BOOK III

PREPARATION OF SPECIES OF FATTY MATERIALS

CHAPTER 1

PREPARATION OF FATTY ACIDS AND ANALYSIS OF THE SAPONIFICATION PRODUCTS OF THE FATTY MATERIAL OF THE FIFTH AND SIXTH GENERA

596. The fatty acids of the fatty material of the fifth and sixth genera are obtained by saponification but it is not necessary to carry out the saponification on purified samples of stearin, olein, phocenin, butyrin and hircin. It suffices to saponify tallow, fat, butterfat or oil, in other words, the substances formed of these immediate principles[1].

SECTION 1

PREPARATION OF THE FATTY MATERIAL TO BE SAPONIFIED

§ 1. PREPARATION OF HUMAN FAT, LARD, BEEF TALLOW, MUTTON TALLOW, ETC.

597. Remove most of the membranes enveloping the fat, place it with some water in a porcelain mortar and press with a pestle. Replace the water repeatedly until the washing water remains uncolored. When the fat has been washed, it is drained, then melted on a water bath and filtered through filter paper positioned between two stoves that are burning[2]. Because it is difficult to avoid the presence of some water in the molten fat poured on to the filter, it must be filtered a second time. The main purpose of filtering the fat is to remove the last traces of cellular tissue.

§ 2. PREPARATION OF DOLPHIN OR PORPOISE OIL

598. This is extracted from the tissue in which it is contained more or less as described above. After this tissue has been cleaned as well as possible, it is cut into small pieces and placed with some water in a narrow flask. Exposing this flask to a temperature of 40 to 60°C in a water bath causes the oil to separate and collect on the surface of the water. It is removed with a small pan and filtered in the same way as the above fats. A further considerable quantity of oil can be recovered by heating the tissue in the water and treating it in a press[3].

§ 3. PREPARATION OF BUTTERFAT

599. The butterfat to be used in experiments to analyze its immediate composition and for the preparation of butyric, caproic and capric acids must be separated from the buttermilk. This treatment is described in Book IV, Chapter 2.

SECTION 2

SAPONIFICATION BY CAUSTIC POTASH OF FATS, DOLPHIN OR PORPOISE OIL AND BUTTERFAT

600. Take 4 parts of the material to be saponified and 4 parts of water in which 1 part of caustic potash has been dissolved, place all that in a porcelain dish and heat to a temperature of 100°C. The water that evaporates must be replenished and care should be taken to ensure that the soap does not stick to the bottom of the dish, especially if the dish is heated on a sand bath. Saponification is complete when the mass is homogeneous, semi-transparent and forms a perfectly clear solution when mixed with boiling water. While saponification proceeds, most fatty materials develop an aromatic odor that is not disagreeable.

SECTION 3

ANALYSIS OF THE ABOVE SAPONIFICATION PRODUCTS

601. Add an amount of water to the soapy mass such that a solution is obtained that does not form threads when exposed to a temperature of 50°C. Then acidulate the solution with tartaric or phosphoric acid while taking care to add just sufficient acid to separate the saponified fatty material from the potassium to which it is bound. When all the material has melted and collected on the surface of the aqueous liquid, let it cool until it solidifies; then the aqueous liquid is decanted and the saponified fatty material is washed with water until nothing more is removed[4]. When treating dolphin oil, butterfat and substances that yield volatile acids like isovaleric acid, butyric acid etc., overheating the soapy mass when this is decomposed by tartaric or phosphoric acid must be avoided and above all, the fatty material that is treated with water to separate the volatile acids should have as little contact with air as possible. When treating small quantities, it is useful to wash the fatty material in a stoppered flask[5].

602. I will now explain the methods used to analyze: 1. the *saponified fatty material*, which can consist of three acids: *stearic, palmitic and oleic*[6], 2. the *aqueous liquid*, which always contains glycerin and in many instances, one or more volatile acids.

§ 1. ANALYSIS OF THE SAPONIFIED FATTY MATERIAL AND PREPARATION OF THE CONSTITUENT FATTY ACIDS

ARTICLE 1

ANALYSIS OF THE FATTY MATERIAL OF SAPONIFIED HUMAN FAT, CONSISTING OF PALMITIC AND OLEIC ACIDS

First method

603. Place the saponified fat with 6 to 7 times its weight of water in a porcelain dish or a flask and heat. Then gradually add aqueous caustic potash while stirring each time and continue until all the fatty material is completely dissolved. Transfer the solution to a recipient containing an amount of water equal to 40 or 45 times the weight of the fatty material. Allow it to stand at a temperature of 12 to 15°C; gradually, a *pearly deposit of potassium bipalmitate*[7] *containing peroleate*[8] *of the same base* is formed. When it no longer visibly increases, the supernatant liquor is decanted and water is poured on the deposit to wash it, after which all of

it is filtered. The washing liquors are concentrated by evaporation. When they have been sufficiently concentrated, they are combined with the supernatant liquor decanted from the pearly deposit and this combined liquid is concentrated. Then enough tartaric acid is added to neutralize most of the alkali that has been liberated by the decomposition of the potassium palmitate[9]. After these processes, the liquor is subjected to successive treatments similar to those I have just described until finally, a liquid is obtained that no longer forms a pearly deposit[10].

Preparation of palmitic acid

604. The pearly deposits are collected and after they have been allowed to drain and dry, they are treated three times with 8 parts of boiling alcohol with a density of 0.820[11] (g/mL). After each treatment, the washing liquor is filtered. The first washing liquor sets as a mass on cooling and normally, the third washing liquor deposits hardly anything although it still contains about 0.03 parts of insoluble residue. This residue consists of calcium and iron palmitate, the bases of which come from the material that has been saponified and the filter. After cooling, the first alcoholic washing liquor is poured into a filter. After the deposit has been well drained, the second and third washing liquors are poured over it, followed by some alcohol, and finally, the filter is pressed. The deposit still retains some potassium peroleate. To remove this, it is dissolved in boiling alcohol[12], after which the solution is allowed to cool and filtered. If the deposit contains an acid that melts below 60°C, the same treatment is repeated.

605. The alcoholic mother liquors from which the potassium bipalmitate had crystallized retained a noticeable amount of salt in solution as well as the peroleate of the same base. By concentrating these liquors and then cooling, the following are obtained: 1. a deposit formed by those two salts; 2. an aqueous[13] mother liquor which contains a material in solution that only differs from the deposit in that it contains more potassium peroleate than potassium palmitate.

606. After having obtained a bipalmitate containing an acid that melts at 60°C, it is heated in a dish with water and hydrochloric acid. The latter combines with the potassium and the palmitic acid floats on top of the aqueous liquid. As soon as this acid has congealed, it is removed and washed with water until it no longer precipitates silver nitrate[14]. If the acid is mixed with any foreign particles, it must be melted and filtered through filter paper that contains no calcium carbonate[15].

Preparation of oleic acid

607. When the soap solution (603) no longer yields a *pearly deposit*, it is concentrated and a slight excess of tartaric acid is added; this combines with the potassium, and the oleic acid separates and floats on the aqueous liquid. It is removed with a pipette and mixed with warm water to wash it. It is finally collected in a small flask and exposed step by step

to an increasingly low temperature, but not so low as to cause the entire mass to solidify. Each time the oleic acid is exposed to a lower temperature, it must be filtered[16] to remove the palmitic acid that crystallized, using filter paper that has been washed with hydrochloric acid[17] .

