Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Chemistry. — *"On the Saponification of Fats."* II. By Dr. J. P. TREUB. (Communicated by Prof. S. HOOGEWERFF).

(Communicated in the meeting of June 30, 1917.)

§ 1. In a previous paper [1]) equations were derived for the case that saponification takes place in emulsion, which equations indicate the quantities of glycerine and fatty acid present in free state after an arbitrary time.

These equations are:

$$g = 1 - \frac{2pq}{(2p-3)(q-3)} e^{-3kt} + \frac{3q}{(2p-3)(q-2p)} e^{-2pkt} - \frac{6p}{(q-3)(q-2p)} e^{-qkt} . \quad (1)$$

$$T = 1 - \frac{1+(2p-1)(q-2)}{(2p-3)(q-3)} e^{-3kt} + \frac{2(q-p)}{(2p-3)(q-2p)} e^{-2pkt} - \frac{2p}{(q-3)(q-2p)} e^{-qkt} . \quad (2)$$

Equation (1) represents: the fraction of the total number of molecules of glycerine, present after the time t in free state. (Relative concentration of the free glycerine after the time t).

Equation (2) expresses · the relative concentration of the free fatty acid after the time t.

In these equations p and q represent: the increase of concentration of di- resp. monoglycerides at the surface of contact between fat- and waterphase, in consequence ot the adsorption.

When the velocity constant k is not constant in reality (as in the saponification in emulsion, where the surface of contact between fat- and water phase constantly varies in size), the equations (1) and (2) have no physical meaning *each in itself*. When, however, we eliminate $k \times t$, which is possible for different numerical values of p and q, we arrive at equations of the general form $f(g, T) = 0$, which give the connection between the relative concentrations of free glycerine and free fatty acid for the assumed values of the adsorption constants p and q. As was proved [2]) these equations are independent of the variability of the constant of velocity k.
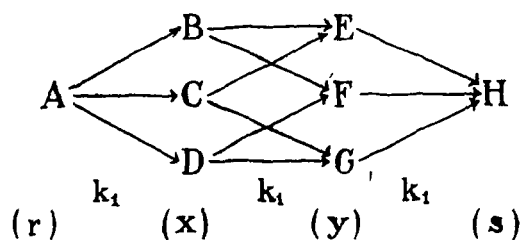
In the saponification in emulsion complications make, therefore, their appearance, which in some cases entirely cover the stagewise

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[1]) These Proc. **20**, 35 (1916).
[2]) loc. cit. 41.

course of the saponification (saponification in alcalic surroundings), and it is now of importance more closely to examine the ideal case, in which such complications do not appear.

Let us consider the saponification of triacetine in solution, and let us assume that the three ester-groups are perfectly equivalent [1]). Then the saponification takes place according to the following scheme:

$$
\begin{array}{ccccc}
 & B & \longrightarrow E & & \\
A & \longrightarrow C & F & \longrightarrow H \\
 & D & \longrightarrow G & & \\
 & k_1 & k_1 & k_1 & \\
(r) & (x) & (y) & (s) &
\end{array}
$$

In this A represents the triglyceride, B, C, and D the diglycerides, E, F, and G the monoglycerides and H glycerine. Let the number of molecules of each of these substances, present after a time t, be represented by r, x, y, and s, in which x and y indicate the number of molecules of the three di- resp. monoglycerides each taken separate, and let the constant of velocity at the splitting off of each fatty acid group be k_1.

Then the equations of velocity are:

$$-\frac{dr}{dt} = 3k_1 \cdot r.$$

$$\frac{dx}{dt} = k_1 r - 2k_1 \cdot x,$$

$$\frac{dy}{dt} = 2k_1 x - k_1 y,$$

$$\frac{ds}{dt} = 3k_1 y.$$

Starting from a molecules of triglyceride, we may calculate from this that the number of molecules of the different stages present after a time t amounts to the values from column 2 of table 1.

The relative concentrations (fraction of the total possible number of molecules) of each of the glycerides is, therefore, represented by the values from column 3 of table 1. The sum of these relative concentrations is of course, always $= 1$.

When we now finally calculate the number of molecules of acetic acid (z) split off after the time t, we find from $z = 3 (x + 2y + s)$:

$$z = 3a (1 - e^{-k_1 t}).$$

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[1]) With regard to the validity of this assumption cf. § 3 and 4.

T A B L E I.

