XXV.—*On the Constitution of Stearine.*

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A specimen of stearine from mutton fat, having its second melting-point at 62°·5, and, therefore, nearly identical with the substances analyzed by Lecanu* and Heintz† respectively, burned with chromate of lead, gave the following results :

I. 0·2989 grm. gave :
  0·8483 ,, carbonic acid, and
  0·3277 ,, water.
II. 0·2706 ,, gave :
  0·7677 ,, carbonic acid, and
  0·3026 ,, water.
III. 0·2670 ,, gave :
  0·7544 ,, carbonic acid, and
  0·2941 ,, water.
IV. 0·2820 ,, gave :
  0·7943 ,, carbonic acid, and
  0·3148 ,, water.
V. 0·3492 ,, gave :
  0·9858 ,, carbonic acid, and
  0·3858 ,, water.

These numbers correspond to the following quantities per cent :

* J. Pharm. [3] XX, 325 ; Ann. Ch. Phys. [2] LV, 192.

† Pogg. Ann. LXXXIV, 229. It is, perhaps, proper to state that it differed from theirs in being the second crop of crystals in the twenty-fifth ethereal solution of mutton fat, instead of the first crop in the sixth or seventh solution.

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	I.	II.	III.	IV.	V.
C.	77·40	77·37	77·05	76·81	76·99
H.	12·18	12·42	12·23	12·40	12·27
O.	10·42	10·21	10·72	10·79	10·74

The following are the numbers obtained by Lecanu and Heintz, also the melting-point given by them. Liebig and Pelouze do not mention the melting-point of the stearine analyzed by them, and Artzbächer's melted at 60°·6, so that a comparison of their results with the others is not admissible.

			Lecanu.	Heintz.	Mean of mine.
Second melting-point			62°	62°	62°·5
C.	.	.	76·90	76·74	77·12
H.	.	.	12·44	12·42	12·30
O.	.	.	10·66	10·84	10·58

1·8297 grm. of this substance was saponified in a small flask by a solution of potash in alcohol; the alcohol nearly all distilled off in the water-bath; and water added, which formed a clear solution of the soap. This solution was heated in the water-bath till all smell of alcohol disappeared; the soap was decomposed by dilute sulphuric acid in slight excess, the liberated fatty acid allowed to collect and solidify; and the water containing the sulphate, or sulphoglycerate of potash, removed by a delicate pipette: it was slightly opalescent from precipitation of a small quantity of silica, which the potash had removed from the flask. The fatty acid was afterwards washed, till the washings ceased to leave any residue on evaporation, and till the acid ceased to lose weight by washing, and subsequent drying at 100°. It then weighed 1·7521 grm.

In a second similar operation, 1·4056 grm. of stearine afforded 1·3426 grm. of acid.

In a third operation, 1·0399 grm. of stearine afforded 0·9931 grm. of acid. A determination of the glycerine produced in this operation was also made; for that purpose, the solution of sulphate of potash, mixed with glycerine, was evaporated by a steam-heat nearly to dryness; dry carbonate of potash added; the glycerine extracted by absolute alcohol; and the alcoholic solution was filtered and evaporated over sulphuric acid in the air-pump vacuum till it ceased to lose weight. From the weight so obtained, was deducted that of the small quantity of sulphate and carbonate of potash left on burning off the glycerine. The glycerine weighed 0·093 grm.

The acid of each operation was fusible at 64°·7 into a perfectly limpid liquid.

These quantities compared to 100 parts of the stearine are as follows :

	I.	II.	III.	Mean.
Acid . . .	95·76	95·51	95·50	95·59
Glycerine . .	—	—	8·94	8·94

The acid, burned with chromate of lead, gave the following results :

   I. 0·2969 grm. of first operation gave :
      0·8258 ,, carbonic acid, and
      0·3320 ,, water.
  II. 0·3164 ,, of second operation gave :
      0·8787 ,, carbonic acid, and
      0·3572 ,, water.