Explanation of the process

608. If there had been no affinity between potassium oleate and palmitate, dissolving these two salts in boiling water and then cooling the solution would have resulted a solution of pure potassium oleate and a deposit of potassium palmitate or bipalmitate, or a mixture of these salts, according to the proportion of water used. The result would still have been the same if cold water had been added to the soap: the oleate would have dissolved but not the palmitic acid. But since there is an affinity, this is not what happens. When the warm potassium hydroxide solution is neutralized by the oleic and palmitic acids and allowed to cool, only part of the palmitic acid will precipitate in the form of an acid salt. The other part remains in solution in the water that contains both caustic potash[18] and potassium oleate. When the cooled liquor is left to stand at a constant temperature, it continues to become more cloudy for a while because the affinity force[19] of the acid salt continues to cause the decomposition of more neutral palmitate until the point when this force is in equilibrium with the dissolving power of the alkali liberated and the oleate. If at this point the temperature of the liquid is lowered, or the energy of the alkali and the oleate is lowered by the addition of water, or if the major part of the liberated alkali is neutralized, the affinity force causes a third deposit of bipalmitate to be formed. Certainly in the last instance, a new equilibrium between the oleate and the palmitates establishes itself that can no longer be shifted without causing the decomposition of the oleate and the palmitate into alkali and acid salts, which precipitate. When preparing oleic acid, it is therefore necessary to decompose the potassium oleate, although it still contains palmitic acid, and expose the resulting oleic acid to lower and lower temperatures in order to cause the palmitic acid to solidify.

Second method

609. 100 parts of well-dried potassium soap made from human fat are treated cold with 200 parts of alcohol with a density of 0.821[20] (g/mL). After soaking for twenty-four hours, it is filtered and the filter cake is washed with alcohol. It consists mainly of potassium palmitate[21], a large part of the oleate of this base having dissolved in the alcohol.

610. The material that remained on the filter is dissolved in 200 parts of hot alcohol. By cooling, a deposit of potassium palmitate is obtained[22]. It must be allowed to drain, then dissolved again in hot alcohol: in this way a new deposit is obtained that must be treated repeatedly in the same manner until it yields an acid that melts at 60°C[23].

611. The palmitate that remains in solution with the oleate in the cooled alcohol is obtained by concentration and cooling, after which it is treated as above.

612. The potassium oleate that has been dissolved by the cold alcohol must be treated as follows: the alcohol is gently evaporated and cold alcohol is applied to the residue; the more concentrated, the better. The oleate dissolves and is thus separated from a substantial amount of palmitate that is not dissolved. After two or three treatments, an oleate is obtained that is completely soluble in cold alcohol[24]. When this stage has been reached, the oleate dissolved in the water is acidulated with either hydrochloric or tartaric acid and the oleic acid is treated as above (607).

ARTICLE 2

ANALYSIS OF THE FATTY MATERIAL CONSISTING OF STEARIC, PALMITIC AND OLEIC ACID ORIGINATING FROM SOAPS MADE FROM MUTTON TALLOW, BEEF TALLOW AND LARD

First method

613. The saponified mutton tallow is dissolved in a weak solution of potassium hydroxide, like the saponified human fat (603), and the solution is then concentrated, which converts it into a *pearly material* and *potassium oleate.*

Preparation of stearic acid

614. The *pearly material* consists of potassium bistearate, bipalmitate and peroleate. It is allowed to dry and is then treated with boiling alcohol in the same way as the *pearly material of the soap of human fat* (604). After several successive treatments of a given amount of pearly material, a deposit of bistearate is obtained, the acid of which melts at 70°C. The acid itself is separated from the potassium by either hydrochloric or tartaric acid (606).

Preparation of palmitic acid

615. The alcoholic washing liquor from which the bistearate has been separated contains potassium bistearate, bipalmitate and peroleate. Concentrating and cooling leads to: 1. a deposit of these three salts and 2. a solution of these three salts but there is a difference between the deposit and the material in solution in that the peroleate occurs only in a small amount in the former whereas it predominates in the solution[25].

616. Treating the deposit (615) with warm alcohol and cooling the solution and then subjecting the new deposit to the same sequence of processes finally yields: 1. potassium bistearate and 2. potassium bipalmitate, the acid of which melts at 56 to 60°C. I tried in vain to split the

latter into peroleate and bistearate. Instead of raising the melting point of the acid, the experiments I carried out to this end[26] actually lowered its melting range by several degrees.

Preparation of oleic acid

617. It is prepared in the same way as oleic acid from soap of human fat (607).

Second method

618. The potassium soap is treated with cold alcohol as described in (609).

619. The matter that does not dissolve in cold alcohol consists of potassium stearate and palmitate and a small amount of oleate of the same base. It is subjected to the same kind of treatment as used to analyze the *pearly material* of mutton tallow soap (614).

620. The treatment of the potassium oleate is as described in (612).

621. This is the method by which I have analyzed the fatty material in mutton and beef tallow, lard and that in butter made from cow's milk.

Observations and experiments concerning the extraction of palmitic acid

622. (A) Because I feared that heat might alter any stearic acid[27] that might be present in the saponified human fat, I used a water bath when saponifying this fat by the procedures described above. The fatty material of this soap that formed a compound with the potassium was separated from its alkali by means of tartaric acid. The soap thus obtained was treated with alcohol. All these treatments were carried out on a water bath but nevertheless, the acid obtained had a melting point of 60°C.

(B) The fatty material from a soap prepared on a water bath was pressed between paper until it no longer stained the paper. In this state, it melted at 53°C. An amount of 75 g of this material was combined with potassium hydroxide[28]. The soap was treated three times with cold alcohol with a density of 0.816[29] (g/mL). This yielded a white salt that was quite shiny, the acid of which melted at 59.5 to 60°C. This deposit was redissolved five times in alcohol and finally yielded a deposit containing an acid with a melting point of 60°C[30].

(C) Another soap was prepared from human fat by using potassium carbonate[31] and the analytical result was the same.

(D) Finally, subjecting potassium stearate dissolved in water and alcohol to a temperature of 60 to 70°C for a hundred and fifty hours while in contact with pure oxygen did not degrade the stearic acid at all.

§ 2. EXAMINATION OF THE AQUEOUS LIQUID; PREPARATION OF GLYCERIN AND VOLATILE ACIDS

623. Since most saponifiable oils and fats do not yield volatile acids on saponification, it is necessary to ascertain their presence before starting the analysis of the aqueous liquid (602). To this end, distill a portion of the liquid, mix an amount of barium oxide that is hematin sensitive[32] into the distillation product, evaporate to dryness and redissolve in water, filter and see if the filtrate contains any salt. If it does not, the examination of the aqueous liquid is very simple.

If the aqueous liquid does not contain any volatile acid

624. The aqueous liquid is evaporated to dryness and the residue is treated with dephlegmated[33] alcohol. When the alcohol is filtered and then evaporated, the glycerin is left as a syrupy liquid. Since alcohol dissolves small amounts of potassium tartrate and phosphate, there will always be traces of these salts in the glycerin. To obtain this substance perfectly free from any saline material, place equal amounts of lard and pure lead oxide in a dish with a certain amount of water. Expose them to a temperature of 100°C while replenishing the water that evaporates. This will saponify the fat but since the fatty acids being liberated form insoluble combinations with the lead oxide, the glycerin is the only solute with just a trace of this oxide[34]. It is a good idea to regularly decant the water that has been boiling with the materials so that the glycerin portions that are formed early on are not exposed to heat during the entire process. Finally, the water is filtered and evaporated on a water bath.