1	2	3
Glycerides	Number of molec. present after the time t.	Relat. concentrations after the time t
Triglyceride	$r = a . e^{-3k_1 t}$	$v = e^{-3k_1 t}$
Diglyceride	$3x = 3a . e^{-2k_1 t}(1-e^{-k_1 t})$	$d = 3e^{-2k_1 t}(1-e^{-k_1 t})$
Monoglyceride	$3y = 3a \; e^{-k_1 t}(1-e^{-k_1 t})^2$	$m = 3e^{-k_1 t}(1-e^{-k_1 t})^2$
Glycerine	$s = a . (1-e^{-k_1 t})^3$	$g = (1-e^{-k_1 t})^3$

Where now $3a$ molecules of acetic acid are possible, the relative concentration T of the free acetic acid is:

$$T = 1 - e^{-k_1 t}$$

The two relative concentrations which are of most importance here, are those of the free fatty acid and of the free glycerine, viz.:

$$g = (1-e^{-k_1 t})^3 \quad . \quad . \quad (3) \quad \text{and} \quad T = 1-e^{-k_1 t} \quad . \quad . \quad (4)$$

from which follows:

$$g = T^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or in words:

In case of stagewise saponification of an ester of a tri-valent alcohol (with equivalent OH groups) and a univalent acid, the relative concentration of the free alcohol, independent of time, is always equal to the third power of the relative concentration of the free acid, provided that no complications (as in case of saponification in emulsion), take place.

When we saponify an ester of a trivalent acid and a univalent alcohol, the reverse holds of course.

The equations (3) and (4) may be derived from (1) and (2) by putting $p = q = 1$.

We may now apply our considerations also to the opposite case, viz. the esterification of glycerine with the equivalent quantity of acetic acid.

In this case the reaction is bimolecular, as the reaction velocity is not only dependent on the number of still unesterized OH groups, but also on the number of molecules of free fatty acid. When we, therefore, draw up equations of velocity as in the case of triglyceride saponification, i e. when in our equations we only express the number of free OH groups, which can become esterized, and *not* the number of acetic acid molecules available to bring about this

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esterification, the velocity constant k_2 occurring in this equation [1]) will in reality not be constant, but vary with the acetic acid concentration, hence with the time.

The formulae for g and T, which we obtain by integration from these equations of velocity, will then have no physical meaning in themselves. If, however, $k_2 \times t$ is eliminated, which is always possible, the equation obtained gives the connection existing between g and T at any moment of the esterification, and that independent of the variation of k_2.

The equations of velocity drawn up like this for the esterification run:

$$-\frac{ds}{dt} = 3k_2 \cdot s,$$

$$\frac{dy}{dt} = k_2\, s - 2k_2\, y,$$

$$\frac{dx}{dt} = 2k_2\, y - k_2 \cdot x$$

$$\frac{dr}{dt} = 3k_2 \cdot x,$$

from which after integration and introduction of the relative concentrations, follows:

$$g = e^{-3k_2 t}, \text{ and } T = e^{-k_2 t}, \text{ and therefore } g = T^3.$$

We see, therefore, that $g = T^3$ holds both for the reaction in saponifying sense and for that in esterizing sense. It follows from this that when the two reactions take place at the same time (i. e. when an equilibrium sets in) $g = T^3$ holds likewise.

This may be proved as follows:

For the reaction of equilibrium holds:

$$\frac{dg}{dT} = \frac{dg_1 + m\, dg_2}{dT_1 + m\, dT_2},$$

when $\dfrac{dg_1}{dT_1}$ refers to the reaction in saponifying sense, and $\dfrac{dg_2}{dT_2}$ to the reaction in esterizing sense, in which m is a quantity varying with the time.

Because at any moment:

$$\frac{dg_1}{dT_1} = \frac{dg_2}{dT_2} = 3T^2$$

also

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[1]) We shall denote here and later the velocity constant in saponifying sense by k_1, that in esterising sense by k_2.

$$\frac{dg}{dT} = 3T^2,$$

independent of the value of m.

As further the equilibrium reaction begins at the same point as one of the finishing reactions (viz. $g = T = 0$, or $g = T = 1$), the equation $g = T^3$ must hold also for the equilibrium reaction:

$$g = T^3.$$

If the saponification did *not* take place stagewise, but if triacetine directly split up into glycerine and acetic acid, then $1/n$ of the acetic acid would be present in free state, when $1/n$ of the glycerine was split off, so that in this case the relative concentrations of glycerine and acetic acid would be equal to each other. For the esterification of equivalent quantities of glycerine and acetic acid the same thing holds of course.