These numbers correspond to the following percentages :

	I.	II.	Mean.
C.	75·85	75·74	75·79
H.	12·42	12·54	12·48
O.	11·73	11·72	11·73

The equivalent weight* of the acid was determined from its silver and soda salts. A portion of the acid was added to a solution of pure carbonate of soda, which was boiled till saponification was complete, and then evaporated to dryness ; the resulting soap was removed from the excess of carbonate of soda† by treatment with boiling absolute alcohol and filtration ; the alcoholic solution of soap was evaporated to dryness, and the remaining soda-salt dissolved in water ; and from this solution the silver-salt was prepared by pre-cipitating with nitrate of silver, washing the precipitate, and drying at 100°, keeping it protected as much as possible from daylight.

0·5893 grm. silver salt of acid of first preparation left on ignition 0·1638 grm. silver.

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* The term "equivalent weight," is here used in preference to that of "atomic weight," as the latter is not strictly applicable in respect to substances consisting of a mixture. In some instances in this paper, where this reason for its use does not apply, it has been retained for the sake of uniformity. Another reason was, that in speaking of equivalents it was not required to take into consideration the fact of the acid being bibasic, which would only have complicated the remarks that follow.

† Carbonate of soda dissolves in small, but, for questions of atomic weight, important quantities, in absolute alcohol ; but I have some reason to think that it is quite insoluble in an alcoholic solution of soap, which is just the opposite of what occurs with aqueous solutions, for here the carbonate of soda renders the soap insoluble. I had not an opportunity of fully investigating this point.

I. 0·4102 grm. soda salt of acid of second preparation afforded :
   0·0986   „   sulphate of soda.
II. 0·3415   „   of same salt afforded :
   0·0811   „   sulphate of soda.

A mixture of acids, of which 4 equivalents consist of **3** equivalents of stearic acid ($C_{34} H_{34} O_4$), and 1 of oleic acid ($C_{36} H_{34} O_4$), would require the following percentages :

	Calculated	Found.
C.	75·82	75·79
H.	12·45	12·48
O.	11·73	11·73

and in its salts :

	Calculated.	Found.	
		I.	II.
Silver . .	28·42	27·79	—
Sodium . .	7·89	7·85	7·76

It is not intended to be implied that the acid analysed actually consisted of stearic and oleic acids in the proportions indicated ; on the contrary, it must have contained, if any, only a trace of oleic acid ; the assumed mixture is taken only for the convenience of calculation, inasmuch as its composition and equivalent weight closely represent those found.

100 parts of the fat contained 77·12 of carbon ; the 95·62 parts of acid derived from them contained 72·44 parts of this carbon ; the difference, viz., 4·68, is all that went to form glycerine.

The equivalent weights of the fat and acid are obviously in the proportion of 100 : 95·62, but the equivalent weight of the acid, according to the foregoing determinations, is 273 ; hence, the equivalent weight of the fat must be 285, which agrees with what we might deduce directly from its own analysis.

It has hitherto been supposed that any fat, such as stearine, which on saponification is resolved into a certain acid and glycerine, consists of this acid combined with a hypothetical base, oxide of lipyl ($C_3 H_2 O$) ; and that the process of saponification is merely a case of substitution, 1 equivalent of the alkali or other oxide employed, changing places with 1 equivalent of the oxide of lipyl, and combining with the acid to form soap, while 2 equivalents of oxide of lipyl, together with 4 equivalents of water combine to form hydrated glycerine ($C_6 H_8 O_6$).

If this represented what took place in the present instance, the loss of carbon sustained by the fat on being converted into acid, should have been to the fat, in the proportion of 3 equivalents of carbon to 1 of fat, or $\frac{18}{285}=6\cdot31$ per cent of the fat. The actual loss was, however, only 4·65 per cent, a result which coincides closely with those found by Chevreul* in similar analyses of mutton, pork and human fats, each in the crude state. These fats, on being converted into acid, lost respectively 4·181, 4·685, 4·493 per cent of carbon.