If the aqueous liquid contains volatile acids

625. If on saponification the fat or oil yielded one or more volatile acids, the aqueous liquid resulting from the acidulation of the soap with tartaric or phosphoric acid (601) must be put into a bottle with a ground-glass stopper. Add enough acid to convert the tartrate or phosphate into acid salts, wait until these have settled if they are not fully dissolved, decant the clear supernatant and distill in a large glass retort connected to a long-necked, round-bottomed flask. The volatile acid product distills with the water[35], leaving a residue consisting of glycerin and potassium hydrogen tartrate or potassium hydrogen phosphate.

626. The salty mass that may have been deposited in the flask in which the salts in the aqueous liquid were further acidified with tartaric or phosphoric acid (625), will be impregnated with one or more volatile acids and it must therefore be washed repeatedly to remove these acids completely. The water that served to wash the *saponified fatty material*

(601) should be used for this purpose. After each wash, the washing liquor should be distilled.

627. Combine all the distillation residues and evaporate them to dryness or treat them with dephlegmated[36] alcohol to dissolve the glycerin. If too much tartaric or phosphoric acid has been used to saturate the aqueous liquid, the excess acid will dissolve at the same time as the glycerin.

628. Combine the distillation products containing the volatile acid or acids and evaporate an aliquot of this to make sure that it leaves no solid material, which would be the case if the distillation had been carried out too hastily. If this is the case, the distillation must be repeated. Finally, when a pure product has been obtained, saturate it with crystalline barium hydroxide[37], then evaporate to dryness if the distillation product contains only a single acid, as is the case for the product originating from the aqueous liquid obtained by the acidulation of the soap made from dolphin or porpoise oil. If the product contains several acids, like the product from the aqueous liquid obtained by the acidulation of the soap made from cow's milk butter, the acids are separated by treating the dried salts they form with barium hydroxide with water, as I will explain below[*].

ARTICLE 1

PREPARATION OF ISOVALERIC ACID[38]

First method

629. 100 parts of dry barium isovalerate are placed in a narrow glass tube that has been sealed at one end and 205[39] parts of aqueous phosphoric acid with a density of 1.12[40] (g/mL) are poured on top of it while agitating with a platinum wire. This produces: 1. solid *barium phosphate*; 2. an *aqueous liquid that is saturated with isovaleric acid*[†]; 3. *free isovaleric acid,* which floats on top of the aqueous liquid.

630. The isovaleric acid is collected by pipette; it usually has a slightly yellow color. At a temperature of 21°C, it has a density of 0.954[41] (g/mL). If it is distilled slowly on a sand bath, a colorless *liquid product* A is collected which separates into two layers, and a *thick brown mass* B remains.

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[*] I have ascertained that when an excess of barium hydroxide is used to neutralize the distillation product of the aqueous liquid from butter, the insoluble residue obtained is pure barium carbonate formed from the carbon dioxide in the air and the excess barium hydroxide.

[†] By saturating the aqueous liquid with baryta water, barium phosphate is precipitated and thereby the phosphoric acid that was not neutralized. All that remains in the liquor, is barium isovalerate, which exhibits all the properties I have observed in this salt.

A. Liquid product

631. The upper layer is the most abundant and it consists of free isovaleric acid with a density of 0.933 (g/mL) at 28°C. To obtain it in a pure state, it is allowed to macerate for four days with 2 to 3 times its weight of calcium chloride[42] in a small glass retort equipped with a recipient. It is then distilled on a water bath[43] until nothing more is distilled off. The acid thus obtained has a density of 0.932[44] (g/mL) at 20°C. It does not form a precipitate with silver nitrate[45].

632. The more dense layer of liquid *A* is very small in comparison with the other layer and it seemed to me to be just an aqueous solution of isovaleric acid. It is more volatile than the acid in the first layer.

B. Thick brown mass

633. This material does not appear to contain phosphoric acid. It originates from part of the isovaleric acid that has been downgraded by the action of air and heat.

Second method

634. 100 parts of dry barium isovalerate are placed in a tube that is closed at one end together with 33.4 parts of 66 degree[46] sulfuric acid diluted with 33.4[47] parts of water. The mixture is agitated with a platinum wire. This yields: 1. *barium sulfate*; 2. an *aqueous liquid*; 3° *free isovaleric acid* which floats on top of the aqueous liquid. The latter is collected with a pipette. By adding 33.4 parts of water to the residue, a further amount of *free isovaleric acid* is obtained; this is also drawn off and added to the other amount. After this treatment, the addition of 33.4 parts of water containing 13 parts of sulfuric acid with a density of 66 degrees to the contents of tube liberates no further *free isovaleric acid*. However, if the aqueous liquid is then neutralized by baryta water, some isovalerate of this base remains in the liquid and this displays all the properties we have observed in this salt.

635. *Free isovaleric acid* is normally colored slightly yellow. It has a density of 0.946 (g/mL) at 28°C. Gentle distillation on a sand bath yields a colorless *liquid product* A that separates into two layers, and a *thick, reddish brown material* B.

A. Liquid product

636. The layer with the lowest density is free isovaleric acid with a density of 0.932 (g/mL) at 28°C. The bottom layer is very small in comparison with the former; it is certainly an aqueous solution of isovaleric acid. It has a higher vapor pressure than the free acid. When left in contact with the latter, it disappears by dissolution. If this solution is distilled from twice its weight of calcium chloride on a water bath and the distillate is collected in separate portions, each portion will be found to have a density of 0.932 (g/mL) at 28°C. It does not precipitate silver nitrate.

B. Thick, reddish brown material

637. This residue contains a brown bituminous oil and an acid liquid that does not yield a precipitate when neutralized by baryta water. But when it is evaporated to dryness and the residue is calcined in a tube, it leaves some barium carbonate mixed with a small amount of sulfide. This experiment demonstrates that if there is any sulfuric acid present in of isovaleric acid (635), it is only an extremely small amount.

ARTICLE 2

PREPARATION OF THE ACIDS PRESENT IN BUTTER

638. The barium salts formed by the acids present in butterfat should be dried and treated as follows (628):

(A) Mix 100 parts of barium salts with 277 parts of water at ambient temperature. After twenty-four hours of maceration, a *first solution* is decanted. By evaporating an aliquot of known weight and weighing the residue, the salt content of this solution can be determined. Having thus determined the proportion of salt to water, the weight of the salt that the 277 parts of water have dissolved can easily be calculated. Subtracting this weight from the 100 parts of salt gives the amount of undissolved material, which I will call the *first residue*.

(B) The *first residue* is mixed with water in the same proportion as that in the *first solution* and after a maceration of twenty-four hours, a *second solution* is decanted and 1. its salt-to-water ratio and 2. the weight of the undissolved material which I will call the *second residue* are determined.

(C) By treating the *second residue* in the same way as the first one, a *third solution* is obtained together with a *third residue* that is also subjected to the same treatment as the first and the second residues. This procedure is repeated until no further residues are left[48] except for some barium carbonate that will be formed during the operations I have just described when carbon dioxide from the air and the water reacts with part of the barium salts.

