CHAPTER 3

ON SAPONIFICATION

979. In this chapter, I will endeavor to determine what changes occur in the proportions of the various elements of which saponifiable oils and fats are composed when they are transformed by contact with alkali, 1. with respect to the proportion of fatty acids and 2. the proportion of glycerin and cetyl alcohol.

SECTION 1

THE SAPONIFICATION OF MUTTON TALLOW, LARD AND HUMAN FAT

§ 1. COMPARATIVE ELEMENTAL ANALYSIS OF MUTTON TALLOW, LARD AND HUMAN FAT

980. The mutton tallow used in my experiments was colorless, odorless and had no effect on vegetable tinctures. On incineration, 5 g did not leave a noticeable amount of ash. When a thermometer was inserted in the fat after it had been melted, the reading dropped first to 40.5°C and then rose to 42°C as the fat solidified.

981. The lard was totally colorless. It had only a very slight smell and did not change the color of vegetable tincture. On incineration, 5 g did not leave a noticeable amount of ash. When a thermometer was inserted in the fat after it had been melted, the reading dropped to 29°C and then rose to 31°C when the fat started to solidify.

982. The human fat was yellow, odorless and had no effect on vegetable tincture. An amount of 5 g left only 1 mg of a yellowish ash. At 17°C, it started to deposit some stearin.

	BY WEIGHT[1]		BY VOLUME		
Oxygen………………………..	9.304	100	1		Mutton tallow
Carbon………………………....	78.996	849.50	11.10	1	
Hydrogen…………………...	11.700	125.75	20.18	1.82	
					Lard
Oxygen………………………..	9.756	100	1		
Carbon………………………	79.098	810.80	10.59	1	
Hydrogen…………………...	11.146	114.30	18.34	1.73	
Oxygen……………………..	9.584	100	1		Human fat
Carbon………………………	79.000	824.29	10.77	1	
Hydrogen…………………...	11.416	119.11	19.11	1.77	

983. The lard and the human fat contained the elements in about the same proportions[2]. Mutton tallow contained relatively more carbon and hydrogen. Conclusions

§ 2. COMPARATIVE ELEMENTAL ANALYSIS OF THE SAPONIFICATION PRODUCTS OF MUTTON TALLOW, LARD AND HUMAN FAT

984. 100 parts* of each kind of fat were saponified by caustic potash. The soaps were acidulated with weak phosphoric acid, yielding *free fatty acids* and aqueous liquids containing glycerin and various potassium phosphates[3]. The aqueous liquids were evaporated to dryness on a water bath and their residues were treated with cold alcohol. The alcoholic liquors were concentrated on a water bath and the residues were exposed to a dry vacuum for twenty-four hours and compared with a reference sample consisting of 0.5 g of glycerin from olive oil that had been brought to the same density as the other glycerin samples; the composition of the reference sample had been determined beforehand. The glycerin samples were then incinerated and the residual inorganic content was deducted from their weight.

100 parts of mutton tallow, 100 parts of lard and 100 parts of human fat gave:

Free fatty acids...............	96.5	95.90	96.18
Glycerin........................	8.00	8.82	9.66
Total..............	104.50	104.72	105.84

Conclusions

985. For each type of fat, the sum of the weight of the glycerin and the free fatty acids exceeds the weight of the fat subjected to the alkali treatment[4].

986. Since saponification can be carried out under vacuum (973) and without evolution of gas, it follows that water must have been bound by the saponification products. There are two moments when this water could have been bound: first, during the reaction with alkali, or subsequently, when the acids were separated from the alkali by means of phosphoric acid. I would like to remark that the increase in weight is certainly much larger than indicated by the experimental results, since the fairly large number of operations by which the glycerin was separated from the free fatty acids cannot have been carried out without loss. Moreover, when the glycerin and the free fatty acids were dried by heating, some must undoubtedly have evaporated since both are susceptible to volatilization, especially when heated while exposed to the atmosphere. In addition to these losses, there is also the loss that must result from the reaction of the oxygen in the air with the carbon and hydrogen of these same materials.