The comparison of the relative concentrations of initial resp. final products furnishes, therefore, a direct quantitative proof whether or no a reaction takes place in stages.

§ 2. The case of the saponification of triacetine in aqueous solution is not easy to study experimentally on account of the difficulty to determine the free glycerine here quantitatively.

Esters, for which free alcohol and free acid is easier to determine, are the fats. Glycerine is soluble in water, the glycerides of the higher fatty acids are hardly so, no more than these fatty acids themselves, so that the split off glycerine will be easily separated from it.

The slight solubility in water of the higher glycerides, however, involves that most of the saponification processes do not take place in solution, but in emulsion.

A procedure, however, that takes place in solution at least partially, is the so-called sulphuric acid saponification.

Van Eldik Thieme[1] has isolated the lower glycerides in this method of saponification, which quantitatively proves the stagewise course of the reaction.

The method comes to this: 5—10°/₀ strong sulphuric acid is added to the fat, which is heated to 120° or higher. The action of the acid is allowed to continue for some time, then the reaction product is led into boiling water, and the formed emulsion is boiled, till the required degree of decomposition is attained.

During the first phase of the process the reaction takes place in solution. The action of the sulphuric acid is here twofold: 1 the

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[1] Thesis for the Doctorate, Delft 1911. J. f. pr. Chem. (2) 85 284 (1912).

strong acid acts saponifying; and 2 it attacks the double binding of the oleic acid present, in consequence of which this is partially found back after the operation is over (saponification in emulsion and distillation), as iso-oleic acid, which is solid at the ordinary temperature. Accordingly this method of saponification is applied, when a yield of solid fatty acid as high as possible is desired.

In order to examine the stagewise course of the saponification with strong sulphuric acid quantitatively, it is necessary to start from a saturate triglyceride in order to avoid this complication. A suitable material is the trilaurine (to be prepared from Tangkallak-fat by re-crystallisation from alcohol), the same triglyceride that was used by van Eldik Thieme

After repeated futile attempts to isolate the partially saponified fat without further saponification in emulsion taking place, the following method was applied :

5 grammes of trilaurine were carefully weighed in a glass beaker of 250 cc. It was carefully melted, a certain quantity of strong sulphuric acid was added, and everything was thoroughly mixed. Then the glass beaker was covered by a watch glass, and left for some time either in a drying oven, or at room temperature, during which the stirring was several times repeated.

After the fixed time had elapsed, the beaker was cooled in ice, and in order to separate glycerine and sulphuric acid from the glycerides and the fatty acid, as much pounded ice was added as was necessary to keep the temperature under 0° C. After mixing, ether was added and it was all brought into a cock-funnel. After shaking and separation of the layers [1]) the water layer was poured off as sharply as possible, and collected for the determination of the quantity of free glycerine.

The ether layer was rinsed with alcohol in a flask and titrated with alcoholic KOH to fix the quantity of split off fatty acid. In this titration a little sulphuric acid is always also titrated. This was gravi-metrically determined after evaporation of ether and alcohol, decomposition of the soap with hydrochloric acid, and removal of the fatty acids with ether, and then deducted.

The glycerine water was repeatedly shaken with ether to remove traces of glycerides, then boiled till all the ether (and alcohol originating from the ether) had again been removed. Then the glycerine was determined by oxidation with potassium bichromate of known strength,

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[1]) If a sufficient quantity of sulphuric acid is present a good separation is obtained in a few minutes.

and retitration with sodium thiosulphate according to STEINFELS' method[1].)

The results obtained thus are recorded in table 2 (curve A of the
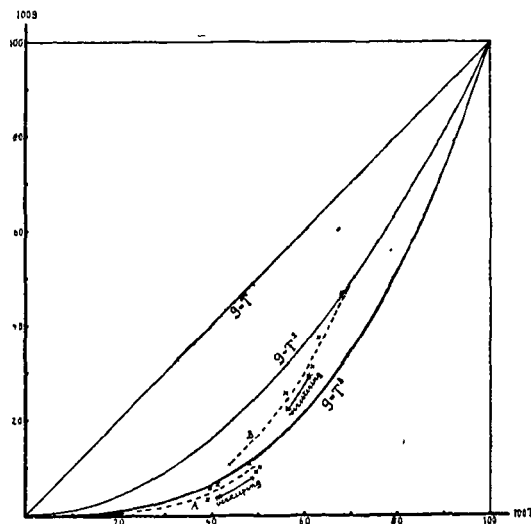
figure). The relative concentrations have here been both given in percentages. It appears that within a short time a state of equilibrium is reached, the situation of which varies with the concentration of the sulphuric acid.

