride.	4451	89.02	100
Sodium oxide...	549	10.98	12.33. of which 3.154 oxygen

102. The product appears as shiny crystals or semi-transparent flakes that at first have no taste but after a while taste alkaline. It has a melting point.

Effect of alcohol

103. 1 part of sodium stearate can dissolve in 20 parts of alcohol with a density of 0.821⁵³ (g/mL). The solution becomes cloudy at between 71°C and 69°C. It sets as a gel that slowly contracts under formation of small,

brightly glittering crystals (See Table 2 at the end of Chapter 3 of the present Book.)

104. At 10°C, 100 parts of a saturated alcoholic solution contain only 0.2 parts of stearate⁵⁴. This means that 100 parts of alcohol can only dissolve 0.2004 parts of sodium stearate.

105. Boiling ether extracts some stearic acid that contains a trace of sodium. When you boil 100 parts of ether with 1 part of sodium stearate, you will obtain a slight deposit on cooling the solution. When cooled to 12°C, the solution contains only 0.15 g stearic acid for 100 parts of ether.

Effect of diethyl
ether with a
density of 0.728
(g/mL)

106. When 1 part of semi-transparent sodium stearate is soaked in 600 parts of water at 12°C for a week, its aspect does not change at all. After two weeks, the stearate has lost its transparency by absorbing some water. When the liquid is evaporated, a trace of alkali is left behind.

Effect of water

107. When 1 part of stearate is heated to 90°C in 10 parts of water, a thick liquid results that is almost transparent; it sets at 62°C as a solid white mass. The addition of 40 parts of water to this mass and heating causes everything to dissolve, even below 100°C. The solution can be filtered. When collected in a recipient containing 2000 parts of water, pearly sodium bistearate is formed⁵⁵ on cooling. The sodium that dissociated from the stearate is retained in the water, which only contains a trace of acid that is too small to be measured on a balance.

108. When 200 mg of sodium stearate are placed at 12°C in an atmosphere that is saturated with water, 15 mg of water are absorbed after six days. A subsequent exposure of twenty-four hours does not noticeably increase the weight of the stearate.

ARTICLE 4

SODIUM BISTEARATE

109. This is obtained by dissolving 1 part of sodium stearate in 2 000 to 3 000 parts of hot water, filtering the liquid after it has cooled, washing the filter cake, letting it dry and then treating it with warm alcohol. The cold solution deposits the bistearate, which is collected on a filter and allowed to dry in the sun.

Preparation

110. An amount of 0.500 g yielded 0.488 g free acid and 0.532 g sodium chloride, which corresponds to 0.2835 g⁵⁶ of sodium oxide. Accordingly, the salt contains:

Composition

Acid anhydride.....	471.65	94.33	100 ⁵⁷
Sodium oxide.....	28.35	5.67	6.01

Properties

111. It has a lower melting point than the stearate; it is white and has no taste or color.

112. It is insoluble in water.

113. It is highly soluble in alcohol. The solution turns litmus red and the liquid turns blue again when water is added.

ARTICLE 5

BARIUM STEARATE

Preparation

114. Boil an aqueous solution of barium hydroxide in a round bottomed flask and filter it while still hot, collecting the filtrate in a long necked flask containing stearic acid and a little boiling water. By proceeding in this manner, any contact with the carbon dioxide in the air is avoided. Boil the material for two hours, close the long necked flask and after it has cooled somewhat, decant the baryta water⁵⁸, which is in stoichiometric excess, wash the stearate with boiling water and treat it with warm alcohol to remove any excess acid.

