

CHAPTER 6

CAN SAPONIFICATION BE ACHIEVED WITH POTASSIUM BICARBONATE AND AMMONIUM CARBONATE¹ ?

1056. After having considered saponification with respect to the nature of the bases that can form salts and the amount of fat that a given weight of alkali can saponify, it would be interesting to investigate whether alkalinity that is counterbalanced by the acidity of a weak acid such as carbonic acid still has the ability² to liberate the acid from a fat with which it is brought into contact.

§ 1. THE EFFECT OF POTASSIUM BICARBONATE ON LARD

1057. I took 30 g of lard with a melting point of 27°C and allowed it to react in boiling water containing 60 g of crystalline bicarbonate; most of the fat was saponified. The soap was then diluted with a large amount of warm water. The fat that had not been saponified gathered on the surface of the liquid; it was collected and treated again with 30 g of crystalline potassium bicarbonate. It saponified completely, except for one gram. This gram was isolated and finally saponified with 2 g of bicarbonate³.

1058. The soap solutions were combined; they were quite clear. When they were concentrated, no oily drops were formed on the surface of the liquid. At a certain degree of concentration, the soap was precipitated from the water by the action of the carbonated alkali. After cooling, the material was poured onto a filter. The filtrate caused a violent effervescence with tartaric acid but did not yield any fatty material to speak of. I therefore concluded that all the soap had remained on the filter. The liquor was saturated with tartaric acid and evaporated to dryness. When the residue was extracted with alcohol, it yielded a large amount of glycerin. The soap was collected from the filter and divided into two parts.

First part

1059. First of all, as much of the mother liquor as possible was removed by pressing between filter paper. Then the material was dissolved in boiling water and the resulting solution was poured into an excess of barium nitrate. The precipitate was collected and dried and on analysis, it showed constituent fatty acids⁴ melting at 36°C and barium oxide⁵. It did not contain any noticeable amount of carbonic acid⁶; *the soap produced by potassium bicarbonate is therefore the same as ordinary soap; consequently,*

in the experiment I have just described, the carbonic acid must have been eliminated from the potassium that combined with the constituent fatty acids.

1060. It was dissolved completely in boiling water. When the solution was left to stand, it yielded: 1. a pearly deposit consisting of *potassium bistearate* and *potassium bipalmitate*; 2. *potassium oleate*.

Second part

1061. When an aqueous solution of potassium bicarbonate was boiled, it was converted into carbonate, as I have ascertained. The saponification was therefore caused by this salt and not by the bicarbonate, because it was carried out in boiling water. It is very likely that it is the excess of potassium in the carbonate⁷ that determines the saponification and that, when this takes place, the carbon dioxide that was combined with the alkali that becomes attached to the soap moves back to part of the carbonate and becomes bicarbonate if the temperature allows this combination to be formed; or, if the temperature makes this impossible, this carbon dioxide is liberated as a gas.

1062. Having mixed lard with potassium carbonate that had previously been heated to a dull red in a platinum crucible⁸ and then dissolved in some boiling water, I observed that saponification took place without contact with air in a bell jar resting on mercury and placed between two heated ovens. I also observed that carbon dioxide was not released until after a large amount of soap had been formed and when the raw materials were exposed to a temperature that was sufficiently high to decompose the potassium bicarbonate. When fat was treated with an excess of a strong solution of potassium carbonate, beautiful crystals of potassium bicarbonate were obtained after some time. It was easy to separate them mechanically from the non-saponified fat and the soapy mass.

§ 2. THE EFFECT OF AMMONIUM CARBONATE ON LARD

1063. 35 g of lard with a melting point of 27°C mixed with sublimated ammonium carbonate were placed in a flask with a cork stopper. The material filled a third of the volume of the vessel. The flask was left in my laboratory in a place where the sun never shines and where the temperature varies between zero and 18°C. After five years, the flask was opened. In some places, the surface of the fat was yellow. The material was treated with amounts of water totalling some 2 liters. A white emulsion was obtained in which a large number of pearly flakes could be observed like those formed by potassium bistearate.