Inasmuch as these fats were analysed by Chevreul in the crude state, while that which I operated upon was comparatively pure, it might be thought that, the conditions being thus different, any coincidence in the results can only have been accidental, and may have originated in a different source from that supposed, but Chevreul has left numerical data sufficient for making the calculations here required independently of the contrary hypothesis.

The crude acid which he obtained from these fats, when heated with oxide of lead, lost in each case the same quantity of water, viz., 3·65 per cent; its equivalent weight was therefore 246; consequently, the equivalent weights of the several fats were to 246 in the proportion of 100 to the percentage of acid obtained from them respectively, or as 100 : 96·5 for the mutton fat, 100 : 95·9 for the pork fat, and 100 : 96·18 for the human fat; that is, as 254, 256 and 255 respectively. Now, if 1 equivalent of each of these fats, on being converted into acid, had lost 3 equivalents of carbon, the difference between the quantity of carbon in 100 parts of the fat, and that in the percentage of acid obtained from it, should have been : in the case of the mutton fat, $\frac{18}{254}=7\cdot08$ per cent, in the case of the pork fat, $\frac{18}{256}=7\cdot03$ per cent, and in the case of the human fat $\frac{18}{255}=7\cdot05$ per cent.

If we admit that the proportion of the fat, which in saponification goes to form glycerine, contains not 3, but 2 equivalents of carbon, we come much nearer the actual result. The agreement between the calculated and found quantities is then as follows :

	Calculated.	Found.	Glycerine found represents
Purified mutton fat . .	4·21	4·68	3·498
Crude mutton fat . .	4·72	4·181	3·130
,, pork fat . . .	4·68	4·685	3·451
,, human fat . .	4·70	4·495	3·780

* Rech. Chim. sur les Corps Gras, Paris, 1823, 333—343.

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Further, upon the lipyl theory, the difference between a fat and the hydrated acid producible from it, is that the latter contains 1 equivalent of water (HO), instead of 1 equivalent oxide of lipyl (C_3H_2O) in the former; consequently, the oxygen in an equivalent of either should be the same; but the analyses do not support this view. The oxygen found in 100 parts fat and their equivalent of acid is as follows:

	Purified mutton.	Crude (Chevreul):		
		Mutton.	Pork.	Human.
Acid . . .	11·21	10·132	10·253	10·633
Fat . . .	10·58	9·304	9·756	9·584
Excess in acid	0·63	0·828	0·497	1·049

According to these experiments, the acid did not derive all its oxygen from the fat. Is the excess only apparent, and belonging really to the errors of experiment; or is it due to the circumstance of any oleic acid present in the acid undergoing oxidation during the operations of drying, weighing, &c.; or does it represent a definite quantity of oxygen taken up in the form of water during saponification? The latter is most probable; for, firstly, the concordance of all Chevreul's analyses with mine in showing an excess, would probably not have occurred, if it had been due to accident. Secondly, there must have been extremely little oleine in the fat, and a correspondingly small quantity of oleic acid in the acid which I operated upon; and if it had arisen from the absorption of oxygen by any oleic acid possibly present, this absorption being gradual would have been discovered by a gradual increase of ·007 to ·01 grm. in the weight of the acid in my determinations; but although the acid was kept melted and exposed to the air for hours, no increase of its weight occurred. Thirdly, Chevreul's experiments* show that free oxygen is not taken up in saponification; the only remaining source of this increase is therefore the water used. Other experiments, to be mentioned presently, show that when alcohol is used instead of water, saponification does not occur in the ordinary way.

Upon the supposition that in the formation of 4 equivalents of acid there is taken up 1 equivalent of water, I should have found the increase of oxygen 0·70 per cent; and in the fats analyzed by Chevreul it should have been 0·78 per cent for each.