115. When an amount of 1 g was burnt in a crucible, an amount of barium oxide was left that yielded 0.34 g of sulfate. Consequently:

Acid anhydride.	77.69	100 ⁵⁹
Barium oxide....	22.31	28.72, containing 3.001 of oxygen ⁶⁰

116. It is white, tasteless and odorless and melts when heated.

ARTICLE 6

STRONTIUM STEARATE

Preparation

117. It is prepared in the same way as the previous compound.

118. When 1 g is burnt in a crucible, it leaves an amount of strontium oxide that corresponds to 0.29 g of sulfate. Accordingly:

Acid anhydride..	83.655	100 ⁶¹
Strontium oxide.	16.345	19.54, containing 3.0189 oxygen ⁶²

119. Its properties are analogous to those of the previous compound.

ARTICLE 7

CALCIUM STEARATE

120. Calcium stearate is prepared by mixing boiling solutions of calcium chloride and of potassium stearate. The precipitate must be washed until the washing liquor no longer forms a precipitate with silver nitrate or with ammonium oxalate⁶³. Preparation

121. If 1g is burned, it leaves an amount of base that corresponds to 0.24 g of calcium sulfate⁶⁴. Composition

Acid anhydride. 90.033 100⁶⁵
Calcium oxide... 9.967 11.06, containing 3.107 g of oxygen

122. Its properties are analogous to those of barium stearate⁶⁶.

ARTICLE 8

LEAD STEARATE

123. It is prepared by mixing two boiling aqueous solutions of lead nitrate and of potassium stearate. The precipitate must be washed until the washing water is no longer colored by hydrogen sulfide. It is then dried in the sun. It is white, it has a melting point and is odorless. Preparation

124. Burning 1 g yields 295 mg of lead oxide. Therefore: Composition

Acid anhydride..... 70.5 100⁶⁷
Oxide..... 29.5 41.84, containing 3 oxygen

ARTICLE 9

BASIC LEAD STEARATE

125. This is prepared while taking the same precautions as with barium stearate with the only difference that a solution of lead subacetate⁶⁸ in water is used instead of baryta water. Preparation

- Properties 126. It is colorless and has a rather low melting point. When molten, it is transparent and can be pulverized by grinding.
- Composition 127. It consists of:

Acid anhydride.....	54	100
Lead oxide.....	46	85.18

128. If the salt is prepared from lead subacetate that contains some copper, the basic lead stearate will also contain this element and there will be a smaller proportion of the base.

ARTICLE 10

AMMONIUM STEARATE

129. An amount of 0.25 g of free stearic acid is introduced into a narrow glass jar that is bent at its top. It is melted and after it has solidified again, the jar is filled with mercury. It is turned upside down and placed in a mercury bath and an amount of ammonia gas is introduced that occupies a volume of 26 cubic centimeters at 760 mmHg and zero degrees. The acid is heated just sufficiently to melt it and left to stand. The absorption is at first rapid and it continues even after the acid has solidified again. When no further absorption takes place, the experiment is concluded. At no point during the experiment could any water be observed.

Below are the details of an experiment that was carried out most carefully. Because the ambient temperature was 22°C and the atmospheric pressure was 753 mmHg, an amount of 0.25 g of free stearic acid was heated for one minute with 30 mL of ammonia gas that had been in contact with lime. The absorption was (in mL):

		mL
After	1 hour.....	9.3
	2 hours.....	9.7
	3	10.1
	24	21.4 ⁶⁹
	48	14.0
	72	16.3
	96	18.0

At the last measurement, the 18 mL amounted to 16.48 mL after normalization to 760 mmHg and 0°C.

The absorption continued for a month, but very slowly. Thereafter it appeared to have stopped and in the course of the second month there was no progress at all.

The gas that had not been absorbed was pure ammonia. Its volume showed that a volume of 21 mL (standard conditions) gas had been absorbed.

According to this result, the composition of ammonium stearate is:

Acid anhydride.....	24125	100
Ammonia.....	1612	6.68

So assuming that 48.81 g of ammonia is equivalent to 117.72 g of potassium oxide⁷⁰ and that 18 g of potassium oxide neutralizes 100 g of stearic acid, it follows that 100 parts of the same acid are neutralized by 6.54 mL of ammonia and that 0.25 g of the free acid absorbs 20.55 mL of this gaseous base.

130. Ammonium stearate is white and almost odorless. It has an alkaline taste. It can be sublimated *in vacuo*; this causes some ammonia to be released but that is absorbed again without the formation of water.

