PART TWO

SAPONIFICATION WITH RESPECT TO BASES THAT CAN FORM SALTS

CHAPTER 4

THE EFFECT ON LARD OF SEVERAL BASES THAT CAN FORM SALTS

1011. The fat used for the following experiments had all the properties we have recognized in lard; when a thermometer was immersed in lard that had been melted at 40°C, its reading dropped to 29°C and went up again to 31°C on agitation.

§ 1. THE EFFECT OF CAUSTIC SODA ON LARD

1012. An amount of 25 g of fat was saponified by 15 g of caustic soda. After saponification, the soap was acidulated with hydrochloric acid, which yielded 23.95 g of acidulated soaps[1]. When these acidulated soaps were melted at 50°C, they started to become very cloudy at 41°C but remained fluid until 39.37°C. They then congealed on agitation while the thermometer reading rose to 39.60°C. When treated with alcohol, they yielded a combination[2] of palmitic acid with stearic acid.

1013. In order to analyze the sodium soap made from lard, I saponified 100 g of lard with 60 g of pure caustic soda[3] dissolved in 100 g of water. I obtained a rather hard soap and a mother liquor containing glycerin and a trace of a red coloring principle.

1014. The soap was put in 26 L of water and exposed to a temperature of 25°C. It gradually swelled and changed into a fairly solid, gelatinous mass with a pearly appearance. I heated these materials until the water boiled and everything dissolved. On cooling, a semi-transparent, gelatinous material separated out from the liquid. It did not settle at the bottom of the flask, as does the pearly material of potassium soap. After a month, when it seemed to me that no more gelatinous material was being formed, I poured the liquor on a filter after having mixed it with water. When dry, the gelatinous material left on the paper turned into semi-transparent, yellowish white flakes that consisted of sodium bistearate and sodium bipalmitate mixed with a significant amount of neutral sodium stearate, palmitate and oleate. After allowing them to dissolve in a warm and very dilute caustic soda solution, pearly sodium bistearate and sodium bipalmitate were obtained on cooling, whereby some sodium oleate remained in solution.

1015. The filtrate was concentrated by evaporation, diluted with water and left to stand. A further deposit was formed that differed from the first one only in that it had a more pearly sheen. It was removed by filtration and the filtrate was concentrated. Sufficient tartaric acid was added to neutralize most of the alkali that had been liberated by the formation of the deposit. The liquor was left to stand for about a month and a further deposit was then separated from the mother liquor. When the filtrate stopped becoming cloudy, it was acidulated with tartaric acid and yielded oleic acid, which started to solidify at 6°C. When it was stored in a small, stoppered bottle for several days at 10°C, it threw a deposit of palmitic acid.

1016. From these experiments it follows that caustic soda saponifies lard in the same way as caustic potash does or in other words, that it makes the lard undergo the same changes in composition.

§ 2. SAPONIFICATION OF LARD BY BARYTA

1017. Equal parts of lard and barium hydroxide were melted. When they were well mixed, 6 parts of water were added and the mixture was boiled for twelve hours; as it boiled, water lost by evaporation was replenished. Finally, when the fat seemed to have been saponified, that is to say when it hardened when put into cold water and had to be brought to the temperature of boiling water to soften again, it was separated from its aqueous mother liquor.

1018. A stream of carbon dioxide was passed through this liquid to precipitate the free barium hydroxide it contained. It was filtered and the filtrate was evaporated: it deposited a small amount of barium carbonate, which was separated. The evaporation residue was slightly yellow. Litmus paper that had been turned red by acid indicated that it was alkaline. It had a bitter and sweetish taste that made me suspect that the glycerin that could be present might have combined with the baryta. When this residue was treated with alcohol, it released a combination of glycerin and baryta that was decomposed by the minimum amount of sulfuric acid required to precipitate the baryta. The glycerin obtained by this method was almost colorless and had a very pleasant, sweet taste. The residue that was not soluble in the alcohol turned out to be a mixture of the same combination together with salts that were present in the baryta I used. I think that if the combination of baryta and glycerin could be perfectly dried, it would be insoluble in alcohol.