T A B L E 2.
Saponification of Trilaurine.

1	2	3	4	5	6	7	8
Time of action (about)	Temperature	Strength of the H_2SO_4	Number of cc. H_2SO_4 to 5 gr. of trilaurine	100 T (found)	100 g. calcu-lated	found	Remarks
1 uur	60°	91.5%	15	39.6	6.2	5.7	
1 »	90	»	»	41.3	7.0	6.4	
2 »	95	»	»	54.0	15.8	(4.9)	carbonization!
4 »	75	»	5.5	39.0	5.9	3.1	
3 »	75	95%	0.25	15.35		—	
1 »	60	»	40	49.4	12.1	8.9	
1 »	20	»	30	50.4	12.8	10.0	
15 min.	20	»	20	48.1	11.15	10.7	

[1]) Seifens. Ztg. **42** 721 (1915).

Somewhat less split off glycerine was always found than corresponds with $g = T^3$. The deviation is slight, but on an average more than the error of observation. In § 3 the importance of this will be further set forth.

As, on account of the setting in of the equilibrium, only a small region could be examined in the saponification, it was tried to complete the found curve by starting from equivalent quantities of glycerine and laurinic acid, and esterizing this in strong sulphuric acid. The procedure was here quite identical with the preceding case, instead of 5 grams of trilaurine 4.705 grams of laurinic acid and 0.710 gram of glycerine were now weighed.

The results obtained in this way are collected in table 3 (curve B of the figure).

It appears that in the esterification always more free glycerine is present than corresponds with $g = T^3$, and the more as the esterification has proceeded less far.

It is now the question: how are the deviations found in the saponification and the esterification, to be accounted for?

TABLE 3.

Esterification of laurinic acid with glycerine

1	2	3	4	5	6	7	8
Time of action (about)	Temperature	Strength of the added H_2SO_4	Number of cc. H_2SO_4 to 4.705 gr. laurinic acid and 0.710 gr. of glycerine.	100 T found	100 T^3	100 g found	100 T_2
5 hours	20°	95%	20	43.8	8.4	10.6	19.2
1 „	„	„	„	55.9	17.45	25.8	31.25
20 min.	„	„	„	61.75	23 5	31 3	38.1
10 „	„	„	„	63.1	25.1	37.3	39.8
5 „	„	„	„	67.9	31.3	46.9	46.1

§ 3. Shortly after I had obtained the results recorded in tables 2 and 3 I imagined the question to be as follows: In virtue of the fact that secondary esters are on the whole more slowly saponified than primary ones it is natural to expect that the middle ester group of the triglyceride will also be slower to react than the two others. We may then expect in the saponification that $g < T^3$. If on the other hand laurinic acid with glycerine is esterized, the secondary alcohol group will probably also in this case react more slowly.

It seemed explicable to me therefore that in the esterification reversely $g > T^3$ was found. On second thoughts the latter, however, appeared to be entirely erroneous.

Let us first study the saponification of the triglyceride, and let the velocity constant of the saponification of the secondary ester-group be $= p \cdot k_1$, those of the two primary estergroups $= k_1$. Then we obtain the following scheme:
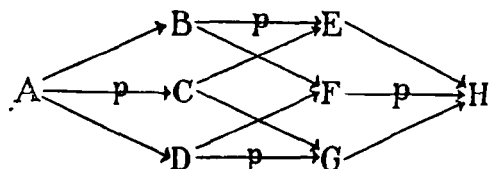
In the calculation of the relative concentrations of the different mono- and di-glycerides we must now bear in mind that these concentrations are *not* mutually equal.

We now find that after the time t:

$$g = (1 - e^{-pk_1 t})(1 - e^{-k_1 t})^2 . \qquad \ldots \ldots \quad (6)$$

$$T = 1 - \tfrac{1}{3} e^{-pk_1 t} - \tfrac{2}{3} e^{-k_1 t}. \qquad \ldots \ldots \quad (7)$$

If in these equations we substitute $p = 1$, we of course find back the equations (3) and (4).