Properties

131. If ammonium stearate is distilled in a retort while in contact with air, there is some release of ammonia. Water is also formed and a stearate mixed with an empyreumatic oil is sublimated.

132. It is soluble in warm water^{*}, at least in water containing some ammonia. On cooling, a perstearate deposit of small glittering flakes is formed which probably contains twice as much acid as the neutral stearate.

¹ The use of the term 'free acid' stems from an analogy with inorganic salts. Nowadays, we write potassium sulfate as K_2SO_4 since it contains two potassium ions and a sulfate ion. At the time of Chevreul, this salt was considered to be a combination of two oxides: K_2O and SO_3 . This sulfur trioxide could also be 'hydrated' and form sulfuric acid. Similarly, the stearic acid as a free acid is hydrated and in soap, it is dry. From now onwards, 'acide hydraté' will be translated as 'free acid'. See also endnote 6.

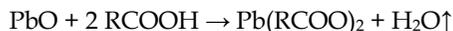
² By assuming that the stearic acid contains two oxygen atoms, the weight percentages in the table lead to the following formula: $C_{20}H_{39}O_2$. The oxygen content is underestimated and should be $(32 : 284) \times 100\% = 11.27\%$ instead of the 10.1488% quoted in the table; consequently, the molecular formula to be derived in sub-section (30) will not be quite correct.

³ In this table, the weight is expressed as a weight percentage. Subsequent tables may have two columns for the weight, the second one of which is again a weight percentage.

⁴ This is the "massicot" referred to in the Foreword.

* In order to dissolve the material, it must be heated in a closed vessel that is entirely filled with water.

⁵ With our present knowledge (relative molecular mass of stearic acid equals 284 and that of water equals 18), we can calculate that this 17 mg corresponds to 0.54 molecule of water per molecule of stearic acid. This corresponds to the reaction:



However, at the time of writing, this was not yet clear and another interpretation (30) of the experiment was sought, which we now consider to be obsolete.

⁶ The text says “l'acide sec de l'hydrate” or ‘the free fatty acid without the water’. Later this has been abbreviated to just “l'acide sec”. Both terms will be translated as ‘acid anhydride’

⁷ The first data column in this table stems from the experimental observation. The next one expresses the values of the first data column as percentages and the last sets the acid anhydride at 100.

⁸ Indeed, $3.5 (16/18) = 3.129$.

⁹ This is the first time that the column heading BY VOLUME appears. The data in the column have been obtained by dividing the data in the column headed BY WEIGHT by the respective atomic weights. The BY VOLUME column therefore gives atomic ratios.

¹⁰ These 3 parts are an approximation of the 3.129 parts listed in the last column in the last table on page 14.

¹¹ The first table on page 15 mentions that 100 parts of acid anhydride contain 7.377 parts of oxygen; this is almost 7.5 parts, so $7.5 : 3 = 2.5 : 1$ or $5 : 2$. However, the correct value is $3 : 1$ and the low oxygen content reported in the first table of this chapter is responsible for this anomaly. See also endnote 2.

¹² The sample must have been very pure since the currently accepted value is 70.1°C .

¹³ The author always expresses the strength of aqueous alcohol (ethanol) by its density. A density of 0.794 (g/mL) corresponds to absolute alcohol. Since nowadays, expressing the strength as a percentage alcohol, either by weight or by volume, is more common, such percentages will be mentioned in endnotes.

¹⁴ The CRC Handbook of Chemistry and Physics gives 0.7138 (g/mL) at 20°C for diethyl ether and also a boiling point of 34.5°C so if indeed diethyl ether is meant, you will have to press your finger down quite hard on the test tube to maintain the pressure inside.

¹⁵ The figure between brackets refers to the corresponding sub-section.

¹⁶ At the time of writing, the salts we now call carbonates were called ‘sous-carbonates’ since they contain less carbon dioxide per alkali metal ion than what we now call bicarbonates, that were formerly called ‘carbonates’.