1019. The barium soap was acidulated with hydrochloric acid. The acidulated soap thus obtained melted between 39.5 and 40.5°C. It was yellow, crystallized into needles and was soluble in less than its weight of boiling alcohol. On cooling, the solution yielded crystals of stearic and palmitic acid retaining some oleic acid. The acidulated soap reacted very easily with potassium hydroxide dissolved in a large amount of water.

1020. From these facts we can conclude that fatty matter saponified with baryta is absolutely the same as that saponified by potassium or sodium hydroxide.

§ 3. SAPONIFICATION BY STRONTIUM HYDROXIDE

1021. Saponification by strontium hydroxide produces the same phenomena and the same results as saponification by baryta. I will therefore not discuss it in detail.

§ 4. SAPONIFICATION BY LIME

1022. Lard was saponified by its own weight of slaked lime that had been diluted with 6 parts of water. The reaction proceeded quite readily. The aqueous liquid yielded an almost colorless glycerin and some yellow flakes; the glycerin combined with the lime. When sulfuric acid was poured into the aqueous liquid after it had been concentrated, it released an aroma of blackcurrants without the slightest whiff of acetic acid, which proves that no acetic acid is produced during saponification (967).

1023. When the calcium soap was acidulated with hydrochloric acid, it produced a white fatty material that crystallized into needles. After having been melted at 50°C, it started to become very cloudy at 41°C and at 39.37°C, it solidified. When a thermometer was immersed in the liquid and used as anagitator, the temperature rose to 39.60°C. When the fatty material was treated with alcohol, it yielded crystals of stearic acid and palmitic acid and it behaved exactly like the acidulated soaps described above.

§ 5. THE EFFECT OF MAGNESIA ON LARD

1024. A paste of equal parts of lard and calcined magnesia, left for two years while exposed to the air, failed to saponify and most remarkably, when the fat was separated from the magnesia, it was not rancid. This led me to investigate how magnesia could be utilized for the preservation of fats and oils and certain other foodstuffs. However, not having finished this investigation, I cannot yet report any results.

1025. When magnesium hydroxide was heated with its own weight of lard with a melting point of 28°C in an aqueous medium, it reacted with the lard in such a way that it could no longer be separated, not even when the temperature was raised to 100°C. After twenty-four hours of boiling, the water did not contain any appreciable amount of glycerin dissolved in it. After taking an aliquot of the solid material and separating the fatty matter from it by means of hydrochloric acid, I found that this material had not undergone any noticeable change. But if the exposure of the fat to the magnesium hydroxide is continued at elevated temperature for a sufficiently long time, saponification does finally take place. An orange colored glycerin can be found in the water in which the saponification took place, which glycerin has a bitter taste because it is combined with oleic acid and a colored principle. These three compounds are combined with some of the magnesia. Treating the soap with hydrochloric acid separates the fatty matter. In one of my experiments, there were only 0.36 parts of fat saponified but after having separated the 0.64 parts that had not been saponified, I managed to saponify these completely in two successive treatments with magnesia. The acidulated soaps resulting from the three treatments had a melting point of 38°C. They were soluble in weak aqueous potassium hydroxide and after this solution had been boiled for five hours and acidulated with hydrochloric acid, it yielded an amount of fatty matter, the weight of which only differed by 0.02 parts from the fat that had been dissolved and that had a melting point of 38°C. This substance consisted of stearic, palmitic and oleic acid.

1026. In my first experiment, I failed to saponify fats with magnesia, but this is because the treatment was not sufficiently long. I also worked in the presence of air, but I do not know whether or not this had any influence on the outcome.

§ 6. THE EFFECT OF AMMONIA ON LARD

1027. Finely comminuted lard was put into water that was then saturated with ammonia. After fourteen months of contact, the fat had a slightly pearly aspect. It was in the form of flakes that were filtered off.

Examination of the liquor

1028. The liquor was opaque and was filtered until it became transparent; then it was evaporated. It left a yellow material with a bitter, slightly astringent and acid taste that seemed to me to consist of *glycerin, oleic acid, an orange coloring principle* and a trace of a water-soluble acid.