1064. One fifth of the emulsion was poured onto a filter; the *filtrate* was very slightly opalescent. When filtered again, it was perfectly clear; it contained a little acid oil dissolved in it, amongst other substances.

Because the filtration took a very long time, the remaining four fifths of the emulsion were placed in a long-necked flask that was heated on a water bath. The emulsion split into three liquid layers. The lower, aqueous layer was almost clear and the two other layers were oily. The lightest one had a citrine yellow color and the heavier one was orangey yellow. After they had been allowed to congeal, the lowest layer was collected, filtered and combined with the *filtrate* obtained from the first fifth of the emulsion. I will examine these liquids, which I will call the *aqueous liquid*. Next I will examine the fatty part of the emulsion, that is to say the two upper layers of the emulsion after it had been heated.

ARTICLE 1

EXAMINATION OF THE AQUEOUS LIQUID

1065. It was yellowish and strongly alkaline; on agitation, it foamed. Hydrochloric acid caused carbon dioxide to be released and produced a slight cloudiness and on separating, a little *orange colored acid oil*.

1066. When heated over a flame, ammonium bicarbonate was given off and droplets of an *orange colored acid oil* appeared on the surface of the liquid. After evaporation of the water, a *syrupy residue* was left that weighed almost 2 g. It was orange in color and acid; its taste was at first sweetish and then became very bitter and pungent. It was highly soluble in alcohol. Cold water dissolved 1.6 g of a *syrupy material* and left 0.2 g of *orange colored acid oil*.

A. Orange
colored acid oil

1067. This oil was still liquid at 3°C but it thickened after having been exposed to the air for a few days. It was insoluble in cold water and released only traces of coloring matter into boiling water. It was very soluble in alcohol; the alcoholic solution turned litmus tincture red and the red color turned blue again when mixed with water. It was soluble in very weak aqueous caustic potash and the resulting solution threw a deposit of pearly material and retained the *oleate* and an *orange coloring matter*. The *orange colored acid oil* is therefore a combination of *oleic acid*, *palmitic acid* and an *orange coloring principle*.

B. Syrupy
material

1068. It was yellow. Its taste, although bitter, was less so than that of the *syrupy residue*. It was noticeably sweeter. It consisted of *glycerin*, *oleic acid*, an *orange coloring principle*, *ammonia* and *water*, and, so it seemed to me, traces of an *acid* that forms a salt with barium hydroxide that is soluble in water and insoluble in alcohol. These are the experiments that led me to this conclusion: when I added a little sulfuric acid to the syrupy material, a small amount of *oleic acid* and *orange coloring principle* separated out. After filtration, the filtrate was boiled with an excess of baryta water; this caused the release of ammonia and the precipitation of *oleate* and an

orange coloring principle combined with baryta as well as a little barium sulfate and carbonate. The filtrate was evaporated to dryness and the residue treated with alcohol. White flakes that looked to me like a *barium salt* separated out. Then the alcohol was filtered and the filtrate evaporated; the residue was redissolved in water. By means of sulfuric acid, a little barium sulfate and orange principle were precipitated from this liquor. When that liquor was subsequently evaporated, it yielded a syrupy *glycerin* that had hardly any color or trace of bitterness in its taste. When this substance was treated with nitric acid, it produced a large amount of oxalic acid.

1069. I ascertained that the *combination of oleic acid and the orange principle* is the cause of the bitterness of the glycerin by taking the same colored acid, dissolving it in alcohol and mixing it with glycerin obtained from olive oil. By evaporating the solution, a syrupy residue was obtained which first tasted sweet but then became very bitter and sharp, just like the *syrupy residue* (1066); remarkably, cold water caused some colored oleic acid to separate. The combination of the oleic acid and the coloring principle has little or no taste when pure, probably because it does not dissolve in saliva.

ARTICLE 2

EXAMINATION OF THE FATTY PART OF THE EMULSION

1070. This material formed an emulsion with water because part of its mass was combined with ammonia. It seemed to congeal at 39°C but several degrees below this temperature it was still soft. By removing the ammonia, hydrochloric acid inhibited the formation of an emulsion with water and simply whitened the surface of the material. After having been melted, the material formed a single layer that started to congeal at 43°C and remained soft at several degrees lower⁹. When allowed to congeal slowly and without agitation, it did not present an uneven surface¹⁰ as lard does. It had the orange color of soft adipocere¹¹. It turned litmus dark red.