As to the relation between the hydrogen in the fat and that in the acid, it is scarcely possible to arrive in this manner at any definite

* Rech. Chim. sur les Corps Gras, 323—329.

expression for it; for where a single equivalent of it does not, as in the present instance, amount to more than $\frac{1}{280}$th part of the substance, ordinary analysis can hardly decide between one equivalent more or less. The hydrogen in 100 parts fat, and in their equivalent of acid, appears from the analyses, as follows:

			Purified mutton.	Crude (Chevreul):		
				Mutton.	Pork.	Human.
Fat	.	. .	12·30	11·700	11·146	11·416
Acid	.	. .	11·93	11·553	11·234	11·040
			0·37	0·147	−0·088	0·376

With the exception of that of the pork fat, these analyses concur to show that the fat, on being converted into acid, loses hydrogen; the analysis of the pork fat shows an increase of 0·088 per cent in the acid.

Upon the supposition that the fat contains 1 equivalent of hydrogen more than the acid, I should have found a difference of 0·35; but this theoretical difference is reduced to 0·26, if we admit that the increase of oxygen has been taken up as an equivalent of water in the formation of 4 equivalents of acid. The hydrated acid contains 1 equivalent of basic hydrogen, which it did not derive from the fat; hence the conclusion is, that the part of the fat which goes to form the acid contains 2 equivalents of hydrogen less than the fat itself.

What I consider particularly established by the foregoing facts is, that an equivalent of fat, in being converted into one of acid, loses 2 equivalents of carbon; and that a given quantity of acid contains more oxygen and less hydrogen than the portion of fat from which it is derived.

Liebig and Pelouze* represented stearine by the formula $2\bar{S}t, GlyO, 2HO$, regarding it as analogous to sulphoglyceric acid; but Heintz has already remarked that the analyses, from which this formula was deduced, are at variance with those made by Lecanu, Artzbächer and himself, and, I may add, with those which I have made.

I have also made the following analyses of mutton stearine, which, after thirty-two crystallizations from ether, melted at 52°, 64°·2 and 69°·7, and furnished an acid melting at 66°·5. Burnt with chromate of lead:

* Ann. Ch. Pharm. XIX, 264; J. pr. Chem. 173; Ann. Ch. Phys. [2] LXIII, 146.

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    I. 0·2760 grm. gave :
        0·7745 ,, carbonic acid, and
        0·3050 ,, water.
    II. 0·3081 ,, gave :
        0·8652 ,, carbonic acid, and
        0·3360 ,, water.
    III. 0·2689 ,, gave :
        0·7218 ,, carbonic acid, and
        0·2927 ,, water.
    IV. 0·2974 ,, gave :
        0·8310 ,, carbonic acid, and
        0·3256 ,, water.
    V. 0·2887 ,, gave :
        0·8075 ,, carbonic acid, and
        0·3106 ,, water.

These numbers correspond to the following per cent :

	I.*	II.	III.	IV.	V.
C	76·53	76·56	76·02	76·20	76·28
H	12·27	12·11	12·10	12·16	11·95
O	11·20	11·33	11·88	11·64	11·77

The following analyses of beef stearine, having its several melting-points at 51°, 63° and 67°, were made with chromate of lead.

    I. 0·4709 grm. gave :
        1·3264 ,, carbonic acid, and
        0·5187 ,, water.
    II. 0·2873 ,, gave :
        0·8098 ,, carbonic acid, and
        0·3143 ,, water.

These numbers correspond to the following quantities per cent :

	I.	II.
C	76·87	76·87
H	12·24	12·15
O	10·89	10·98

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* Analyses I. and II. were made of the substance after it had been dried at 100° ; the others were made of the crystals from ether, after they had been dried over sulphuric acid in the air-pump vacuum till they ceased to lose weight. It is probable that the difference between the carbon in the two series of analyses, arose from the crystals in the latter case having retained a trace of ether, and hence, that the numbers in the first two analyses are most nearly correct.

Beef stearine has accordingly the same composition as mutton stearine. In beef stearine, having its second melting-point at 60°·6, Artzbächer* found 2 per cent more carbon. The difference in the purity, as indicated by the melting-point, of the substances which we analysed, cannot, I think, account for this discrepancy in our results. He has fallen into an error in supposing that his results agree with those of Chevreul and Lecanu; for in Chevreul's " Recherches Chimiques sur les Corps Gras," I can find no account of any ultimate analysis of either crude or purified beef fat; and Lecanu† appears to have analysed stearine from mutton fat only.