Examination of the fat

1029. It had a pearly aspect. After it had been melted, a thermometer immersed in the melt showed that it began to solidify at 37°C but it did not solidify completely until 28°C. By treating it with twice its weight of alcohol with a density of 0.821[4] (g/mL), filtering the liquor after it had cooled and then evaporating the filtrate, a yellowish, acid fat was obtained that represented about 1/13th of the fat used in this experiment. This fat was almost entirely saponified since when treated with alcohol, most of it dissolved. When this was then dissolved in caustic potash and isolated, I found that it had hardly lost any weight and its melting point remained unchanged.

1030. I conclude from this experiment that aqueous ammonia at ambient temperature only saponifies fats with great difficulty.

§ 7. THE EFFECT OF ALUMINA[5] ON LARD

1031. I took 15 g of gelatinous aluminum hydroxide that had been dried in the sun, reduced it to a fine powder and heated it with 15 g of fat that was free of any humidity. The materials formed a kind of paste. When the alumina was perfectly mixed into the fat, water was added and the mixture was boiled for six hours. The next day, it was boiled for three hours, after which the fat seemed to separate completely from the alumina. It was boiled for a further thirty hours, by which time the fat had collected at the surface of the liquid and most of the alumina had been deposited at the bottom of the flask. The liquor was decanted and evaporated. It left traces of alkaline aluminum salts originating from the aluminum hydroxide, which had not been completely washed out, but it did not yield any glycerin.

1032. After the fat had been melted by heating to 40°C, it solidified at 30°C, although it still contained alumina. Together with the alumina that had formed a deposit, it was treated with hydrochloric acid and this yielded a fat that was still liquid at 29°C. The alumina had therefore not noticeably changed the melting point of the fat. When the fat was treated with four times its weight of boiling alcohol, only very little of it dissolved and the residue was still liquid at 28°C. The alcohol deposited some oily globules on cooling. The filtered liquor left several droplets of yellow oil after evaporation which turned litmus slightly red but did not display the characteristics of a saponified fat, since it was only slightly more soluble in boiling alcohol than the ordinary fat and it did not saponify more readily than this fat.

1033. From these facts it can be concluded that aluminum hydroxide does not saponify lard, at least not under the circumstances in which I worked.

§ 8. SAPONIFICATION BY ZINC OXIDE

1034. I heated 15 g of fat in boiling water with 15 g of zinc oxide that I had prepared by combustion[6]. This gave a soap that was almost fluid at a temperature of 100°C. When the supernatant water was decanted and evaporated, it left a reddish residue that was slightly acid towards litmus paper and had a sweet, bitter and astringent taste. I thought it might contain a zinc salt. Consequently, I looked for the presence of sulfuric acid, nitric acid and hydrochloric acid but I detected only a trace of acetic acid and a principle that smelled like blackcurrants. I took another aliquot of the residue and dispersed it in water containing hydrogen sulfide. This caused a small amount of yellow, oily material and some zinc sulfide[7] to separate out. Evaporating the water yielded a glycerin with a taste that, although quite sweet, was still bitter and disagreeable. I tried to produce the same taste in pure glycerin by boiling it with zinc oxide but without success. I do not know the cause of the unpleasant taste of the glycerin that is formed during the saponification of lard by zinc oxide.

1035. In order to get rid of all the zinc oxide that had combined with the fat, the soap had to be boiled a number of times with dilute hydrochloric acid. After this treatment, the fat was slightly yellow. After it had been melted at 55°C, it became cloudy at 45°C, very cloudy at 39°C but did not completely solidify until 35°C. It seemed to be completely miscible with boiling alcohol and on cooling, the solution deposited crystals of stearic acid and palmitic acid that retained some oleic acid.