It is now the question: what is the situation of the curve $f(g, T) = 0$, when $p \gtrless 1$, with regard to the curve $g = T^3$.

For $p \gtrless 1$ we have according to (6):

$$g = (1 - e^{-k_1 t})^2 . (1 - e^{-pk_1 t}) = (1 - e^{-k_1 t})^3 . \frac{1 - e^{-pk_1 t}}{1 - e^{-k_1 t}},$$

or

$$g = (1 - e^{-k_1 t})^3 . \left\{ 1 + \frac{e^{-k_1 t} - e^{-pk_1 t}}{1 - e^{-k_1 t}} \right\} . \qquad \ldots \ldots : \quad (8)$$

Further:

$$T = 1 - \tfrac{2}{3} e^{-k_1 t} - \tfrac{1}{3} e^{-pk_1 t} = 1 - e^{-k_1 t} + \tfrac{1}{3} (e^{-k_1 t} - e^{-pk_1 t}),$$

or

$$T = (1 - e^{-k_1 t}) \left\{ 1 + \tfrac{1}{3} \frac{e^{-k_1 t} - e^{-pk_1 t}}{1 - e^{-k_1 t}} \right\} \qquad \ldots \ldots \quad (9)$$

If we now put the fraction:

$$\frac{e^{-k_1 t} - e^{-pk_1 t}}{1 - e^{-k_1 t}} = \Delta ,$$

in which, therefore Δ is positive or negative according as p is greater or smaller than unity, the following equation follows from (8):

$$g = (1 - e^{-k_1 t})^3 . (1 + \Delta) \qquad \ldots \ldots \ldots \quad (10)$$

and from (9)

$$T = (1 - e^{-k_1 t})(1 + \tfrac{1}{3}\Delta)$$

or

$$T^3 = (1 - e^{-k_1 t})^3 (1 + \tfrac{1}{3}\Delta)^3 . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

From (10) and (11) follows:

$$\frac{g}{T^3} = \frac{1 + \Delta}{(1 + \tfrac{1}{3}\Delta)^3} = \frac{1 + \Delta}{1 + \Delta + \tfrac{1}{3}\Delta^2 + \tfrac{1}{27}\Delta^3} \quad . \quad . \quad . \quad (12)$$

This fraction is always < 1, also when Δ is negative, because the third power term can never preponderate. The latter is easily proved as follows:

If $\Delta < 0$, it is required for the preponderance of the 3rd power term that:

$$-\tfrac{1}{27}\Delta^3 > \tfrac{1}{3}\Delta^2, \text{ hence } \Delta < -9,$$

hence:

$$e^{-k_1 t} - e^{-p k_1 t} < -9 + 9 e^{-k_1 t},$$

or

$$8 e^{-k_1 t} + e^{-p k_1 t} > 9,$$

and this can never be fulfilled, because $e^{-k_1 t}$ and $e^{-p k_1 t}$ are always smaller than 1.

It follows therefore from what precedes that when p deviates from the value 1, no matter whether $p > 1$, or < 1, always *less* glycerine will be liberated during the saponification than corresponds with $g = T^3$.

§ 4. Let us now consider the esterification which proceeds according to the same scheme. Then we find:

$$g = e^{-(p+2) k_2 t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and

$$T = \tfrac{1}{3} e^{-p k_2 t} + \tfrac{2}{3} e^{-k_2 t} . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

We now put the question: what is for values of $p \gtrless 1$ the situation of the $f(g, T) = 0$ determined by (13) and (14) with regard to the curve $g = T^3$.

We find from (13) and (14) in the same way as before:

$$g = e^{-3 k_2 t} . \left\{ 1 + \frac{e^{-p k_2 t} - e^{-k_2 t}}{e^{-k_2 t}} \right\} . \quad . \quad . \quad . \quad (15)$$

and

$$T = e^{-k_2 t} . \left\{ 1 + \tfrac{1}{3} \frac{e^{-p k_2 t} - e^{-k_2 t}}{e^{-k_2 t}} \right\} \quad . \quad . \quad . \quad (16)$$

Let us put the fraction:

$$\frac{e^{-p k_2 t} - e^{-k_2 t}}{e^{-k_2 t}} = \Delta,$$

in which Δ is now positive or negative according as p is smaller or greater than unity. Then follows again from (15) and (16):

$$\frac{g}{T^3} = \frac{1 + \Delta}{(1 + \frac{1}{3}\Delta)^3} < 1 \quad \ldots \quad \ldots \quad (12)$$

We see therefore that also in the esterification g is always $< T^3$, when p departs from the value 1, as here too $\Delta < -9$ is impossible.