* A sample size of 5 g was used throughout. Each time the sample was exposed to heat on a water bath.

ELEMENTAL ANALYSIS OF THE FREE FATTY ACIDS AS OBTAINED AFTER SEPARATION FROM POTASSIUM BY MEANS OF PHOSPHORIC ACID

987.

	BY WEIGHT		BY VOLUME		
Oxygen……………………	10.500	100	1		Free fatty acids from mutton tallow, melting at 52°C
Carbon……………………	77.528	738.36	9.65	1	
Hydrogen…………………	11.972	114.02	18.30	1.896	
Oxygen……………………	10.692	100	1		Free fatty acids from lard melting at 42 to 45 °C
Carbon……………………	77.594	725.72	9.48	1	
Hydrogen…………………	11.714	109.56	17.58	1.854	
Oxygen……………………	11.056	100	1		Free fatty acids from human fat solidified from 31°C
Carbon……………………	77.466	700.66	9.15	1	
Hydrogen…………………	11.478	103.81	16.66	1.82	

For an equal weight, the free fatty acids contain more oxygen and hydrogen than their respective fats[5] before saponification. Conclusions

988. When the free fatty acids are heated with lead oxide, I found that each type of fat released the same amount of water. This was shown by the following experiments:

100 parts of free fatty acids from mutton tallow, 100 parts of free fatty acids from lard and 100 parts of free fatty acids from human fat each released 3.65 g water composed of:

Oxygen………………………………………………	3.245
Hydrogen……………………………………………	0.405

989. Consequently, given the elemental compositions of the free fatty acids, the composition of fatty acid anhydrides are as shown in the following table :

COMPARATIVE ELEMENTAL COMPOSITION OF THE ANHYDROUS FATTY ACIDS

	BY WEIGHT		BY VOLUME		
Oxygen……………………	7.529	100	1		Fatty acids from mutton tallow
Carbon……………………	80.465	1068.80	13.97	1	
Hydrogen…………………	12.006	159.47	25.59	1.83	

Fatty acids from lard

	By weight		By volume	
Oxygen	7.729	100	1	
Carbon	80.533	1041.96	13.61	1
Hydrogen	11.738	151.90	24.38	1.79

Fatty acids from human fat

	By weight		By volume	
Oxygen	8.106	100	1	
Carbon	80.400	991.85	12.96	1
Hydrogen	11.494	141.79	22.75	1.75

Conclusions

990. In the fatty acid anhydrides, or the fatty acids as they were after having reacted with the lead oxide at elevated temperature, the carbon to hydrogen ratio was about the same as in the natural fats but the proportion of oxygen present was lower.

ANALYSIS OF THE GLYCERIN

991. Glycerin originating from the action of litharge[6] on pure olive oil was treated with hydrogen sulfide and then concentrated on a water bath. It was almost colorless and had a very distinct, sweet taste; it was not at all acid. An amount of 1 g heated in a platinum crucible only left 1 mg of alkaline ash. At a temperature of 17°C, it had a density of 1.252[7] (g/mL). This particular sample was analyzed and found to consist of:

	By weight		By volume[8]
Oxygen	53.278	100	1
Carbon	37.666	70.70	0.92
Hydrogen	9.056	16.99	2.72

992. When 25 g of glycerin were exposed to a dry vacuum at a temperature between 15 and 20°C, they showed the following weight loss profile:

	grams
51 hours	0.705 of water
120	1.025
216	1.200
1 month	1.420.
1½ month	1.450
2 months	1.500
2½ months	1.500*

* When 0.500 g of glycerin with a density of 1.252 (g/mL) was exposed to a dry vacuum for 116 hours, it reached the same degree of dehydration as the 25 g, that is to say, it reached a density of 1.27 (g/mL).