To 1·019 grm. of mutton stearine, having its second melting-point at 62°·5, and 3·075 grms. of pure oxide of lead in fine powder, absolute alcohol was added in quantity sufficient to dissolve the stearine readily when heated. The whole was kept boiling in the water-bath, and frequently agitated during four hours, the alcohol being replaced as it evaporated. At the end of this time the oxide of lead retained its yellow colour, and nearly the whole of the stearine was recovered unaltered, except for the admixture of a trace of impalpably fine oxide of lead. No lead-soap appeared to have been formed. The difference between the circumstances of this experiment and those of the ordinary process of forming lead-plaster, was that the water of the latter operation was replaced by alcohol, yet this was sufficient to prevent saponification.

The following experiment was performed before those already detailed, accordingly in the belief that the fats were analogous to ordinary salts, and that saponification consisted, as represented, in an exchange of places between the alkali employed and the oxide of lipyl or other base of the fat; the only question was, as to what this base was. The intention was to procure a body corresponding to ordinary glycerine, but in which the water taken up by the base of the fat, on its liberation and conversion into glycerine, should be substituted by ether.

The experiment consisted in acting in the first instance upon stearine by the compounds procured by the action of the alkali-metals on pure alcohol, which, from their analogy with the hydrates of the alkalies, have been called the ethylates of the alkalies by Dr. Williamson. Two grms. of sodium were dissolved in a quantity of absolute alcohol sufficient to dissolve 23·803 grms. of stearine, which were added. (The propor-

* Ann. Ch. Pharm. LXX, 239; Compt. Rend. des Trav. de Chim. 1849, 343.

† J. Pharm. [3] XX, 325; Ann. Ch. Phys. [2] LV, 192.

tions of sodium and stearine are nearly those of equivalent quantities, the sodium being slightly in excess.) The whole was boiled for some time, and on being allowed to cool, it stiffened into a jelly, showing that a soap had been formed; the alcohol was then distilled off in the water-bath, and the soap dissolved in water. On the surface of the solution an oily stratum formed, which was removed by a pipette, washed with water, and the washings added to the solution of soap. The soap, being decomposed by hydrochloric acid, the fatty acid was collected, washed, dried, and weighed; it amounted to 17·481 grms. The oily substance when dried, weighed 5·571 grms. A quantity of glycerine, which was not weighed, was found in the liquid from which the acid had been removed. The oily substance solidified on cooling into a semi-transparent mass, melting again at 29°. It dissolved readily in alcohol and ether. By crystallisation, from the former, its melting-point was raised to 33°·7. It did not crystallise from ether, was not sensibly affected by aqueous solution of potash, but was readily saponified by an alcoholic solution of potash. On distillation, the temperature rose gradually to 224° C., the substance came over partially decomposed, and a black mass remained in the retort.

The crystals from alcohol, after being dried over sulphuric acid in the air-pump vacuum till they ceased to lose weight, gave the following results when burned with oxide of copper:

> I. 0·3200 grm. gave:
>   0·8980 „ carbonic acid, and
>   0·3600 „ water.
> II. 0·4255 „ gave:
>   1·1720 „ carbonic acid, and
>   0·4920 „ water.
> III. 0·3273 „ gave:
>   0·8999 „ carbonic acid, and
>   0·3796 „ water.

These numbers correspond to the following percentages:

	I.	II.	III.
C.	76·53	75·12	74·99
H.	12·50	12·85	12·88
O.	10·97	12·03	12·13

Although the analyses are not satisfactory, there can be no doubt, after all these facts, that this is the same substance as the stearic

ether prepared by Redtenbacher.* In short, I prepared this substance in the same manner that he did; viz. by passing a current of hydrochloric acid gas into a solution of stearic acid in alcohol, and found all its physical characters the same as those of the substance prepared by the action of ethylate of soda upon stearine.