¹⁷ Nowadays, hydrogen is considered to be odorless but according to W. Ostwald, *Grundlinien der Anorganischen Chemie*, 3rd edition, 1912, footnote on page 134, hydrogen was prepared by allowing water vapor to react with iron and could have an unpleasant smell not unlike petroleum. It originates from the reaction of the carbon in the iron. In the early 20th century, when Normann invented a process for the hydrogenation of

triglycerides, hot iron was still used on an industrial scale to provide him with the hydrogen required and in 1953 the Steam-Iron ore process was apparently still widely used (J.P. Hughes, Hydrogenation of fatty oils, *J. Am. Oil Chem. Soc.*, **30**, 506-515).

¹⁸ This translation is guesswork. The French is “succin empyreumatique”. According to *Le Roberts & Collins Super Senior*, succin was the same in English but then, according to the *Oxford English Dictionary*, this word does not exist; *Collins Concise Dictionary*, *Chambers Science and Technology Dictionary* and Webster don't list it either. However, my Ernst: *Dictionnaire Général de la Technique Industrielle* gives amber as a translation and this word is also mentioned when consulting the www through Google. The latter route also provided meanings for ‘empyreumatique, which I preferred to the literal translation ‘empyreumatic’ given by Ernst. And so, at least a quarter of an hour has been spent on something that is neither here nor there

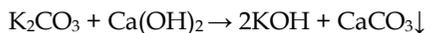
¹⁹ Lead vinegar (sous-acetate de plomb) is obtained by dissolving lead oxide in lead acetate. It is also called basic lead acetate and its formula is $\text{PbOPb}(\text{CH}_3\text{COO})_2$ or also $\text{Pb}(\text{CH}_3\text{COO})(\text{OH})$. The French name indicates that it contains less acetic acid moieties than normal lead acetate.

²⁰ According to Berzelius, this “protoxyde de manganese” contains 28.105 parts of oxygen for 100 parts of manganese. Nowadays, its formula is therefore MnO .

²¹ The reaction product obtained when nitric acid is allowed to react with lactic acid.

²² See endnote 17.

²³ The French text refers to “potasse à l'alcool” and according to Jean-Baptiste Dumas in *Traité de chimie appliquée aux arts* (1848), alcohol (ethanol) was used to produce potassium hydroxide that was almost free from potassium carbonate. The standard way to produce potassium hydroxide was by causticization, allowing potassium carbonate (potash) to react with lime according to:



After removal of the chalk by filtration, a solution of caustic potash results and isolation of the latter can be achieved by evaporation to dryness. However, this evaporation is in contact with the air so that the caustic attracts carbon dioxide and becomes impure. But adding ethanol when the solution is already quite concentrated and allowing the mixture to cool yields two phases, the lower one of which is aqueous and contains all the carbonate and other impurities, whereas the supernatant is an alcoholic solution of almost pure potassium hydroxide. Hence the name “potasse à l'alcool”. See also the preface by the translator.

²⁴ Given the molecular weights of stearic acid (284) and potassium hydroxide (56), it is quite clear that a large stoichiometric excess of potassium is used and that the resulting solution will be quite alkaline, with a pH that must be well above 10. Accordingly, the stearic acid is almost entirely dissociated so that on cooling, when the solubility of potassium stearate is reached, this salt will crystallize as such.

²⁵ The text refers to ‘potasse’, which can mean potassium (the metal or the element), potassium oxide or its equivalent, potassium hydroxide (caustic potash) and even potassium carbonate (potash). The word ‘potassium’ originates from the Dutch ‘potas’ meaning the ashes left over in a pot after burning vegetable matter, but quite unexpectedly, potassium is referred to in Dutch as ‘kalium’.

