CHAPTER 6

CAPROIC ACID AND SOME CAPROATES

SECTION 1

CAPROIC ACID

§1. COMPOSITION

389. Burning caproic acid as present in lead caproate gave:

	BY WEIGHT	BY VOLUME[1]
Oxygen	22.67	1.00
Carbon	68.33	3.94
Hydrogen	9.00	6.33

389 *bis* 100 parts of 'dry' caproic acid neutralize an amount of base that contains 7.5 parts of oxygen. Consequently, in the neutral caproates, the ratio of the oxygen content of this acid to the oxygen content of the base equals 3 : 1. Therefore, if caproic acid anhydride consists of (by volume):

Oxygen	1
Carbon	4
Hydrogen	6.334

its composition will be:

	ATOMS	BY WEIGHT	
Oxygen	3	300.00[2]	22.439
Carbon	12	918.36	68.692
Hydrogen	19	118.56	8.869
TOTAL		1136.92	100.000

Composition of the free acid

389 *ter* When 0.551 g of 'free' caproic acid with a density of 0.922 (g/mL) is mixed with 5 to 6 g of lead oxide, they react under evolution of heat. When the reaction mixture is heated, an amount of 43 mg of water is given off and this will be alkaline rather than acid. Accordingly, the hydrate consists of[3]:

Acid	508	100
Water	43	8.660[4], containing 7.698 oxygen;

this amount of oxygen is just over a third of the amount in the 'dry' acid*.

§ 2. PHYSICAL PROPERTIES

390. The acid is liquid at ambient temperature; it is very fluid like a volatile oil. It does not solidify at 9°C below zero and it can be distilled without decomposing.

391. At 26°C, its density is 0.922 (g/mL) since a flask with a volume corresponding to 0.647 g of water can hold 0.597 g caproic acid.

392. It is colorless and it smells slightly of acetic acid or rather like sweat. It is not at all reminiscent of the aroma of butyric acid.

393. It has a sharp acid taste and a sweetish aftertaste that is more pronounced than that of butyric acid. It whitens those parts of the tongue with which it has come into contact.

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

Effect of water

394. Water dissolves only a very small amount since, when 0.14 g of acid was mixed with 13.40 g of water at a temperature of 7°C, it did not dissolve completely. Consequently, 100 parts of acid did not completely dissolve 1.04 parts of acid.

Effect of alcohol

395. Alcohol with a density of 0.794[5] (g/mL) is miscible with the acid in all proportions.

396. It dissolves in concentrated sulfuric acid with evolution of heat. If water is added to this solution, it causes some of the caproic acid to separate out.

397. At ambient temperature, nitric acid with a hydrometer reading of 35 degrees dissolves it with difficulty and does not seem to alter the acid.

398. It reacts with iron in the same manner as isovaleric acid.

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* Assuming that the water given off is formed from of the hydrogen in the caproic acid and the oxygen in the lead oxide, the acid moiety that is bound to the lead will consist of:

	BY WEIGHT	BY VOLUME
Oxygen……	28.20	1.00
Carbon……	63.44	2.94
Hydrogen……	8.36	4.75

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

399. When caproic acid is distilled in the presence of air, it behaves like isovaleric acid.

400. It burns with a flame like volatile oils.

401. When a sulfuric acid solution of caproic acid is heated to 100°C, it discolors only slightly. At a more elevated temperature, it discolors earlier than a solution of butyric acid in sulfuric acid. When it starts to boil, caproic acid is evolved with only a little sulfurous acid[6]. The carbon residue is larger than the residue resulting from a sulfuric acid solution of butyric acid.

§ 5. PREPARATION

402. (See Book III, chapter 1)

§ 6. NOMENCLATURE

403. *Caproic* comes from *capra* or "goat".

§ 7. OCCURRENCE

404. It is present in soap made from cow's milk butter and goat's milk butter.

§ 8. HISTORY

405. I discovered it in 1818.

SECTION 2

CAPROATES

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ARTICLE 1

BARIUM CAPROATE

406. When barium caproate flakes, which are enamel white, were exposed to a dry vacuum for a week, no weight loss was observed. Composition

407. When an amount of 100 mg of dry caproate was placed in a platinum crucible and heated with an alcohol burner, the salt melted without showing any signs of change. Very gradually it darkened and released a very pronounced aroma. The residual basic barium carbonate yielded 64 mg of sulfate[7], which corresponds to 41.9 mg of base; therefore:

Caproic acid anhydride.	58.00	100
Barium oxide……....	42.00	72.41, containing 7.57 oxygen

408. When the temperature to which the barium caproate solution is exposed is 18°C or less, the salt crystallizes into flakes, some of which are hexagonal. These flakes are very shiny as long as they are humid but when they are exposed to air, they effloresce and take on the greasy appearance of tallow. They are often arranged like cockscombs; I have managed to obtain samples that were 0.01 to 0.03 m long. Morphology

409. When the temperature to which the barium caproate solution is exposed is 30°C or even lower, the salt crystallizes into needles of 0.01 to 0.025 m long, arranged in various configurations.

410. When the caproate is humid and exposed to air, it smells like caproic acid. It has an alkaline barium flavor and a taste of caproic acid. Aroma and taste

411. 100 parts of water at 10.5°C dissolve 8.02 parts of barium caproate. Effect of water

ARTICLE 2

STRONTIUM CAPROATE

412. When 100 mg of effloresced flakes that lost no weight at 100°C were heated in a platinum crucible, they melted while giving off a strong Composition

aroma of basil oil. They left an amount of base that corresponds to 58 mg strontium sulfate, which contains 34.8 mg of base[8]; thus:

Caproic acid anhydride.	67.31[9]	100
Strontium oxide……..	32.69	48.56 containing 7.50 oxygen

Morphology

413. Strontium caproate crystallizes into flakes that are 0.03 to 0.04 m long and remain transparent as long as they are kept in the solution in which they were formed; on exposure to air, they become white like enamel.