993. In this condition, the glycerin had a density of 1.27 (g/mL) at a temperature of 10°C and in accordance with the previous analysis, it must have consisted of:

	BY WEIGHT[9]		BY VOLUME	
Oxygen…………………..……	47.944	51.004	100	1
Carbon…………………..……	37.666	40.071	78.56	1.02
Hydrogen……………….....	8.390	8.925	17.50	2.81

Carbon……………………..……………………	40.071
Hydrogen……………………..…………………	2.557
Oxygen…… / Hydrogen… } Water……..…………..………………	57.372[10]

994. Let us now see if the elements of the saponification products of each type of fat correspond quantitatively to the elements of the fats from which they originate.

TABLE 1
SAPONIFICATION OF MUTTON TALLOW

995. Mutton tallow consisting of[11]:

Oxygen………………………………………..…….	9.304
Carbon……………………………………...……...	78.996
Hydrogen……………………………………………..	11.700

100 parts of this fat yielded[12]:

Free fatty acids………………………………………….	96.5
Glycerin…………………………………………………	8.0

A. 96.5 parts of the free fatty acids consist of[13]:

Oxygen…………………………………………..…	10.132
Carbon……………………………………….…...	74.815
Hydrogen……………………………………………..	11.553
Total…………………………….	96.500

or

Water[14]………………	3.522	Oxygen……………	3.131
		Hydrogen…………	0.391
Oxygen[15]…………….	7.001		
Carbon………………	74.815		
Hydrogen…………...	11.162		
Total…….	96.500		

B. 8.0 parts of glycerin consist of[16]:

Oxygen	4.080
Carbon	3.206
Hydrogen	0.714

or

Carbon	3.206
Hydrogen	0.205
Water[17]	4.589

Calculating the sum of these products and comparing them with the elements of the natural fat gives the following results:

				Mutton Tallow	Difference in saponification products
Oxygen[18].	of the 'dry' acid..	7.001	11.081	9.304	+1.777
	of the glycerin….	4.080			
Carbon….	of the 'dry' acid	74.815	78.020	78.996	-0.976
	of the glycerin….	3.205			
Hydrogen	of the 'dry' acid	11.162	11.876	11.700	+0.176
	of the glycerin….	0.714			
	Total		100.977	100.000	

TABLE 2[19]

SAPONIFICATION OF LARD

996. Lard consisting of:

Oxygen	9.756
Carbon	79.098
Hydrogen	11.146

100 parts of this fat yielded:

Free fatty acids	95.9
Glycerin	8.82

A. 95.9 parts of the free fatty acids consist of:

Oxygen	10.253
Carbon	74.413
Hydrogen	11.234
Total	95.900

or

Water	3.500	Oxygen	3.111
		Hydrogen	0.389
Oxygen	7.142		
Carbon	74.413		
Hydrogen	10.845		
Total	95.900		

B. 8.82 parts of the sweet principle consist of:

Oxygen	4.499
Carbon	3.534
Hydrogen	0.787

or

Carbon	3.534
Hydrogen	0.225
Water	5.061

Calculating the sum of these products and comparing them with the elements of the natural fat gives the following results:

				Lard	Difference in saponification products
Oxygen	of the 'dry' acid	7.142	11.641	9.756	+1.885
	of the glycerin	4.499			
Carbon	of the 'dry' acid	74.413	77.947	79.098	-1.151
	of the glycerin	3.534			
Hydrogen	of the 'dry' acid	10.845	11.632	11.146	+0.476
	of the glycerin	0.787			
	Total		101.220	100.000	

TABLE 3

SAPONIFICATION OF HUMAN FAT

997. Human fat consisting of:

Oxygen	9.584
Carbon	79.000
Hydrogen	11.416

100 parts of this fat yielded:

Free fatty acids	96.18
Glycerin	9.66

A. 96.18 parts of the free fatty acids consist of:

Oxygen	10.633
Carbon	74.507
Hydrogen	11.040
Total	96.180

or

Water	3.510	Oxygen	3.12
		Hydrogen	0.39
Oxygen	7.513		
Carbon	74.507		
Hydrogen	10.650		
Total	96.180		

B. 9.66 parts of glycerin consist of:

Oxygen	4.927
Carbon	3.871
Hydrogen	0.862

or

Carbon	3.871
Hydrogen	0.247
Water	5.542

Calculating the sum of these products and comparing them with the elements of the natural fat gives the following results:

				Human fat	Difference in saponification products
Oxygen	of the 'dry' acid	7.513	12.440	9.584	+2.856
	of the glycerin	4.927			
Carbon	of the 'dry' acid	74.507	78.378	79.000	-0.622
	of the glycerin	3.871			
Hydrogen	of the 'dry' acid	10.651	11.513	11.416	+0.097
	of the glycerin	0.862			
	Total		102.331	100.000	

RESULTS AND CONCLUSIONS

998. 1. *Not all the carbon present in the natural fats is found in the saponification products. For mutton tallow the difference is 0.976 parts, for lard it is 1.151 parts and for human fat it is 0.622 parts.*

This finding can be attributed to two causes: 1. the imperfection of my analyses; 2. the losses of fatty acids and glycerin resulting from the experiments I carried out to determine the ratio of the saponification products (984). But according to the degree of accuracy of my analyses and what I have said earlier (986), I think that the latter cause is more significant than the former.

2. *Water has been bound in both the free fatty acids and the glycerin.* But since the hydration water of the free fatty acids could have been combined with the acids at the point in time when they were detached from the potassium rather than during saponification, I disregarded this water since it may be immaterial to the saponification reaction itself, and only considered the acids in their anhydrous state.

3. *The 92.978*[20] *parts of 'dry' acids from mutton tallow, the 92.400 parts of 'dry' acid from lard and the 92.670 parts of 'dry' acid from human fat contain less oxygen and less hydrogen than the 100 parts of fat from which they originate**.

Although I recognize that the determination of the ratio of the saponification products led to the loss of a certain amount of these products (986), these losses are nevertheless not sufficiently large to explain all the oxygen and hydrogen missing from the 'dry' acids in comparison with the amounts present in the natural fats. Consequently, I do not hesitate to conclude that *the oxygen and hydrogen of the fats combined with the carbon of the same fats to produce glycerin.*

When calculating the ratio of the missing oxygen to the missing hydrogen in the 'dry' acids from mutton tallow and human fat, in comparison with the ratio of oxygen to hydrogen present in the natural fats from which these acids originate, the oxygen was found to be insufficient to convert all the hydrogen into water; therefore *an amount of oxygen and hydrogen, represented by water + hydrogen, must have passed into the glycerin,* which result is in accordance with the analysis of the glycerin†.

When making the same calculation for the oxygen and the hydrogen missing from the 'dry' acids from lard in comparison with the amounts of these elements present in the natural fat, it turns out that *the oxygen to hydrogen ratio is slightly higher than in water.* This result is not in

*

	Mutton tallow	Lard	Human fat
Oxygen content of natural fat	9.304	9.756	9.584
Oxygen content of 'dry' acid	7.001	7.142	7.513
DIFFERENCE	2.303	2.614	2.071
Hydrogen content of natural fat	11.700	11.146	11.416
Hydrogen content of 'dry' acid	11.162	10.845	10.650
DIFFERENCE	0.538	0.301	0.766

† The following fats give:

	Mutton tallow	Human fat
Water	2.591	2.330
Hydrogen	0.250	0.507

accordance with the previous one and seems to me to stem from experimental errors [*].

4° *Glycerin with a density of 1.27 (g/mL) is formed from elements that derive from the fat plus an amount of water or these elements that derive from the alkaline liquid in which the saponification takes place.*

999. In fact, during saponification, the fat splits into two very unequal portions:

(A) One portion is at least equal to 92% of the weight of the fat and consists of oxygen, carbon and hydrogen. The last two occur in a ratio that is not very different from the ratio in which they are found in the fat but the ratio of carbon and hydrogen to oxygen is higher than in the fat.

(B) The other portion also consists of oxygen, carbon and hydrogen and binds water to form glycerin with a density of 1.27 (g/mL).