639. By allowing the solutions to crystallize spontaneously[49], a considerable number of different crops of crystals is obtained which comprise eight main species, including the four crops that pertain to barium butyrate, caprate and caproate[50] and which I have described in the sections dealing with those salts (Book II). But before describing those first crystal crops, I think that I should return to the four last ones and describe the experiments that made me conclude that they belong to definite species, whereas the other crops represent undefined combinations or mixtures of two or more salt species[51].

FIRST CROP OF CRYSTALS

BARIUM BUTYRATE

640. It is not possible to isolate different materials from barium butyrate by crystallization. These are the experimental conditions I used.

641. An amount of 20.4 g of powdered barium butyrate, which would have required 57.7 g of water to dissolve at 20 to 25°C, is mixed with 9.45 g of water in a stoppered flask. After twenty-four hours, the materials formed a paste and since they could not be filtered in this state, 9.45 g of water were added and after a further twenty-four hours, the mixture was filtered.

1st *solution,* consisting of:

Water	100
Salt	36.05

The residue left on the filter was allowed to drain and then washed with 9.45 g of water; both the washing water and the first solution were left to evaporate spontaneously.

The residue was mixed with 9.45 g of water and filtered twenty-four hours later.

2nd *solution,* consisting of:

Water	100
Salt	36.05

The residue left on the filter was allowed to drain and then washed with 9.45 g of water; both the washing water and the second solution were left to evaporate spontaneously.

The residue was mixed with 9.45 g of water and filtered after twenty-four hours.

3rd *solution,* consisting of:

Water	100
Salt	35.2

The residue left on the filter dissolved in the 9.45 g of water that had been poured on to it to wash it[52].

Because I have not been able to note any difference between the crops of crystals obtained from the spontaneous evaporation of the four solutions at a temperature in the range of 20 to 25°C nor between the crops resulting from washing the residues, I have concluded that water does not split the barium butyrate into different compounds[53].

642. The following experiments were also carried out: 13 g of the barium butyrate that had been dissolved in the first step and 5.8 g of the barium butyrate dissolved in the second step were combined and treated as described in (641). The following results were obtained:

A. Butyrate dissolved in the first step

An amount of 13 g mixed with 12 g of water at 21°C gave a *first solution*:

Water	100
Salt	36.34

The *1st residue* mixed with 6 g of water at 26°C yielded a *2nd solution:*

Water	100
Salt	36.61

The *2nd residue* mixed with 6 g of water at 26°C yielded a *3rd solution:*

Water	100
Salt	36.2

The *3rd residue* mixed with 6 g of water at 26°C yielded a *4th solution*:

Water	100
Salt	36

Finally, all these solutions crystallized in the same way.

B. Butyrate dissolved in the second step

Then 5.8 g mixed with 5.32 g of water at 26°C yielded a *1st solution*:

Water	100
Salt	36

The *1st residue* mixed with 5.32 g of water at 27°C yielded a *2nd solution*:

Water	100
Salt	36.51

The *2nd residue* mixed with 5.32 g of water at 22°C dissolved entirely. Consequently, we do not know if the solution was saturated. It consisted of:

Water	100
Salt	28

All solutions crystallized more or less in the same manner as the butyrate solutions *A*.

Calcium butyrate treated with water

643. When calcium butyrate is treated with water at a temperature of 15°C, it is not split into different types of salt, as demonstrated by the following experiments[54].

5 g of this salt mixed with 8 g of water yielded a *1st solution:*

Water	100
Salt	17.58[55]

The *1st residue* mixed with 8 g of water yielded a *2nd solution*:

Water	100
Salt	17.64

The *2nd residue* mixed with 4 g of water yielded a *3rd solution*[56]:

Water	100
Salt	17.64

When the *3rd residue* was dissolved in a sufficient amount of water, its solution yielded crystals that were exactly like those of the previous three.

Strontium butyrate treated with water

644. When strontium butyrate was treated with water in the same way as barium and calcium butyrate, it gave the same results.

SECOND CROP OF CRYSTALS

BARIUM CAPRATE

Barium caprate treated with water

645. An amount of 2.718 g of this salt was reduced to a fine powder and mixed with 75 g of distilled water in a closed bottle that was shaken from time to time; the temperature was 25°C. After forty-eight hours, the water, referred to as the *1st solution,* was decanted and allowed to evaporate spontaneously. The residue was treated with 75 g of water, yielding

a 2nd *solution* and a 2nd *residue* that was again treated with 75 g of water, and so on. The solutions consisted of:

	1st solution	2nd solution	3rd solution	4th solution	5th solution	6th solution
Water	100	100	100	100	100	100
Salt	0.54	0.56	0.56	0.50	0.50	0.30

646. I feared that the *6th solution* had not had enough time to become saturated because there was only a small amount of the salt residue left and it consisted of the largest particles of the salt used in the experiment which meant that the particles had a relatively smaller surface area than those in the first solutions. I therefore evaporated the 6th solution to dryness and reduced the resulting solids to a fine powder. I did the same with the *6th salt residue* and mixed everything with water. This time, I obtained a solution consisting of:

Water……………………………………………..	100
salt………………………………………………..	0.65[57]

All the solutions that were allowed to evaporate spontaneously yielded only crystals of caprate.

Strontium caprate treated with water

647. When strontium caprate was treated in the same way as barium caprate, it gave the same results.

THIRD AND FOURTH CROPS OF CRYSTALS

FLAKES AND NEEDLES OF BARIUM CAPROATE

Barium caproate treated with water

648. An amount of 11.7 g of powdered barium caproate was mixed with 24.36 g of water in a closed flask. The materials were left in a place where the temperature was between 20 and 23°C. After twenty-four hours, they were filtered and the filter cake was washed with 12.18[58] g of water. This treatment resulted in a *1st solution*, a *1st washing liquor* and a *1st residue.* The latter was treated with 24.36 g of water, yielding a *2nd solution,* a *2nd washing liquor* obtained in the same way as the previous one by using 12.18 g of water, and a *2nd residue* that was subjected to the same treatments as the first, and so on. The solutions consisted of:

	1st solution	2nd solution	3rd solution	4th solution after three days
Water…	100	100	100	100
Salt……	8.1	7.88	7.24	7.58

649. When I noted that the *4th residue* was in the form of flakes, this made me think that if the last three solutions contained less salt than the

first, this could be because the particles of the material to be dissolved were not sufficiently fine. Consequently, I reduced the *4th residue* to a powder that was as fine as possible, which was quite difficult because of the flexibility of the caproate crystals. When 1.4 g of this powder was mixed with 10 g of water and kept at 21°C for eight days, it gave a solution consisting of:

Water	100
Salt	8.10[59]

650. The residue was mixed with 7 g of water and after forty-eight hours, a liquid was decanted consisting of:

Water	100
Salt	7.2

The amount that had not dissolved was negligible.

651. After spontaneous evaporation, all the solutions and washing liquors yielded absolutely identical crystals with respect to shape, appearance and indeed all physical properties.