Here are the numbers obtained by Redtenbacher in the analysis of stearic ether:

$$
\begin{aligned}
&\text{C.} \quad . \quad . \quad . \quad . \quad 76 \cdot 13 \\
&\text{H.} \quad . \quad . \quad . \quad . \quad 12 \cdot 88 \\
&\text{O.} \quad . \quad . \quad . \quad . \quad 10 \cdot 99
\end{aligned}
$$

In order to determine whether any more volatile products were formed in this reaction, $0 \cdot 8187$ grm. of stearine was acted upon by a quantity of ethylate of soda containing $0 \cdot 0772$ grm. of sodium. The stearine was placed in a tube inside a small flask, in such manner that no communication occurred between the stearine and the ethylate of soda, till the flask was filled with alcohol vapour, and all the air expelled from it. The orifice of a conducting tube, inserted in the neck of the flask, was then introduced under a mercury barometer standing in a mercury trough; by a slight inclination of the flask, the melted stearine was allowed to flow out of the tube into the ethylate of soda, the heating being continued. By this arrangement, any gaseous products formed in the decomposition would have been collected above the mercury in the barometer, and have produced a depression corresponding to their elastic force; but there were none, unless alcohol vapour; for the depression of the column was only from $30° \cdot 15$ inches before the operation, to $28° \cdot 6$ after it, or $1 \cdot 55$ inch, the temperature being $20°$; and the same depression exactly was produced by a few drops of alcohol admitted into another similar barometer. Stearic ether was found to have been formed.

When stearic acid is substituted for stearine in this reaction, no ether is produced. To a quantity of ethylate of soda, containing $0 \cdot 02$ grm. of sodium, $0 \cdot 25$ grm. of stearic acid was added; stearate of soda was the only product.

Amylate of soda was formed by adding $0 \cdot 445$ grm. of sodium to pure amylic alcohol, and to this $5 \cdot 46$ grms. of stearine were added; a quantity of oily substance was formed which, being freed from soap by washing, and from amylic alcohol by being heated in an oil-

* Ann. Ch. Pharm. XXXV, 51.

bath for some time at 185°, melted at 25°·5, and was in every respect similar to stearate of amyl prepared by passing hydrochloric acid gas into a solution of stearic acid in amylic alcohol. At temperatures below its melting-point, it was semi-transparent, soft and glutinous ; above its melting-point, it passed into a clear transparent fluid; it was readily soluble in alcohol and ether ; it solidified as a jelly on cooling its solution in the former by a freezing-mixture, but did not crystallise from either ; it was not acted upon by aqueous solution of potash, but was readily converted by an alcoholic solution of potash, into stearate of potash and amylic alcohol, which then exhaled its well-known odour.

When palmitine was substituted for the stearine, a corresponding result was obtained. To 0·231 grm. of sodium in amylic alcohol 2·598 grms. of palmitine, having its second melting-point 61°, were added. After boiling for some time, a solution of chloride of calcium in amylic alcohol was added, which gave a precipitate ; every trace of the amylic alcohol was afterwards driven off ; nothing else escaped at the same time ; the residue was digested successively with anhydrous ether, absolute alcohol, and water. The ether, when filtered and evaporated, left 0·693 grm. of a substance having a close resemblance to the stearate of amyl, but melting at 13°·5. Its solution in alcohol, when cooled by a freezing-mixture, became opaque and gelatinous, but not sensibly crystalline. It resembled in every respect palmitate of amyl, which I prepared in the ordinary way with palmitic acid from the same specimen of palmitine.

Burned with oxide of copper and chlorate of potash, 0·246 grm. gave 0·709 grm. carbonic acid and 0·286 grm. water, which correspond to the following numbers per cent :

	Found.	Calculated.
C_{42}	78·60	77·30
H_{42}	12·91	12·88
O_4	8·48	9·82

The excess of carbon found may have arisen from the palmitine used containing oleine, or a trace of some other fat. I had not enough substance to repeat the analysis.

What was removed by treatment of the lime-soap with alcohol consisted of glycerine, a small quantity of palmitate of amyl, some palmitate of lime, and chlorides.

Water removed inorganic salts only.