[*] But lard gives:

Water	2.937
Hydrogen	0.003

SECTION 2

THE SAPONIFICATION OF SPERMACETI

1000. Spermaceti consists of[21]:

	BY WEIGHT	BY VOLUME
Oxygen…………………………	5.478	1.00
Carbon…………………………..	81.660	19.48
Hydrogen……………………….	12.862	37.70

1001. When 100 parts of spermaceti were treated with aqueous potassium hydroxide, they yielded[22]:

1. Free fatty acids with

a melting point of 45°C…...	60.96	Idem, anhydrous…….	58.735
Cetyl alcohol……………….	40.64	Cetyl alcohol…………	40.640
Total	101.60		99.375

2. An amount of 0.90 parts of a syrupy liquid that was not at all sweet and that consisted of a very small amount of colored organic material.

1002. On analysis, the free fatty acids were found to consist of[23]:

	BY WEIGHT			BY VOLUME
Oxygen……………	11.888	100	7.247	1
Carbon…………….	76.290	641.70	46.507	8.38
Hydrogen…………	11.822	99.44	7.206	15.96
Total……..…………………			60.960	

1003. 100 parts of these acids lose 3.65[24] parts of water when heated with lead oxide. Therefore the 'dry' acids consist of:

	BY WEIGHT			BY VOLUME[25]
Oxygen…………..….	8.97	100	5.268	1
Carbon…………..….	79.18	882.8	46.507	11.54
Hydrogen………….	11.85	132.1	6.960	21.20
Total….……………………			58.735	

1004. The cetyl alcohol consists of:

	By weight		By volume[26]
Oxygen	6.2883	2.556	1
Carbon	79.7660	32.417	16.60
Hydrogen	13.9452	5.667	35.54
Total		40.640	

1005. Now that the composition of the fatty acids and the cetyl alcohol has been determined by analysis and the weights of these two materials obtained from a given weight of spermaceti are known, let us examine whether these results are in accordance with the composition of spermaceti and let us then attempt to explain what happens during saponification.

1006. According to the results above, it is evident that:

1. The weight of the materials obtained from the saponified spermaceti exceeds that of the spermaceti, even if the 0.90 parts of water-soluble material are not taken into account;

2. When the sum of the elements present in the free fatty acids and the cetyl alcohol is calculated as follows:

Oxygen	from the acids	7.247[27]	9.803
	from the cetyl alcohol	2.556	
Carbon	from the acids	46.507	78.924
	from the cetyl alcohol	32.417	
Hydrogen	from the acids	7.206	12.873
	from the cetyl alcohol	5.667	
	Total	101.600	101.600

the saponification products show the following:

Excess oxygen in comparison with spermaceti	4.325[28]
Shortfall of carbon	2.736
Shortfall of hydrogen	0.011

3. A calculation of the sum of the elements in the dry acids and those in the cetyl alcohol:

Oxygen	from the acids	5.268[29]	7.824
	from the cetyl alcohol	2.556	
Carbon	from the acids	46.507	78.924
	from the cetyl alcohol	32.417	
Hydrogen	from the acids	6.960	12.627
	from the cetyl alcohol	5.667	
	Total	99.375	99.375

reveals the following in the saponification products:

Excess oxygen in comparison with spermaceti…..	2.346
Shortfall of carbon………………………………..	2.736
Shortfall of hydrogen……………………………..	0.235

4. Since saponification proceeds *in vacuo* and without gas being released, one cannot but conclude that water is bound by the saponification products of spermaceti.

5. The amount of oxygen contained by the acids that are *assumed to be 'dry'* minus 0.209 equals the amount in the spermaceti from which they originate[30].

6. The cetyl alcohol can be expressed as a sum of the elements of water and ethylene[31].

1007. Let us draw some conclusions from these facts to form an idea of what happens during the saponification of spermaceti.

During this operation, *all the oxygen of the spermaceti binds to carbon and hydrogen in the same ratio as in palmitic and oleic acid, whereas the remainder of these combustible elements, which occur in the same ratio as in ethylene, bind water to form cetyl alcohol.* I disregard the small amount of soluble organic matter, which is less than 1% of the weight of the spermaceti, because the appearance of this material seemed to me to be accidental rather than essential to the reaction.