Calcium caproate treated with water

652. Treating calcium caproate with water at a temperature of 14°C does not split it into different types of salt, as shown by the following experiments:

3 g mixed with 13 g of water yielded a *1st solution*:

Water	100
Salt	2.04[60]

Mixing the *1st residue* with 25 g of water yielded a *2nd solution*:

Water	100
Salt	2.04

Mixing the *2nd residue* with 25 g of water yielded a *3rd solution*:

Water	100
Salt	1.99

Mixing the *3rd residue* with 25 g of water yielded a *4th solution*:

Water	100
Salt	1.99

Mixing the *4th residue* with 25 g of water yielded a *5th solution*:

Water	100
Salt	1.94

The *5th residue* was dissolved in just sufficient water. This concentrated solution gave crystals exactly like those from the previous five solutions. The mother liquor of those crystals consisted of:

Water	100
Salt	2

FIFTH CROP OF CRYSTALS

653. These crystals are in the form of small flakes agglomerated in the shape of cockscombs or spheroids. These crystals remain transparent when exposed to air and even in a dry vacuum. Under the latter circumstances, they do not lose any water. For 100 parts of 'dry' acid, they contain 95 parts of barium oxide[61]. Their aroma is not as strong as that of barium butyrate, which makes them smell even more like fresh butter. 100 parts of water at 10.5°C dissolve 37.55 parts of crystals. At that temperature, I was not able to split them into different types of crystals. The only indication that made me suspect that they are made up of several kinds of salts is that when I examined them closely, I observed among them a few groups of crystals that were opaque white, like enamel.

654. I dissolved them in water. On spontaneous evaporation at an ambient temperature of 25 to 32°C, the solution yielded crystals that I separated from the mother liquor. By redissolving those crystals in water and allowing this mother liquor to crystallize, I split the *5th crop of crystals* into:

1° *Enamel white crystals which appear to be impasted*
They will be discussed under *7th crop of crystals*
2° *Transparent needles*
They will be discussed under *6th crop of crystals*

Comment

655. When the aqueous liquid containing the acids from butterfat (602) has been distilled only once, it always contains a significant amount of glycerin and acid potassium tartrate or phosphate, which was *projected* from the retort into the recipient when the liquid boiled. If the distillation product is then saturated with baryta water, the tartaric or phosphoric acid is precipitated by part of this baryta, and the potassium in these acid salts then attaches itself to part of the acids from the butterfat. Consequently, the crystallization of the liquor containing the barium salts yields mother liquors that contain much more salt than the liquors that produced the *6th crop of crystals*. The first kind of mother liquor comes in

two types: one is a liquor that sets as a mass and consists mainly of barium butyrate, potassium butyrate and potassium caproate. The other type does not crystallize when exposed to air and consists mainly of potassium butyrate and glycerin. If these liquors contain caprate, it is only in very small amounts.

SIXTH CROP OF CRYSTALS

656. The *transparent needles* were split into:

1° *Barium butyrate* crystallized in long prisms. This salt was very abundant and was purified by recrystallization.

2° A mother liquor that was evaporated to form *fine, transparent needles* and *octahedra.* The latter were present in very small amounts since 150 parts of salt derived from butter yielded barely 1 part of octahedral crystals.

A. Fine, transparent needles

657. When 100 parts of these needles were decomposed by sulfuric acid, they yielded 72 parts of sulfated residue. 100 parts of barium butyrate yielded 75.2 parts[62].

658. These needles were treated with an equal weight of water to produce the *1st solution,* consisting of:

Water…………………………………………	100
Salt……………………………………………	37.45

It yielded *fine needles* and *octahedra.*

The residue was treated with the same amount of water as used for the *1st solution.*

2nd solution consisting of:

Water…………………………………………	100
Salt……………………………………………	36.5

It yielded *fine transparent needles* that were quite similar to those that had been treated.

The *2nd residue* was dissolved in just sufficient water and the solution yielded *barium butyrate* crystallized in elongated prisms.

It follows from these experiments that the *fine transparent needles* consisted of *barium butyrate* and *octahedral crystals.*

B. Octahedral crystals

659. The water that had remained on an excess of octahedral crystals at a temperature of 18°C formed a solution consisting of:

Water…………………………………………	100
Salt……………………………………………	26.1

660. When 100 parts of these crystals were decomposed by sulfuric acid, they gave 68[63] parts of sulfated residue. Given this result and the buttery aroma of the crystals that was just as strong as that of pure butyrate, I suspected that they could have been formed by two butyrates and this was confirmed by analysis and synthesis: 1. analysis of the crystals identified barium and calcium; 2. by dissolving 2 parts of calcium butyrate and 3 parts of barium butyrate in water, I obtained beautiful octahedral crystals after spontaneous evaporation.

661. The calcium butyrate found in the barium salts from butterfat originated from the reaction of the calcium carbonate in the filter paper with the barium butyrate.

SEVENTH CROP OF CRYSTALS

662. Since this crop comprises at least three species of salt, present in very varied proportions, the crystals that we retrieve differ from each other by their physical properties and their solubility in water. Their aroma is more or less butyric but always less pronounced than that of the previous crystals (656). Their shape is very difficult to describe. However, in general they appear as small needles or opaque flakes, which appear to be embedded in a material the color of white enamel. I split them into *caproate* and *caprate* crystals like those of the *5th crop of crystals*, but the latter was always present as a small fraction. I always started by treating them with twice their weight of water and the residue was also treated with twice its weight of water. As soon as a difference in crystal shape could be discerned in the crystals that were formed from a liquor, the mother liquor was decanted and allowed to crystallize separately.

663. Applying this treatment to:

1. S*ample* A of the 7th crystallization yielded solutions consisting of:

	1st solution	2nd solution	3rd solution
Water……………………	100	100	100
Salt………………………	38.30	31.75	19

2. *Sample* B of the 7th crystallization yielded solutions consisting of:

	1st solution	2nd solution	3rd solution
Water……………………	100	100	100
Salt………………………	35.32	19	17

3. S*ample* C of the 7th crystallization yielded a solution consisting of:

	1st solution	2nd solution	3rd solution
Water………………..…	100	100	100
Salt…………………….	16.96	9.28	8.28

What was left was a mixture of barium caproate and barium caprate.

EIGHTH CROP OF CRYSTALS

664. The crystals were in the form of flakes of varying thicknesses, always opaque and smelling not like butter but like sweat. Some samples also gave off an aroma of billy goat. The flakes were sometimes agglomerated into a cauliflower-shaped configuration[64].

665. 100 parts of the salt were mixed with 500 parts of water at 23°C and left for twenty-four hours.

Treatment of sample *A*

1st solution:

Water……………………………………………	100
Salt………………………………………………	8.29

The *1st residue* was mixed with 500 parts of water and left for twenty-four hours.

2nd solution:

Water……………………………………………	100
Salt………………………………………………	7.41

The 2nd residue was mixed with 290.5 parts of water.

3rd solution:

Water……………………………………………	100
Salt………………………………………………	2.67

The 3rd residue, which weighed 13.8[65] parts, required more than 517[66] parts of water to dissolve.

The first two solutions were evaporated spontaneously at a temperature of 23°C and yielded: 1. *small flaky crystals* that I split into caproate and caprate and 2. *caproate.*

The 3rd solution yielded: *small flaky crystals* that I split into: 1. *caprate* and 2. *small flakes* made up of caprate and caproate.

The 4th solution yielded: 1° *small flaky crystals* similar to those from the 3rd solution, and 2. *caprate.*

Treatment of sample *B* in a cauliflower configuration

666. 100 parts were mixed with 800 parts of water at 10°C. The first residue was mixed with water in the same the proportion as used in the 1st solution, and so on.