-
- ²⁶ This corresponds to some 90.7% alcohol by weight or 93.7% by volume at 15°C.
- ²⁷ Potassium stearate does not dissociate when dissolved in alcohol. Consequently, it will crystallize as potassium stearate and not as a mixture of this soap and free stearic acid, which the author calls potassium bistearate.
- ²⁸ The amount of 'dry acid' has been calculated from the amount of 'free acid' by using the lead oxide data in (29) where it is reported that 500 mg stearic acid loses 17 mg of water. So, $860 (500 - 17)/500 = 830.8$.
- ²⁹ Given the molecular weights of potassium stearate and potassium chloride of 322 and 74.5 respectively, the theoretical amount of potassium chloride originating from 1000 mg potassium stearate equals: $1000 (74.5/322) = 231$ mg which compares extremely well with the 237 mg found.
- ³⁰ In modern terms, the statement that 237 mg of potassium chloride contain 149.9 mg of 'potasse' can only be explained by translating the 'potasse' as potassium oxide K_2O equivalent. (MW = $2 \times 39 + 16 = 94$); equivalent MW equals $94 : 2 = 47$ and then, the 'potasse' can be calculated according to: $237 (47/74.5) = 149.5$.
- ³¹ Because the base part of the salt has been quoted as an oxide, the acid part should be the anhydride.
- ³² This is absolute alcohol.
- ³³ The degree is most likely the 'degree Gay-Lussac', which is the volume percentage measured at 15°C. Because no temperature is mentioned, it is presumably also 15°C.
- ³⁴ The author regularly uses the expression "an atom" when he wants to indicate 'a trace'.
- ³⁵ Alcohol with a density of 0.821 (g/mL) contains 90.7 % ethanol by weight or 93.7 % by volume.
- ³⁶ Dissolving a weak acid like stearic acid in a solution of potassium carbonate is something quite different from adding a strong acid to a potassium carbonate solution. The strong acid will liberate so much carbon dioxide that its solubility is exceeded so that it is released as a gas. This release can be quite sudden. The weak stearic acid will be hardly dissociated at all and thus form little carbon dioxide, which will therefore remain in solution. Raising the temperature decreases the solubility of carbon dioxide, which will then be released.
- ³⁷ According to the author's footnote on this page, 500 mg of bistearate correspond to 470 mg free acid and 37.3 mg potassium oxide. Consequently 100 parts of free acid correspond to $37.3 \times 100/470 = 7.94$ parts of oxide, which is close to the 8.22 parts mentioned in sub-section (75).
- ³⁸ When potassium stearate (straight soap) is dissolved in water, it will dissociate and some of the stearate anions formed will react with water to form undissociated stearic acid and hydroxyl ions; the latter give the solution its soapy taste. When the solution is cooled and the solubility of various compounds decreases, they will crystallize. Deposits of potassium stearate and stearic acid will therefore be formed rather than a stoichiometrically defined 'potassium bistearate'. The latter only results from the laudable desire to introduce some system into an otherwise chaotic world.

³⁹ As shown in (57), potassium stearate is purified by dissolving it in alcohol. On cooling, it crystallizes as potassium stearate because on dissolving in alcohol, it does not dissociate into its constituent ions as it does in water, but dissolves as a salt.

⁴⁰ This is only to be expected since the 'bistearate' contains free stearic acid that will react with lead oxide under liberation of water.

⁴¹ The text refers to 'surstéarate'. The prefix 'sur-' indicates that the salt contains more acid than normal, neutral salts. By analogy with permanganate, the word 'perstearate' has been coined.

⁴² In this section, the author approaches the various soapy substances with Gay-Lussac's law in mind. In a textbook published in 1934, my father described this law as follows: "When during a chemical reaction gases are formed or disappear, the ratios of the volumes involved can be expressed in small, whole numbers."

⁴³ Chemical nomenclature has evolved in that nowadays, numbers would be derived from Greek, *cf.* octadecanoic acid. So if the quadrostearate had been a compound, it would have been called tetrastearate.

⁴⁴ Rather than using the term 'energy', the author uses the term 'force' which at that time had a very broad and ill-defined meaning.

⁴⁵ Alcohol with a density of 0.794 (g/mL) is absolute alcohol.

⁴⁶ Hematin is a dye derived from the tree *Haematoxylon Campechianum*. In 1810, Chevreul (!) discovered that the active ingredient is hematoxyline, $C_{16}H_{14}O_6$ or *cis(+)-7,11b-dihydrobenz[b]indeno[1,2-d]pyran-3,4,6a,9,10 (6H)-pentol*.