When in these decompositions of stearine and palmitine, the proportion of sodium was increased beyond that of 1 equivalent, the quantity of ether obtained diminished, and eventually, with a quantity of sodium which was certainly not less than 2 equivalents, no ether was obtained.

I need hardly state that the effect was similar when ethylate of potash was used. A solution of anhydrous ammonia in absolute alcohol, and which from analogy is ethylate of ammonia, seemed to produce no change on stearine, even when boiled with it for some time.

Considering this reaction of importance with reference to saponification and the constitution of the fats, I have repeated it under every variation of circumstances deemed likely to elicit its explanation, but the preceding are the principal results obtained; and, although several probable reasons might be assigned for it, I know none that can at present be advanced with much confidence.

It is interesting to observe that, while the ethers formed by stearic and palmitic acids, with vinous alcohol, melted respectively at $33°·7$ and $21°·5$,* the corresponding ethers of these acids with amylic alcohol melted at $25°·5$ and $13°·5$; showing an elevation of melting-point with an increase of atomic weight in the acid, and a depression of melting-point with an increase of atomic weight in the alcohol. I was unsuccessful in the attempt to obtain those of methylic alcohol, by passing hydrochloric acid gas into a solution of the acids in purified wood spirit. Should the character alluded to be found to be an instance of a general law as regards the series of fatty acids, we might predicate that cetine and substances of its class are not ethers.

ACTION OF PERCHLORIDE OF PHOSPHORUS ON GLYCERINE.

The intimate connection between the subject principally discussed in this paper and that of the constitution of glycerine, obviously requires that any conclusion admitted of the former must be controlled by results established of the latter. The inferences to be drawn from the results obtained with stearine are not easily reconciled with what is at present admitted of the constitution of glycerine. For this reason, it was intended to investigate the action of perchloride of phosphorus on glycerine.

When glycerine is added to perchloride of phosphorus, a strong

* Frémy found palmitic ether, prepared by means of sulphuric acid, to melt about $21°$ (Ann. Ch. Pharm. XXXVI, 46).

heat is developed, the mixture becomes glutinous, and in the cold hard.   On treatment with water, or better, with carbonate of soda, a substance considerably denser than water, and very like precipitated silica, is obtained.   In performing the reaction, it is advisable to have the glycerine as concentrated as possible, to add it in small quantities to the perchloride, stirring the mixture after each addition, and to cease adding glycerine as soon as all the perchloride is decomposed.   When the glycerine contains much water, or is added at once in large quantity, the perchloride is resolved chiefly into phosphoric and hydrochloric acids, which have the power of dissolving, and at the same time decomposing the new product afterwards formed.   The operator must protect himself, particularly his eyes, from the action of the hydrochloric acid fumes necessarily produced in large quantity.

A portion of this new substance was washed till free from every trace of hydrochloric and phosphoric acids, then fused with pure soda; in the nitric acid solution of the fused mass, nitrate of silver gave a copious precipitate of chloride of silver.   Nitric acid has very little action on it in the cold, but when warmed dissolves it readily. This solution, rendered alkaline by ammonia, gave no precipitate with sulphate of magnesia.   It therefore contains chlorine, but no phosphorus.   It dissolves readily in cold solution of potash, very slowly in boiling solution of ammonia, very slowly also in boiling solution of acetic acid; it is not reprecipitated from any of these reagents by neutralisation; it seems quite insoluble in alcohol and ether.   Cold water does not act upon it; but when kept in boiling water, it is very slowly dissolved, being converted into a substance which, on evaporation of its solution, remained as a hard, perfectly transparent body, highly hygrometric, absorbing in a damp atmosphere in four days its own weight of water, and being converted thereby into a glutinous mass.   The aqueous solution of this latter substance was found acid to test-paper, but gave no reaction for hydrochloric or phosphoric acid, and did not appear to decompose bicarbonate of soda.   The hydrochloric acid solution of the original substance being neutralised, was examined for glycerine; it furnished none.   Hydrochloric acid converts it probably into the same substance, as does water.

I was prevented from analysing these substances by the circumstance of my period of study terminating.