1008. In the Table below, I present what appears to happen during the saponification of spermaceti, while taking into account:

1. My analysis of spermaceti;
2. My analysis of the 'dry' acids;
3. That all the oxygen present in the spermaceti is found in the acids;
4. That 96.35 parts of these acids bind 3.65 parts of water on hydration;
5. That cetyl alcohol can be represented by 100 parts of ethylene and 7.61 parts of water;
6. That cetyl alcohol and free fatty acids are the only saponification products of spermaceti.

TABLE

SAPONIFICATION OF SPERMACETI

1009.

'DRY' ACIDS containing all oxygen present in 100 parts of spermaceti:

Oxygen…………………………………………	5.478[32]
Carbon…………………………………………	48.360[33]
Hydrogen………………………………………	7.236
Total………………………	61.074 which bind
	2.313 [34]parts of water
FREE FATTY ACIDS containing all oxygen present in 100 parts of spermaceti	63.387

If then the carbon and hydrogen contained in the acids are subtracted from the carbon and hydrogen in the spermaceti, there remains:

Carbon……………………………………………..	33.300[35]
Hydrogen………………………………………….	5.626

These quantities are very close to:

Carbon……………………………………………..	33.300
Hydrogen………………………………………….	5.425

which is the ratio of these elements in ethylene[36]. If we take this latter ratio, this gives the following amounts for the carbon and hydrogen which form the cetyl alcohol:

Carbon…………………………………………	33.300
Hydrogen………………………………………	5.425
Total………………………..	38.725 which bind
	2.947 parts of water
Cetyl alcohol from 100 parts of spermaceti.	41.672

Therefore 100 parts of spermaceti give:

Free fatty acids……………………………….	63.387[37]
Cetyl alcohol………………………………….	41.672
Total…………………………	105.059

The experimental data[38] are:

Free fatty acids………………………………….	60.960
Cetyl alcohol………………………………………	40.640
Total……………………………	101.600
Difference…………………………...	3.459

This difference is due to losses during the analyses, the production of the soluble material and perhaps also to the formation of a small amount of water and carbon dioxide by reaction with atmospheric oxygen.

SECTION 3

REFLECTIONS ON THE REASON WHY CHOLESTEROL IS NOT SAPONIFIED

1010. For saponification to take place, there are two essential contributing factors: the influence of an alkali and the nature of the fatty material such that its elements can form part of new compounds, whereby at least one of these elements has a great affinity for alkalis and occurs in a proportion that would seem to have to be at least half the weight of the fatty material. In view of this and the composition of cholesterol[*39], it is easy to understand why this substance is unsaponifiable. In fact, if all the oxygen were to be concentrated on 14 parts of carbon and 27 parts of hydrogen so as to form stearic acid, this would leave 22.77 parts of carbon and 36 parts of hydrogen. So, since the amount left is quite considerable and the carbon and hydrogen do not seem to occur in a ratio that is suitable to form a compound with water, it is clear why cholesterol does not yield stearic acid when brought into contact with an alkali.

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[1] The first data column in this table lists the analytical data in percentages. The next column provides the same data but with the oxygen content set at 100. Then these data are converted to atom equivalents whereby the oxygen content is set at unity in the third data column and the carbon content is set at this value in the last one.

[2] Human fat shows many similarities with lard. Their average carbon chain length is shorter than that of mutton tallow so more carbon atoms are expected per oxygen atom for the latter. Moreover, mutton tallow has been biohydrogenated so the hydrogen to carbon ratio in mutton tallow is also higher than in lard.

[3] The original mentions 'potassium superphosphate', which will be a kind of acid phosphate such as K_2HPO_4, or even KH_2PO_4 and 'potassium phosphate'. Accordingly, the presence of free phosphoric acid is avoided so that evaporation to dryness produces solid salts. When these are extracted with cold alcohol, the resulting glycerin should not contain any phosphoric acid.

[4] Assuming an average relative molecular mass for lard of 872, 100 parts would require (100 : 872) x 3 x 18 = 6.2 parts of water for complete hydrolysis. This is only slightly more than the 104.70 – 100 = 4.7 parts determined experimentally for lard. It would appear that some material was lost .