⁴⁷ See sub-section (63).

⁴⁸ At 15°C, this corresponds to 98.1% by weight and 98.8% by volume.

⁴⁹ The term 'equivalent' had not yet been introduced at that time, but the concept clearly existed.

⁵⁰ This corresponds to 52.0% by weight and 59.8% by volume at 15°C.

⁵¹ Like 'potasse', 'soude' can also have several meanings. In this instance, soda ash is the most likely. Again a large excess of alkali is used.

⁵² Rather, sodium oxide equivalent. See also endnote 28.

⁵³ Surprisingly, no temperature is mentioned but boiling alcohol is probably meant.

⁵⁴ The text says "margarate" which is palmitate; this must be a typesetting error. The first edition of 1823 contains the same error.

⁵⁵ Several of the endnotes discussing the formation of potassium bistearate also apply to the formation of sodium bistearate.

⁵⁶ Again two typesetting errors. Both the amounts of sodium chloride and sodium oxide are out by a factor of 10; they should read 0.053 and 0.028 respectively.

⁵⁷ The three data columns are related in that the first data column reports the analytical results and refers to 500 mg of sample; the second data column expresses the data from the previous one in percentages and the last column sets the acid at 100 parts and thus expresses the oxide in parts per 100 parts of acid.

⁵⁸ 'Baryta water' is an aqueous solution of barium hydroxide.

⁵⁹ The data allow the relative molecular mass of the acid anhydride to be calculated as 533, which is close to the actual value of 550 especially when taking into account that the sample may well have contained some palmitic acid.

⁶⁰ Assuming the atomic weight of barium to be 137.2 and the formula of the oxide BaO, the amount of oxygen can be calculated as: $28.72 \times 16 / (137.2 + 16) = 2.9995$, a figure that differs only marginally from the reported value of 3.001.

⁶¹ Accordingly, the relative molecular mass of the anhydride equals:

$$83.655 \times (87.6 + 16) : 16.345 = 530$$

which is close to the value of 533, calculated from the barium stearate data.

⁶² Assuming the strontium oxide to be SrO, the oxygen content of 3.0189 g in 19.54 g of oxide allows the atomic weight of strontium to be calculated as 87.56, which is very close to the value of 87.62 used nowadays.

⁶³ Whereas silver nitrate is used to show the presence of free chloride ions, the oxalate is used to demonstrate the presence of free calcium ions.

⁶⁴ The molecular weight of calcium stearate, $\text{Ca}(\text{CH}_3(\text{CH}_2)_{16}\text{COO})_2$, is 606 and that of calcium sulfate, CaSO_4 , equals 136. Accordingly, $136 : 606 = 0.2244$.

⁶⁵ Like endnote 50: $90.033 \times (40 + 16) : 9.967 = 506$, which is much lower than expected.

⁶⁶ The text mentions barium "margarate" (palmitate) but again, this is a typesetting error.

⁶⁷ The relative molecular mass can be calculated as $70.5 \times (207 + 16) : 29.5 = 533$, a figure close to the figures derived from the barium and strontium data.

⁶⁸ Lead subacetate is also called 'monobasic lead acetate' $\text{Pb}(\text{OH})(\text{CH}_3\text{COO})$. It is easily prepared by dissolving lead(II) oxide in lead(II)acetate. Its official name is 'lead acetate hydroxide' and since the two anion names must be cited in alphabetical order, the lead 'substearate' is officially called: 'lead hydroxide stearate'.

⁶⁹ This must be a typesetting error. A more logical value would 11.4 mL.

⁷⁰ The equivalent of potassium oxide has a relative molecular mass of 47. Given the value for ammonia of 17, the ammonia equivalent of 117.72 g potassium oxide can be calculated to be 17 ($117.72 : 47$) = 42.58 \neq 48.81. A calculation of the amount of ammonia that is equivalent to 0.25 g stearic acid results in a value of 19.58 mL under standard conditions.