When now equilibrium sets in, the reactions in saponifying and esterizing sense take place simultaneously. When one estergroup deviates from the two others, every change in either direction leads to a relation $g < T^3$. in other words $g < T^3$ holds also here for the reaction of equilibrium.

When we shortly sum up what precedes, it appears that:

Both in the saponification of triglycerides and in the esterification of equivalent quantities of glycerine and fatty acid the relative concentration of the free glycerine is equal to or smaller than the third power of the relative concentration of the free fatty acid, according as the different groups are equivalent or not, provided no further complications (as e. g. in the saponification in emulsion) take place.

The situation of the experimentally determined curve A (see the figure) under the curve $g = T^3$ can therefore have been caused either by a saponification of the secondary estergroup that proceeds more rapidly and by one that proceeds less rapidly compared with the primary ester groups.

It is, however, natural to assume that the latter is the case.

§ 5. After the foregoing it is clear that the experimentally determined curve B of the figure can never find its explanation in inequivalence of the ester groups; accordingly there must be another reason that causes g to be $> T^3$ in the esterification. This reason is probably the bivalence of the sulphuric acid which serves as medium.

To realise this let us first inquire a little more closely into the process of saponification:

When trilaurine is put in contact with sulphuric acid, addition compounds are formed. The sulphuric acid is very loosely bound in these compounds, in water it is immediately split off again. The binding between sulphuric acid and laurinic acid may perhaps be most fitly compared with that between water and salt in a salt hydrate. However this may be, the saponification may now be imagined as follows:

The sulphuric acid bound to an estergroup, expels the laurinic acid from it under formation of glycerine sulphuric acid, so that, finally glycerine trisulphuric acid is formed. This may be expressed as follows:

$$CH_2OOC . R (H_2SO_4) \rightarrow CH_2OSO_2OH (R . COOH)$$
$$CH OOC . R (H_2SO_4) \rightarrow CH OSO_2OH (R . COOH)$$
$$CH_2OOC . R (H_2SO_4) \rightarrow CH_2OSO_2OH (R . COOH)$$
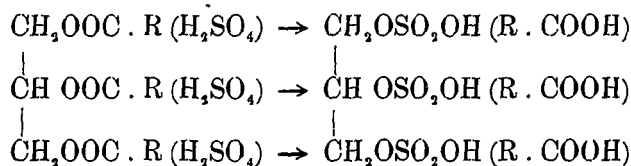
What takes place now on the other hand in case of esterification in sulphuric acid surroundings? When glycerine, laurinic acid, and sulphuric acid are mixed the glycerine will immediately be bound with the sulphuric acid, but certainly not *only* glycerine trisulphuric acid will be formed then. When a molecule of sulphuric acid combines with one of the alcohol groups of the glycerine, the chance is great that the free acid group of the sulphuric acid still combines with a second alcohol group of the same glycerine molecule, and that we therefore get the compounds:.

$$O_2S\begin{cases} O-CH_2 \\ O-CH \\ H_2C-O . SO_2 . OH \end{cases} \quad \text{and} \quad O_2S\begin{cases} O-CH_2 \\ HC-O . SO_2 . OH \\ O-CH_2 \end{cases}$$
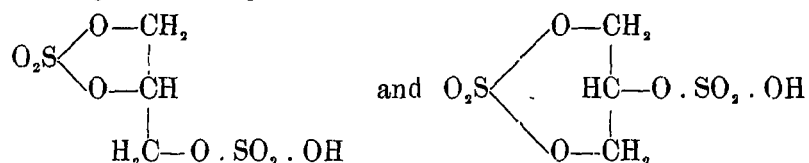
i.e. sulphates of glycerine mono sulphuric acid.