[5] For the oxygen, this remark is correct since free fatty acids weigh less than the fat from which they originate and contain the same amount of oxygen. For hydrogen on the other hand, the difference is much smaller and not correct.

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[*] By volume this composition equals:

Oxygen	1
Carbon	36.77
Hydrogen	63.03

[6] Litharge is PbO, just like 'massicot'. At this stage it is not clear what the difference might be, if any.

[7] At 20°C, glycerin has a density of 1.2613 (g/mL).

[8]The molecular formula of glycerin is $C_3H_8O_3$.

[9] The carbon content in the first data column is the same as that in the first data column in the table in sub-section (991). The other data in the first data column are experimental data that have been normalized to the carbon content. In the second data column, the figures from the previous column have been expressed as percentages and in the third, they have been normalized to oxygen = 100. In the final column, the atomic equivalents have been worked out.

[10] Here the weight percentage of the oxygen content as listed in the second data column of the previous table has been converted into a weight percentage of water. This requires part of the hydrogen and what was left has been listed separately, again as a weight percentage.

[11] These data are the analytical data that have been reported in sub-section (982).

[12] These data underneath have already been reported at the end of sub-section (984).

[13] According to the top third of the first data column in sub-section (987), the oxygen content of the free fatty acids equals 10.500 %. This means that 96.5 parts will contain 10.500 x 0.965 = 10.1325 parts of oxygen. Similarly, the carbon and hydrogen contents equal 77.528 x 0.965 = 74.815 parts and 11.972 x 0.965 = 11.553 parts respectively.

[14] As mentioned in sub-section (988), 100 parts of free fatty acids originating from mutton tallow yield 3.65 parts of water. Thus 96.5 parts yield 3.65 x 0.965 = 3.522 parts of water and this water is formed of 3.522 : 9 = 0.391 parts of hydrogen and an amount of oxygen equalling 3.522 – 0.391 = 3.131 parts.

[15] The amount of oxygen of 3.131 parts already having been accounted for, this leaves 10.132 – 3.131 = 7.001 parts for the oxygen content of the 'dry' acids. The carbon content is the same (74.815 parts) as in the table above since water does not contain carbon but the hydrogen content of the dry acid has again to be corrected 11.553 – 0.391 = 11.162 parts.

[16] These data are in accordance with the glycerin analysis reported in sub-section (993) where the second data column quotes its oxygen content as 51.004 %. For 8 parts of glycerin, this amounts to 8 x 0.51004 = 4.080 parts. Carbon and hydrogen content can be calculated the same way.

[17] The 4.080 parts of oxygen correspond to (4.080 : 16) x 18 = 4.590 parts. The author mentions 4.589 parts since he used slightly different atomic weights. This amount of water corresponds to 0.509 parts of hydrogen so the total hydrogen content of 0.714 parts has to be corrected. This leaves 0.714 – 0.509 = 0.205 parts. Again, the carbon content is not affected.

[18] The oxygen content is arrived at by calculating the sum of the oxygen of 96.5 parts of dry acid as listed in the second table in *A* and the oxygen content of 8 parts of glycerin as listed in the first table in *B*: 7.001 + 4.080 = 11.081. This sum is then compared with

the 9.304 parts determined experimentally (982) and the difference between the theoretical and actual values (11.081 – 9.304 = 1.777) is given in the last column.

As we now know, the theory used to arrive at the table was not quite correct. It assumed that heating free fatty acids with lead oxide would release the same amount of water as needed for hydrolysis of the fat, whereas it equals half this amount. So the 'dry' acids had the formula of an anhydride rather than that of a carbonyl radical and thus contained more oxygen than these radicals. This is clearly shown in the last column of the table.

[19] Table 2 is analogous to Table 1. Accordingly, *mutatis mutandis,* the endnotes in Table 1 also pertain to Table 2 and the subsequent Table 3.