1071. The weight of the material, including the fatty material that had remained on the filter, came to slightly more than 32 g although some of it had been lost.

1072. 100 parts of fatty matter were treated with 750 parts of boiling alcohol with a density of 0.835¹² (g/mL). The solution was allowed to cool and the liquid was decanted together with the fatty material that had been dissolved and precipitated on cooling. I will now examine:

A. the fatty material that dissolved in the boiling alcohol; B. the fatty material that did not dissolve in the alcohol.

A. FATTY MATERIAL THAT DISSOLVED IN BOILING ALCOHOL

1073. The fatty material amounted to 62.5 parts after the alcohol had been removed. It was orange in color and started to congeal at 36°C but did not become hard until 28°C. It had all the characteristics of consisting of just free fatty acids because it colored litmus very red, released water when heated with lead oxide and with barium hydroxide it formed a soap from which alcohol did not extract a significant amount of neutral fatty matter, as demonstrated by the following experiments.

1074. The 62.5 parts were allowed to react with barium hydroxide. The resulting soapy mass was treated with warm alcohol.

1075. The material was not acid. When separated from the alcohol, it started to congeal at 53°C. It was orangey yellow. Hydrochloric acid split off the barium and released 37.5 parts of an orangey acidulated fat that melted at 35°C. When this fat was again neutralized by barium hydroxide and treated with slightly warm alcohol, it divided into two parts: a soluble part amounting to 28.75 parts of free fatty acids with a melting point of 30°C; an insoluble part amounting to 8.75 parts of free fatty acids with a melting point of 36.5°C. Both parts of free fatty acids dissolved completely in weak caustic potash.

1076. After elimination of the barium, it amounted to 25 parts. It melted at 37.5°C. On cooling, it crystallized as intertwined needles just like the free fatty acids from lard. It was almost white.

1077. The proof that all the acid fats were completely hydrolyzed is as follows. After combining these fats, 100 parts with a melting point of 33.5°C were mixed with 70 parts of caustic potash dissolved in water. This was heated for eight hours and when the soap was decomposed with hydrochloric acid, 98 parts of acidulated oil with a melting point of 33°C were obtained, together with an aqueous liquid that left a residue after evaporation from which alcohol extracted only 3 parts of soluble material which did not contain a significant amount of glycerin but only a small amount of potassium tartrate and potassium oleate; the acid in the oleate amounted to 0.1 part by weight as determined by treating the residue with very weak acetic acid which did not dissolve the oleic acid.

B. MATERIAL THAT DID NOT DISSOLVE IN BOILING ALCOHOL (1072)

1078. It amounted to 37.5 parts; it was white and melted at 31°C but it was still soft at a lower temperature. It was slightly acid when tested

A. Material dissolved by warm alcohol

B. Material not dissolved by warm alcohol

with litmus. It was treated with a barium hydroxide solution and then with boiling alcohol.

1079. This material amounted to 25 parts and melted at about 29°C. It contained 5 parts of fatty acids that were removed by treating it with hydrochloric acid and then with warm alcohol. The latter retained the fatty acids and allowed a deposit of a fat to separate out; after this fat had been dissolved several times in alcohol, it was perfectly free from fatty acids.

A. Material dissolved by alcohol

1080. After this material had been treated with hydrochloric acid to remove the barium, 12.5 parts of material were obtained from which alcohol removed 1 part of fatty acids. The neutral fat was combined with the previous sample and given the following treatment.

B. Material not dissolved in boiling alcohol

1081. The material was white and still smelled like lard. It melted at 31°C. When it solidified slowly and without agitation, it presented an uneven surface, like lard. It was not more soluble in alcohol than lard and the solution had no effect on litmus. Treating 2.1 g neutral fat with potassium hydroxide yielded 1.954 g of oleic and palmitic acid with a melting point of 44°C and a syrupy glycerin weighing 0.265 g. It was almost colorless and it tasted very sweet without a hint of bitterness.