1036. The acidulated zinc soaps resulting from the experiment I have just described had a slightly different melting point from those saponified by potassium. I therefore repeated the experiment in order to ascertain whether this difference was fortuitous: the resulting acidulated soaps melted at 55°C and became cloudy at 40.5°C; at 39.5°C, they were almost completely solidified but still slightly soft and at 38.5°C they were completely solid. This experiment shows that zinc oxide saponifies lard in the same way as alkalis.

§ 9. THE EFFECT OF COPPER OXIDE ON LARD

1037. Equal parts of lard and brown copper oxide were boiled in water for thirty-six hours: the aqueous filtrate did not contain any glycerin or copper oxide. After evaporation, it left only a trace of an oily, bitter and acid material with a reddish color. The fat that had solidified on the surface of the liquor was greenish black because it retained a little oxide. It melted at 40°C and solidified again at 26°C. It was relatively insoluble in boiling alcohol but nevertheless, the solution turned litmus tincture slightly red. When water was poured into the reddened liquor, the blue color was re-established. This property was due to a small amount of the fat that had been changed by the action of air and heat. Most of the copper oxide formed a deposit at the bottom of the flask used for the experiment. When the fat was treated with hydrochloric acid[8], it melted at about 29°C and behaved like ordinary fat.

1038. From this experiment I concluded that brown copper oxide does not saponify lard.

§ 10. SAPONIFICATION BY LEAD OXIDE

1039. Equal parts of lard and lead oxide were placed in boiling water. After ten hours, saponification seemed to be complete: the lead oxide had lost its yellow color and become white[9]. The liquor in which the saponification had taken place was completely colorless. After having been concentrated, it left a glycerin syrup that had almost no color and a few fawn-colored flakes. The syrup was neither acid nor alkaline. When it was placed in a narrow glass jar with sulfuric acid diluted with an equal volume of water, no noticeable traces of acetic acid were released. It produced an odor similar to that observed when the mother liquor of a sodium or potassium soap is distilled with an acid, and at the same time a trace of lead sulfate was deposited.

1040. The lead soap was digested at a gentle heat with nitric acid that had been highly diluted with water. The fatty matter that separated had a melting point of 50°C; it started to get cloudy at 41°C and solidified between 39.5 and 39.75°C. It showed all the properties of a fat that had been saponified by alkalis. It readily combined with lead oxide in the absence of water. When separated from this oxide by nitric acid, it demonstrated all the properties that it had shown before it had reacted. Consequently, during its first reaction with lead oxide (1039) it had undergone all the changes this base was capable of producing in it.

SUMMARY OF CHAPTER 4

1041. From the experiments I have described above, it follows that:

sodium hydroxide, baryta, strontium oxide, lime, zinc oxide and yellow lead oxide convert lard into stearic, palmitic and oleic acid and glycerin, just as potassium hydroxide does; and that:

the saponification products appear in the same ratio irrespective of which base was used, since in all saponifications the fat releases the same amount of material to the water and the acidulated soaps always have the same melting point.

1042. Since baryta, strontium oxide, lime, zinc oxide and yellow lead oxide form combinations with stearic, palmitic and oleic acid that are insoluble in water, it follows that the action of water as a solvent for the soap is not essential for saponification to take place. It is remarkable that the oxides of zinc and lead, which are insoluble in water and which yield compounds that are equally insoluble in water, produce the same results as potassium and sodium hydroxide. This proves that they have a very strong alkalinity[10].

1043. Generalizing the saponification process in this way shows that the production of lumps by litharge is a true saponification reaction. Since lead oxide has the same effect on fat as potassium or sodium hydroxide, it follows that in principle, lumps could also be made from acidulated alkali soaps[11]. Before doing this, one should first establish whether an amount of non-saponified fat is present in the lumps to be imitated so that, if this is the case, the same proportion of non-saponified fat can be added to the acidulated soap before allowing it to react with litharge.

1044. It is remarkable that magnesia, which is otherwise strikingly similar to the alkalis proper[12], converts the fat into soap with far less ease than the oxides of lead and zinc that are generally considered to be less alkaline than this salt-forming base. But even though magnesia saponifies fat only very slowly, before saponification starts, it displays the behavior of a base in that it forms a bond with fats and oils such that the resulting species is homogenous and that the fat cannot be separated by exposure to boiling water, even though under those circumstances, two forces tend to separate the substances: 1. their difference in density ; 2. the ability of pure magnesia to absorb water. Readers will no doubt remember that fat separates from alumina when this mixture is treated with boiling water (1031).