[20] This figure can be arrived at by using the data in the last table in Table 1 listing the oxygen, carbon and hydrogen contents of the 'dry' acids from mutton tallow and the glycerin: 7.001 + 74.815 + 11.162 = 92.978. The totals for lard and human fat can be calculated analogously by using data from Table 2 and Table 3 respectively.

[21] These data have already been reported in sub-section (510).

[22] As mentioned in endnote 4 on page 120, the 60 : 40 ratio indicates incomplete saponification.

[23] Again, the first data column expresses the analytical results as percentages. Then they are normalized to oxygen = 100, this being the atomic weight as introduced by Berzelius, and in the third data column they are normalized to their sum equalling 60.96 parts, which is the weight percentage of free fatty acids mentioned in sub-section (1001).

[24] According to endnote 4 in Chapter 11 of Book II (page 120), the average relative molecular mass of the fatty acids in spermaceti equals 263. When these fatty acids are heated with lead oxide, one molecule of water is liberated for every two fatty acid molecules. Therefore, the amount of water that is liberated on a percentage basis is: 18 x (100 : 263) : 2 = 3.42 %.

[25] According to the same endnote, the molecular formula of the free fatty acid is $C_{16.5}H_{32}O_2$ so that the 'dry acid' will be $C_{33}H_{62}O_3$ or $C_{11}H_{20.7}O$. This is close to the values reported in the table.

[26] According to the same endnote, the average relative molecular mass of the alcohols in spermaceti equals 247 and the molecular formula is $C_{16.5}H_{33}O$. Again, the composition reported by the author is very close to what would be expected.

[27] The data in this column have already been reported in sub-sections (1002) and (1104).

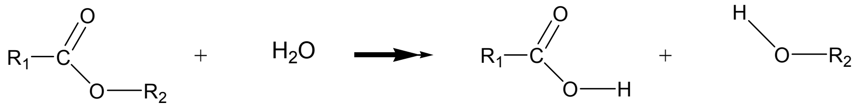
[28] This value of 4.325 has been arrived at by deducting the oxygen content of the spermaceti as given in sub-section (1000) from the sum of the oxygen contents of the saponification products (1006): 9.803 – 5.478 = 4.325. Similarly: 78.924 – 81.660 = -2.736 and 12.873 – 12.862 = -0.011.

[29] Instead of transferring the data from the table giving the free fatty acids (1002), the data from the 'dry' fatty acids (1003) have been listed in this column.

[30] According to the table in sub-section (1000), the oxygen content of spermaceti equals 5.478 % and according to the table in sub-section (1003) the oxygen content of 58.735 parts of 'dry' acids originating from 100 parts of spermaceti equals 5.268 parts. There-

fore, the 'dry' acids contain somewhat less oxygen rather than more as mentioned in the text.

When interpreting this and similar arguments, taking the number of oxygen atoms present in the various compounds involved in the hydrolysis of fatty acid esters makes it much easier to understand:



[31] See also sub-section (480) on page 126.

[32] This is the oxygen content listed in the table in sub-section (1000) giving the elemental analysis of spermaceti.

[33] This figure has been arrived at by using the oxygen to carbon ratio for the 'dry' acids given in sub-section (1003) of 5.268 : 46.507 and the actual oxygen content of 5.478 according to: (46.507 : 5.268) x 5.478 = 48.360. The hydrogen value in the line below is arrived at according to: (6.960 : 5.268) x 5.478 = 7.237, which value is listed as 7.236 in the table.

[34] This value has been arrived at on the basis of the observation that 100 parts of free fatty acids liberate 3.65 parts of water, according to: (61.074 : 96.35) x 3.65 = 2.313.

[35] According to the table in sub-section (1000), the carbon content of spermaceti equals 81.660 %; deducting the carbon content of the 'dry' acids gives 81.660 – 48.360 = 33.300. Equally for the hydrogen contents: 12.862 – 7.236 = 5.626.

[36] In ethylene (C_2H_4) the weight ratio is 24 : 4 = 6, whereas 33.300 : 5.425 = 6.138.

[37] These are the totals arrived at above.

[38] These are the data that have already been reported in sub-section (1001).

[39] These data have been reported in sub-section (455) on page 105.