	1st solution	2nd solution	3rd solution	4th solution	5th solution
Water………	100	100	100	100	100
Salt…………	7.76	4.44	0.7	0.5	0.4

The 1st solution yielded almost pure caproate and the last three solutions yielded almost pure caprate.

The 2nd solution yielded small flakes consisting of caproate and caprate.

Treatment of sample *C* in a cauliflower configuration

When 100 parts were treated like sample B, they gave:

	1st solution	2nd solution	3rd solution	4th solution	5th solution	6th solution
Water…	100	100	100	100	100	100
Salt……	8.54	6.1	3.3	1	0.65	0.5

PREPARATION OF BUTYRIC ACID

First method

667. 100 parts of barium butyrate are placed in a glass tube that is sealed at one end, together with 135 parts of phosphoric acid with a density of 1.12[67] (g/mL) that are added gradually: *oily butyric acid* separated out and finally dissolved. When 12 parts of phosphoric acid with a density of 1.66[68] (g/mL) were added, some oily acid separated out immediately. This was decanted and a further 59 parts of phosphoric acid with a density of 1.12 (g/mL) were added; more *oily acid* then separated and this was added to the first.

668. When the aqueous liquid is diluted with water and subsequently neutralized with baryta water, filtered and evaporated, it gives a salt that has all the typical properties of barium butyrate. It smells like butter and crystallizes in long prisms.

669. The *oily acid* has a density of 1.0007 (g/mL) at 18°C[*]; it is nearly always colored slightly yellow and it solidifies between 7 and 8°C[69] below zero to form a white material. It dissolves in water in all proportions and a solution of 1 part butyric acid and ½ part of water has a density of 1.018[70] (g/mL). It dissolves in alcohol with a density of 0.794[71] (g/mL) while precipitating a small amount of acid barium phosphate[72].

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[*] A flask that could hold 7.032 g water, held 7.037 g of the acid.

670. When the oily acid was distilled on a water bath, it yielded a *first distillate.* When it was then distilled on a sand bath, it yielded a *second distillate*. The residue was black and contained barium superphosphate[73].

First product

671. At 17°C, its density was 1.0055 (g/mL), which clearly shows that the first fractions of the butyric acid distillate contain more water than later ones.

4 g of this acid was mixed with 17.5 g of calcium chloride and heated. After sixteen hours, a product with a density of 0.979 (g/mL)[74] was obtained by distillation on a water bath.

Second product

672. At 17°C, its density was 0.977 (g/mL).

When distilled from 3 times its weight of calcium chloride on a water bath, a product was obtained with a density of 0.968 (g/mL).

Second method

673. 100 parts of barium butyrate were placed in a glass tube that had been sealed at one end together with 63.36[*] parts of sulfuric acid that had a strength of 66 degrees before being diluted with 63.36 parts of water. This yielded a clear acid liquid, which was decanted. When a further 63.5 parts of water were added to the residue, no more acid liquid separated out, nor did it after the addition of 63.5 parts of sulfuric acid.

674. The barium sulfate formed a whitish paste with the water that did not participate in the formation of the free butyric acid, and also with the sulfuric acid that had not yet become part of the barium sulfate. When this was diluted with water and then neutralized with baryta water, a solution of barium butyrate resulted, the acid of which had been dissolved in the sulfuric acid. This butyrate displayed all the properties that we have determined for this salt.

675. Butyric acid is clear and virtually colorless. Its density at 5°C is 0.976[†] (g/mL). It does not form a precipitate with barium nitrate.

676. Gentle distillation on a sand bath while in contact with air yielded 1. *an acid* that was perfectly clear and colorless and had a density of 0.968 (g/mL) at 10°C, and 2. a brown *residue* containing pure butyric acid and butyric acid that had altered and turned brown. Baryta water dissolved the pure acid and a small amount of the altered acid. It left colored flakes, an aliquot of which was insoluble in nitric acid. It did not contain sulfuric acid.

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[*] This amount is twice the amount needed to neutralize the barium oxide present in the butyrate and this excess is necessary to obtain the maximum amount of free butyric acid.

[†] I have also obtained material with a density of 0.971 (g/mL) at 28°C.

677. Butyric acid with a density of 0.968 (g/mL) was distilled on a water bath from its own weight of calcium chloride after it had been in contact with the latter for three days. This yielded a product with a density of 0.9675 (g/mL) at 10°C.

PREPARATION OF CAPROIC ACID

678. 100 parts of barium caproate are placed in a glass tube that has been closed at one end with 29.63 parts of 66 degree sulfuric acid that had previously been diluted with 29.63 parts of water. After twenty-four hours, a clear acid liquid is decanted; this is free caproic acid. By adding 29.63 parts of sulfuric acid diluted with 29.63 parts of water, a further small amount of caproic acid is obtained and added to the first amount. All together, the material obtained amounts to almost 50 parts[75].

679. The barium sulfate forms a whitish paste with water and an excess of sulfuric acid. By diluting it with water and subsequent neutralization with baryta water, a salt is obtained that is similar to the one that has been decomposed.

680. Caproic acid is clear and virtually colorless. At 23°C, its density is 0.928[76] (m/gL) since a small flask with a capacity of 6.287 g of water contains 5.838 g caproic acid.

681. The acid does not contain sulfuric acid. If it is distilled on its own and placed it in a small retort with its own weight of calcium chloride for forty-eight hours and then distilled on a water bath, a first product is obtained that has a density of 0.923 (g/mL) at 26°C.

PREPARATION OF CAPRIC ACID

First method

682. By placing 2.60 g of barium caprate in a tube that is closed at one end together with 2.06 g of vitreous phosphoric acid[77] dissolved in 8 g of water, free capric acid was obtained in its oily state.

683. This acid is colorless. At 12°C, its density was 0.915[78] (g/mL) and it solidified at 11.5°C.

684. When 120 mg were heated with lead oxide, the water loss was 10 mg[79].

685. When the free acid was heated in a small retort on a water bath for fifteen hours, it seemed to lose only acidified water and the residue had

all the properties of free capric acid as ascertained by allowing it to react with baryta water.

Second method

686. In a closed tube, 2.95 g of barium caprate was decomposed by 1.40 g of concentrated sulfuric acid that had been diluted with 1.40 g of water.

687. The free acid obtained in this way had the properties described in Book II, Chapter 7, Section 1[80].

688. After the aqueous liquid from which the acid had been separated had been diluted with water and neutralized with baryta water to precipitate the sulfuric acid, spontaneous evaporation yielded barium caprate.

PREPARATION OF HIRCIC ACID

689. Potassium soap made from mutton tallow is decomposed with tartaric or phosphoric acid. The aqueous liquid is distilled and the hircic acid volatilizes with the water. After having obtained a liquid that is free from potassium salts that could have been carried over mechanically into the recipient (655), it is neutralized with baryta water. The liquid is evaporated to dryness and the barium salt of hircic acid is decomposed by sulfuric acid diluted with its own weight of water.

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[1] The immediate principles referred to are the various fatty acids and according to the author, the only fatty acid present in pure stearin was stearic acid, just as the only fatty acid in pure butyrin was butyric acid. According to this theory, pure stearic acid could be prepared either by saponifying pure stearin, or by saponifying any fat containing stearic acid and isolating stearic acid from the soaps. The author does not mention why he prefers the latter route but it could well be that he prefers purifying fatty acids to purifying fats.