1045. The above illustrates that bases that can form salts show three types of behavior towards fats:

1. They convert this substance into glycerin and stearic, palmitic and oleic acids. This holds for baryta, strontium oxide, potassium and sodium hydroxide, lime, the oxides of lead and zinc, magnesia and ammonia, although the last two only act very slowly.

2. They form a combination or rather a kind of bond with the fat without causing it to change in any way. This is the case with magnesia before it causes saponification.

3. They do not form a strong combination. This holds for bases that, after having been mixed with the fat, separate out again when the mixture is treated with boiling water.

1046. I think that there are various conditions under which soluble bases can exert an effect on non-saponified fats that falls short of full denaturation, either because the contact is not sufficiently long or because the alkalis have been weakened by the presence of too much water. It seems to me that it is this kind of affinity that enables alkalis and soluble alkali carbonates to remove stains made by neutral fats.

1047. When classifying bases that can form salts according to the strength of their alkaline properties, their saponifying energy[13] must be taken into account since this property is in essence the strength of their alkalinity.

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[1] See also endnote 11 on page 218 at the end of Chapter 2 of Book IV.

[2] A literal translation of the original would be “palmitic acid united with stearic acid”, as if it were a kind of compound. Accordingly, the author may well have contemplated the possibility that fatty acids formed compounds that are characterized by fixed ratios between their constituent acids. After all, looking for such fixed ratios had greatly improved understanding in other areas of chemistry.

[3] The author refers to ‘soude à l’alcool’. In endnote 22 of Book II, chapter 1, some background information has been given on its potassium equivalent. Accordingly, the sodium variety has been translated as ‘pure sodium hydroxide’ or ‘pure caustic soda’.

[4] A density of 0.821 (g/mL) corresponds to a weight percentage of 90.7 or 93.7 % by volume.

[5] Just as the French word ‘potasse’ can mean the potassium metal, the element potassium, potash or potassium carbonate and potassium hydroxide or caustic potash, the word ‘alumine’ can have different meanings such as the oxide and the hydroxide. However, it being gelatinous indicates that the hydroxide is meant here; after drying, this becomes aluminium oxide or alumina. Presumably, first preparing the hydroxide and then washing it is also a way to purify commercial reagents. In fact, this process is not fundamentally different from the way alumina is prepared industrially from bauxite.

[6] This will be combustion of the metal.

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[7] The text refers to ‘zinc hydrosulfate’ but since this salt is also mentioned as a constituent of lithopone, a white pigment made by mixing zinc sulfate and barium sulfide, it is clear that zinc sulfide is meant.

[8] In general, the titer of a fat, *i.e.* the melting point of its fatty acids is higher than that of the non-saponified fat. Acidulation of a possibly partially saponified fat and measuring its melting point can therefore indicate whether or not any fatty acids are present and thus if there has been any saponification.

[9] Lead oxide, PbO, is yellow and lead hydroxide, $Pb(OH)_2$ is white. Since both the fatty acids and the lead hydroxide are weak, the lead soaps will comprise both undissociated fatty acids and undissociated lead hydroxide. Hence the formation of something white.

[10] The concept of strength for acids and bases presumably already existed since the author does not explain it any further. And indeed, bases derived from alkali metals and alkaline earth metals are stronger than those from metals like aluminium and copper. Amongst the weaker bases, lead hydroxide has a pK value of 3.02, zinc hydroxide has a pK value of 4.36 and both of these are effective in saponifying fats, but ammonium hydroxide with a pK of 4.76 is not.

[11] These ‘alkali soaps’ are sodium or potassium soaps.

[12] Again, the ‘alkalis proper’ are just sodium or potassium based.

[13] At the time of writing, words like energy, power, strength etc. did not yet have their current, strict definitions.