Neutral material

1082. I cannot confidently state that oxygen from the atmosphere had no influence on the saponification by ammonium carbonate.

§ 3. EFFECT OF POTASSIUM AND SODIUM PYROBORATE ON LARD

1083. An amount of 30 g of potassium pyroborate¹³ was melted and then crystallized and exposed to the temperature of boiling water for a period of about fifty hours, together with some water and 10 g of lard. A large amount of unchanged fat solidified on the surface of the liquor on cooling and this was removed. More was recovered by concentrating the liquor. Finally, an almost clear liquid was obtained. When this was mixed with tartaric acid it yielded about 0.2 g of *fatty acids melting at about 34°C* that were slightly yellow and truly saponified. After this material had been dissolved in a small amount of warm aqueous potassium hydroxide, it separated out into a pearly material and potassium oleate on cooling.

1084. Borax gave the same results

* Because more olein than stearin was dissolved during the purification treatment with alcohol.

1085. It follows from the above that although the pyroborates of potassium and sodium can cause saponification, it is only very slight, probably because the boric acid, which cannot be precipitated or volatilized, resists the energy of the potassium and the sodium.

¹ As usual, is not immediately obvious which compounds are meant but Google helps. According to the *Traité de chimie élémentaire, Théorique et pratique* de Louis Jacques Thenard, 'sous-carbonate d'ammoniaque' is simply ammonium carbonate since it results from the combination of 50 volumes of carbon dioxide and 100 volumes of ammonia. 'Carbonate de potasse' is described as the residue resulting from burning wood. In sub-section (1061), the author mentions that when 'carbonate de potasse' is heated in boiling water, it is converted into a 'sous-carbonate de potasse'. Similarly, Ostwald (*Grundlinien der anorganischen Chemie*, third edition, Verlag von Theodor Steinkopf, Dresden und Leipzig, 1912, page 503) mentions in his sub-section (467) (Potassium bicarbonate) that when a solution of potassium bicarbonate is heated, bubbles are formed before the boiling point has been reached, and that these bubbles consist of carbon dioxide. Accordingly, the 'carbonate de potasse' can be safely assumed to be potassium bicarbonate, KHCO_3 .

² Again, the author uses words like 'force' and 'energy' that have precisely defined meanings today, which was not the case at the time the author was writing. Using these terms here would not give an accurate rendering of what he meant. Accordingly, some less well-defined terms have been chosen.

³ The unsaponifiable in lard is mainly cholesterol and is present in amounts of 3000 to 4000 mg/kg.

⁴ See endnote 5, Book IV, Chapter 1.

⁵ Just as the quantitative analytical data on soaps gave the acid anhydride and the metal oxide contents, the presence of a metal is also indicated by mentioning its oxide.

⁶ The mother liquor that was not removed by pressing would have contained carbonate. Accordingly, a small amount of carbonate ended up in the water used to boil the soaps. This soapy water was then mixed with a barium nitrate solution, causing precipitates of barium soaps and some barium carbonate to be formed. Apparently, the amount of barium carbonate was so small that on acidulation with sulfuric acid, no noticeable amount of carbon dioxide was liberated.

⁷ The excess of potassium in the carbonate is in comparison with the potassium content of the potassium bicarbonate.

⁸ This treatment provides further support for translating 'sous-carbonate de potasse' as 'potassium carbonate'.

⁹ Pure substances have a sharp melting point. If a substance remains rather soft on solidification, this may indicate that it has a melting range and is not a pure substance.

¹⁰ Fats that crystallize in the β -polymorph tend to form uneven surfaces. Solidified fully hydrogenated soybean oil can look like a cauliflower.

¹¹ See Book IV, Chapter 4, § 2.

¹² The density of 0.835 (g/mL) corresponds to an ethanol content of 85.3 % by weight or 89.7 % by volume.

¹³ The text refers to “sous-borate de potasse” and this term is used in the heading as well. Both Google hits state that “sous-borate de soude” is also known as borax and this compound ($\text{Na}_2\text{B}_4\text{O}_7$) is also referred to as sodium pyroborate, presumably because it can be made by heating the decahydrate. Accordingly, the “sous-borate de potasse” has been translated as potassium pyroborate.