[2] The actual set-up is not explained in detail and therefore difficult to envisage. The purpose is to prevent the molten fat from solidifying.

[3] This is what a modern rendering plant also does.

[4] The author does not indicate whether or not he remelts the solidified material before washing it with water. Doing so would certainly increase the efficiency of the water washing operation.

[5] Nowadays, we would use a separating funnel for this operation. It has a stopper, can be shaken and permits decantation and removal of the bottom layer. They had apparently not yet been invented at the time of writing.

[6] The author only describes a single fatty acid that is both liquid and insoluble in water and he call this ‘oleic acid’. His samples will also contain linoleic acid etc.

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[7] When adding caustic potash to a potassium soap, the potassium equivalent exceeds the fatty acid equivalent. Nevertheless, the author reports a deposit of potassium bipalmitate in which the fatty acid equivalent exceeds the potassium equivalent. Perhaps this can be explained by the fact that potassium hydroxide is a strong base and fatty acids are weak acids. Even when there is an excess of potassium cations over fatty acid moieties, a large proportion of the acid moieties will not be dissociated especially when the solution has been diluted. Accordingly, it is not unthinkable that bipalmitate, a combination of potassium soap and free fatty acid, will be deposited. See also subsections (147) where the bipalmitate was obtained by treating the neutral potassium palmitate with water.

[8] See endnote 5, page 62.

[9] The decomposition of potassium palmitate yields potassium bipalmitate and potassium hydroxide.

[10] This liquid is oleic acid and the treatment presumably involves the neutralization of the acid and the formation of a deposit comprising palmitic acid moieties.

[11] This density corresponds to an alcohol content of 91.0 % by weight.

[12] Here the author describes the purification of potassium palmitate that contains some oleate by recrystallization from alcohol whereby hopefully, the potassium oleate remains in solution.

[13] The solution may well have become aqueous since the acid used to acidulate the soaps was dissolved in water and alcohol disappeared by evaporation.

[14] Silver nitrate is used to indicate the presence of chloride anions. When no more silver chloride is precipitated, all chloride anions can be assumed to have been washed out.

[15] The text mentions ‘sous-carbonate de chaux”. According to Mathieu J.B.P. Orfila, *Leçons de Chimie Appliquée à la Médecine Pratique et à la Médecine Légale*, 1830, page 192, this salt is what is found in marble so it is calcium carbonate. A few pages earlier, he also mentions ‘carbonate de chaux’, which is presumably calcium bicarbonate.

[16] Nowadays, this treatment would be called “multi-stage fractionation”.

[17] Treating the paper this way removes any calcium salts and thus avoids the formation of any calcium soaps.

[18] The only reason it contains caustic potash (potassium hydroxide) is because fatty acids are weak acids. In soaps, the fatty acids are present as anions and the potassium as cation. When water is added, the oleic acid anions are protonated under formation of a residual hydroxyl anion. This gives the resulting aqueous solution a ‘soapy’ taste, indicative of its alkalinity. So a potassium oleate soap solution contains the following species: water, non-dissociated oleic acid, dissociated oleic acid anions, hydroxyl anions, potassium cations and a negligible amount of hydrogen cations. Macroscopically, this composition can be described as: water, free oleic acid, potassium oleate and potassium hydroxide.

[19] The original mentions “force the solidité” which could be interpreted as the specific latent heat of crystallisation but the term “affinity force” is more in line with thinking at the time, when energy was a notion that was very much open to interpretation; this

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remark also holds for notions like power, affinity and forces referred to in the same paragraph.

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

[21] Since human fat also contains stearic acid moieties. According to literature quoted by Boekenoogen (D.L. Cramer and J.B. Brown, *J. Biol. Chem.* **151**, p. 427, 1943), human fat contains small amounts of lauric and myristic acid, 24.0-25.7% palmitic acid and 5.2-8.4% stearic acid. More recent literature like *The Lipid Handbook* does not mention the composition of human fat but only that of human milk fat. Human fat soap will therefore contain potassium stearate and the method described does not attain a separation.

[22] First of all, the author arrives at a rough separation between saturated and unsaturated fatty acids by making use of their difference in solubility in alcohol at ambient temperature. Then the saturated fatty acids are purified by repeated recrystallization.

[23] Using melting point as a criterion of purity is something that may well have been introduced by the author; it is still used today.

[24] Here the solubility in cold alcohol is what is important. If the alcohol were not cold, some palmitic acid would also dissolve and the oleic acid would be less pure.

[25] Again the author makes clever use of the difference in solubility of the various compounds he wants to separate from each other.

[26] The author was the first to discover stearic acid and palmitic acid. Consequently, he had to make sure that these acids were indeed different compounds and that they were not mixtures. Hence the attempts to split them into different fatty acids.

[27] Of course, the reason why fatty acids turn rancid was not known. Even the concept of unsaturated fatty acids was not known. All acids were probably presumed to be equally likely to turn rancid and care had to be taken with each of them.

[28] The French word 'potasse' continues to pose translation problems. It derives from the Dutch word 'potas', meaning the ashes that are left when wood has been burned. Accordingly, 'potasse' can mean potash (potassium carbonate) but it also denotes the element potassium and even potassium hydroxide. Sometimes, the author makes it clear that he means the hydroxide by talking about 'caustic potash', but not always.

[29] This corresponds to a strength of 92.5 % by weight.

[30] The value of 60°C is what the author determined for palmitic acid.

[31] The text says: "sous-carbonate de potasse". This is potassium carbonate since it contains less carbon dioxide per potassium atom than potassium bicarbonate, which the author refers to as 'carbonate de soude'.

[32] Hematin is the bluish black compound derived from hemoglobin by removal of the protein part and oxidation of the iron. According to Kolbe (*Ausführliches Lehrbuch der Organischen Chemie,* Vol IIIb) it is insoluble in water, alcohol and ether but readily soluble in aqueous and tartaric alkali and in ammonia. Consequently, hematin is a useful reagent to make sure that the barium hydroxide is still effective as a base and has not yet been inactivated by reacting with carbon dioxide.

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[33] Although the Oxford English Dictionary does not explain this word, an old (1913) Webster does: To deprive of superabundant water, as by evaporation or distillation; to clear of aqueous matter; to rectify; used of spirits and acids.

[34] According to the CRC *Handbook of Physics & Chemistry*, 75th edition (1994), the solubility of lead oxide in water at 22°C is only 0.0032 (g/100 cc); in hot water, it is simply insoluble.

[35] This is the principle of steam distillation, which the author has used quite regularly.

[36] See endnote 11 on page 131.

[37] Crystalline barium hydroxide may well have 8 molecules water of crystallization.

[38] The text mentions 'hydrated' acid, meaning the free acid which will liberate water when reacting with a base such as lead oxide.

[39] The author does not explain why he decided to use this particular amount.

[40] This corresponds to a strength of 21 % by weight.

[41] The *Handbook of Physics & Chemistry* gives a density of 0.931 (g/mL) at 20°C for isovaleric acid.

[42] The calcium chloride has been used to dry the upper layer since the lower layer was an aqueous solution of isovaleric acid (632).

[43] The boiling point of isovaleric acid is 176.5°C so it is certainly less volatile than the water in the dense layer. Given this boiling point, the acid will not have boiled when heated on a water bath. Presumably, distilled acid was collected in accordance with James Watt's principle stating that in a confined space, a volatile compound will condense at the coldest spot. Then this distillation of isovaleric acid must have taken a long time.