Odor and taste

414. Their odor and taste are the same as for barium butyrate.

Effect of water

415. At 10°C, 100 parts of water dissolved 9.05 parts of strontium caproate.

ARTICLE 3

CALCIUM CAPROATE

Composition

416. When 100 mg of calcium caproate was melted, it gave off a strong aroma of basil oil and left an amount of ash that yielded 50 mg of calcium sulfate or 20.77 mg of base.

Acid anhydride..	79.23[10]	100
Lime…….	20.77	26.22, containing 7.36 of oxygen

Morphology

417. Calcium caproate comes in the form of very shiny flakes, amongst which some square ones can be seen.

Effect of water

418. At 14°C, 100 parts of water dissolved 2.04 parts of calcium caproate.

ARTICLE 4

POTASSIUM CAPROATE

Properties

419. It is prepared by neutralizing potassium carbonate by heating it with caproic acid; afterwards, the liquid is allowed to evaporate[11].

Composition

420. An amount of 100 mg of potassium caproate that released no water when exposed in a glass tube to a temperature approximately equivalent to the temperature at which it starts to change, was decom-

posed by hydrochloric acid. It yielded 47 mg potassium chloride, which represents 2.97 mg of potassium oxide.

Acid anhydride...	70.26[12]	100
Potassium oxide..	29.73[13]	42.30 containing 7.17 oxygen

421. The evaporated solution sets into a gelatinous mass that is beautyfully transparent. If this mass is heated, it loses its transparency and takes on the color of white enamel. Properties

ARTICLE 5

SODIUM CAPROATE

422. It is prepared like the previous salt. Preparation

423. 100 mg of sodium caproate released no water before decomposing when heated in a glass tube and yielded 41 mg of sodium chloride, which represents 21.3 mg of sodium oxide; thus: Composition

Acid anhydride..	78.15[14]	100
Sodium oxide….	21.85	27.96 containing 7.15 oxygen

424. In the air, the concentrated solution sets into a white mass that appears to have a surface bloom. Preparation

ARTICLE 6

AMMONIUM CAPROATE

425. In contact with ammonia gas, the caproic acid 'hydrate' behaves like butyric acid. Therefore there is likely to be a solid caproate and a liquid caproate.

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[1] Because the author regards the lead caproate as the sum of two oxides, he calculates the composition of a kind of caproic acid anhydride $(C_5H_{11}CO)_2O$. The oxygen to carbon ratio he arrives at is quite accurate but as has happened before, he is short on hydrogen. In theory, this should have been 2 x 11 : 3 = 7.33. In the table below giving the composition, only 19 hydrogen atoms are given instead of 22.

In the footnote on page 108, the author also mentions the possibility that the oxygen could stem from the lead oxide and thereby moves close to the ionic character of soaps. He then arrives at 4.75 hydrogen per oxygen, which should have been 5.5 hydrogen per oxygen. With respect to carbon (3 carbon per oxygen), the author is spot on.

[2] These are again the Berzelius figures where the relative atomic mass of oxygen is set as 100.

[3] The relative molecular mass of caproic acid anhydride is 214. When it is calculated from the amount of water, a value results of: 18 x 508 : 43 = 212.7 which is very close indeed.

[4] When normalizing the 503 mg to 100 parts, the 43 mg becomes 43 x 100 : 503 = 8.464 parts which contains 7.5241 parts of oxygen. Three times this amount equals 22.57 parts which is in fact slightly less than the 22.67 parts of oxygen in the acid anhydride and not more as stated at the end of the sub-section. Because the value of 43 mg appears twice and the other values tie in (43 + 508 = 551), it looks very much as if this is not a typesetting error but an arithmetical error by the author who expected a lower value and noticed its being slightly higher.

[5] This is absolute alcohol.

[6] Nowadays, the vapors would be referred to as 'sulfur dioxide'.

[7] These figures allow the relative molecular mass of the caproic acid 'anhydride' to be calculated as 100 x 233 :64 – (137 +16) = 211, where:

- 100 is the mass of the sample barium caproate;
- 233 is the relative molecular mass of barium sulfate;
- 64 is the mass of barium sulfate resulting from the sample, and
- 137 is the relative atomic mass of barium
- 16 is the relative atomic mass of oxygen

This value of 211 is quite close to the actual value of 214 for caproic acid anhydride $(C_5H_{11}CO)_2O$ which indicates that the author used a relatively pure fatty acid.

[8] As before, 'base' stands for the oxide, in this case strontium oxide.

[9] Again the relative molecular mass of the caproic acid anhydride can be calculated as: (67.31 : 32.69) x (87.6 + 16) = 213.3 which again is very close to the actual value of 214.

[10] Using the relative atomic mass of calcium of 40, the relative molecular mass of the anhydride becomes: (79.23 : 20.77) x (40 + 16) = 213.6.

[11] The side note of sub-section (419) reads "Properties"; "Preparation" would have been more appropriate. However, to balance this typesetting error, sub-section (424) reads "Preparation" where it should have been "Properties". The errors have not been corrected.

[12] Similarly: (70.26 : 29.73) x (2 x 39.1 + 16) = 222.6.

[13] This is the figure in the original, which does not add up to 100%.

[14] And again: (78.15 : 21.85) x (2 x 23 + 16) = 221.7.