[44] According to the endnote 40, this is spot on.

[45] So there was no chloride from the calcium chloride present.

[46] If these degrees are Bé (degree Baumé), the specific volume v can be calculated according to: Bé = 144.3 (1 – v). So 66 Bé correspond to a specific volume of 0.543 (mL/g) or a density of 1.843 (g/mL), which corresponds to highly concentrated acid. An amount of 100 g of barium isovalerate (MW = 137 + 2 x 101 = 339) corresponds to 0.295 mol. If the acid is assumed to have a strength of 95%, 33.4 g corresponds to (33.4 x 0.95) : 98 = 0.324 mol, or a slight excess.

[47] Again, the author does not explain why he chose these amounts and this strength.

[48] Since the author determined the solubility of the residue by evaporating an aliquot of known weight to dryness and weighing the evaporation residue, he could have calculated how much water to add to dissolve the entire first residue.

[49] It is not quite clear what is meant by spontaneous crystallization. The author does not mention that he heated the liquid to encourage dissolution so it seems that crystallization does not result from the solution cooling down. Perhaps it is just evaporation of the solvent when the solution is set aside that causes it to crystallize.

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[50] The author lists only three and not in the right order.

[51] This is true chemistry: distinguishing between a true compound and a mixture of different compounds. It also illustrates why in Dutch, chemistry is called "scheikunde" which can be literally translated as 'the art of separating'.

[52] By this time, the total amount of water the barium butyrate had been in contact with was 6 x 9.45 = 56.7 g, which is close to the 57.7 g mentioned as the amount of water required to dissolve all of it. It is therefore not surprising that the last amount of water added caused what was left to dissolve.

[53] Moreover, the author reports that all solutions show the same solute concentration, which also points to the fact that they contain identical solutes.

[54] Nowadays, authors would have summarized the outcome of the whole series of experiments in a single table and if they had not done so, they would have been urged by their editor to do so.

[55] Apparently, calcium butyrate is less soluble than barium butyrate, which is remarkable since calcium sulfate is somewhat less insoluble than barium sulfate.

[56] The solubility of calcium butyrate is apparently some 17.5 g per 100 g of water. By expressing the composition of the solution per 100 g solvent, it is easy to compare them.

[57] The value of 0.65 is higher than the values for the previous solutions. This raises the question of whether finer grinding of the material would have raised those values.

[58] Here the amount of water used to wash the filter cake is half the amount used for the extraction of the filter cake. No reason for this method is given.

[59] The value of 8.1 should therefore be regarded as the actual solubility of barium caproate.

[60] Again the calcium soap is less soluble than the barium soap.

[61] Assuming the barium salt has the following formula: $BaO(CH_3(CH_2)_nCO)_2O$, the 'dry' acid will have a molecular weight of (100 : 95) x (137 + 16) = 161, which corresponds almost exactly to n = 2, or butyric acid.

[62] In theory, 100 parts barium butyrate (MW = 311) should give 74.9 parts of barium sulfate (M.W. = 233).

[63] This value of 68 parts of sulfated residue is far less than the 75 parts arrived at in the previous endnote for barium butyrate. For calcium butyrate, the sulfated residue would be 63.6 parts so a mixture of 2 parts of calcium butyrate and 3 parts of barium butyrate should lead to 70.4 parts of sulfated residue per 100 parts of butyrate mixture.

[64] This is a most illustrative comparison. Some β-tending fats, like soybean flakes, when solidifying from the melt, can also develop into a solid that is indeed most aptly described by likening it to a cauliflower.

[65] Since the 1st solution contained 8.29 parts of salt per 100 parts of water, the 500 parts of water used must have dissolved 41.5 parts of salt. The 2nd solution must have

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dissolved 37.5 parts of salt and the 3rd solution only 5.6 parts. Together they dissolved 84.6 parts leaving a 3rd residue of 15.4 parts in theory and 13.8 parts in practice.

[66] The solubility of the salt dissolved in the 3rd solution was 2.67 g per 100 g water. Since the 13.8 parts of the 3rd residue require >517 parts of water to dissolve it, it looks as if the salt in the 3rd solution is identical to that in the 3rd residue: (517 : 100) x 2.67 = 13.8.

[67] The acid will have contained about 35 % phosphoric acid by weight.

[68] This acid contains just over 80 % by weight phosphoric acid and should be compared with the 85 % by weight, which is nowadays a standard commercial grade.

[69] Nowadays, literature reports melting point of – 5.3°C for butyric acid so a congealing point of – 7 to – 8°C indicates a high purity.

[70] The reason why the author reports this density could well be that it is significantly higher than the weighted average of the two constituents.

[71] This is near absolute alcohol.

[72] Acid barium phosphate could be $BaHPO_4$ but another possibility is $Ba(H_2PO_4)_2$ or a mixture of both.

[73] Consulting the francophone pages in Google for "surphosphate de baryte" gives a single hit: the text being translated. However, calcium superphosphate is a well-known fertilizer ingredient. According to D.W. Dijkstra, *Scheikunde en Technologie Deel I*, Nijgh & Van Ditmar, Rotterdam, 1934, superphosphate is $Ca(H_2PO_4)_2$, a compound that is much more soluble in water than straight calcium phosphate $Ca_3(PO_4)_2$ from which the superphosphate is made by reaction with sulfuric acid. By analogy, the "surphosphate de baryte" might well be $Ba(H_2PO_4)_2$ but this is guesswork.

[74] According to *The Lipid Handbook*, 2nd edition, the density of butyric acid is 0.9853 (g/mL) when measured at 20°C.

[75] With a molecular weight of 116 for 'free' caproic acid and an atomic weight of 137 for barium, the molecular weight of barium caproate equals 351. Accordingly, 100 parts of barium caproate can in theory release (100 : 351) x 2 x 116 = 66, which is well above the less than 50 parts observed.

[76] The 2nd edition of *The Lipid Handbook* (1994) gives a value of 0.9276 (g/mL) at 20°C.

[77] According to Victor Regnault *Cours élémentaire de chimie,* page 305 (1854), vitreous phosphoric acid is not anhydrous phosphoric acid since it still contains 11.2 % of water. If we were to assume that the anhydrous phosphoric acid is P_2O_5 (MW = 142), adding one mol of water would lead to a water content of (18 x 100) : (142 + 18) = 11.25%. Accordingly, the vitreous phosphoric acid could have the formula HPO_3. Its modern name is metaphosphoric acid. It occurs as a transparent polymer $(HPO_3)_n$ on the phosphorus pentoxide used to dry the atmosphere within a desiccator.

[78] This value of 0.915 (g/mL) at 12°C is much closer to the density of caprylic acid (0.9105 (g/mL) at 20°C) than that of capric acid (0.8854 (g/mL) at 40°C).

[79] These figures lead to a relative molecular mass for the free acid of (120 : 10) x 18 = 216. This value is unduly high and even exceeds that of lauric acid (MW = 200). Presumably, some water got lost during the experiment.

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[80] The endnotes pertaining to this section provide further data supporting the likelihood that the acid named capric acid by the author is the acid that is now called caprylic acid. See also: A.J. Dijkstra, Which goat is which? *Inform*, **19** (4), 207-208 (2008).