We may imagine the esterification of these sulphates as follows:

$$CH_2-O\begin{cases} \\ CH-O \end{cases}SO_2 (R . COOH) + R . COOH (H_2SO_4) \xrightarrow{(1)} \begin{array}{l} CH_2 OOC . R (H_2SO_4) \\ CH OOC . R (H_2SO_4) \end{array}$$

$$CH_2-O . SO_2 . OH (R . COOH) \xrightarrow{(2)} CH_2 OOC . R (H_2SO_4),$$
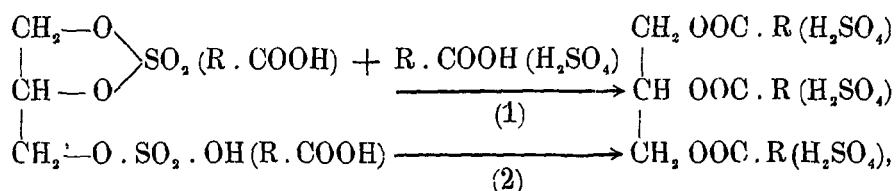
i.e. the two OH groups that are bound to one molecule of H_2SO_4 are esterized at the same time.

Let us now examine what relation there will be between the relative concentrations of free glycerine and free laurinic acid. Let us put the "constant of velocity" $= pk_2$ for reaction (1), and $= k_2$ for reaction (2), we obtain the following scheme for the esterification:

$$\begin{array}{ccccc} & \overset{k_2}{\nearrow} B & \overset{p.k_2}{\searrow} \\ A & & & D \\ & \underset{p.k_2}{\searrow} & C & \overset{k_2}{\nearrow} \end{array}$$

$$(s) \qquad (y) \qquad (x) \qquad (r)$$
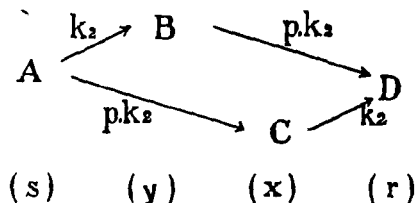
In this A represents the glycerine, which can be converted to monoglyceride B with a "velocity constant" k_2, and into diglyceride C with a "velocity constant" pk_2. Either of these can be converted into triglyceride D with the given "constants of velocity".

When we now determine the equations of velocity, then p and k_2 occur in them, which are both variable:

$$-\frac{ds}{dt} = (p + 1)\,k_2\,.\,s,$$

$$\frac{dy}{dt} = k_2\,.\,s - pk_2\,.\,y,$$

$$\frac{dx}{dt} = pk_2\,.\,s - k_2\,.\,x,$$

$$\frac{dr}{dt} = k_2\,.\,x + pk_2\,.\,y.$$

We may, however, put p and k_2 constant during a short period from the beginning of the reaction, and ascertain the form of $f(g, T) = 0$ at the end of this short period.

As was already discussed before, k_2 does not occur in this last function, from which follows that $f(g, T) = 0$ is independent of the value and of the variations of k_2. It is now, however, the question whether the factor p can likewise be eliminated, or whether it remains in the equation. In the former case $f(g, T) = 0$ is also independent of p, in the latter case it is not. It is, of course, directly to be seen that the factor p will certainly have influence, and can, therefore, not be eliminated.

This, however, causes the relation holding at the end of the short period that p is considered constant, to change if the reaction progresses. From this results that the found $f(g, T) = 0$ does not hold throughout the course of the reaction, but only represents a curve which may be serviceable as an orientation whether $g > T^2$ is possible at the supposition made.

Moreover when equilibrium comes near, the reaction in opposite sense begins to exert more and more influence. In view of the fact that the sulphates considered are esterized to glycerides, but are not restored to their original form by the opposite reaction, it is clear that at last the same equilibrium is reached as' in the saponification of triglyceride.

It is, therefore, now the question: is there an initial value of p to be found by means of which the curve B found experimentally is to be explained.

Integration of the equations of velocity yields for the relative concentrations of free glycerine and free fatty acid after the very short time t:

$$g = e^{-(p+1)k_2 t} \qquad \ldots \ldots \ldots \ldots \quad (17)$$

and:

$$T = \tfrac{1}{3} \{ 2e^{-pk_2 t} + e^{-k_2 t} \} \qquad \ldots \ldots \ldots \quad (18)$$

from which:

$$T = \tfrac{1}{3} \left\{ \frac{p}{2g^{p+1}} + \frac{1}{g^{p+1}} \right\} \qquad \ldots \ldots \ldots \quad (19)$$

Equation (19) gives for:

$$p = 1 \qquad T = g^{1/2} \qquad \text{or} \qquad g = T^2$$

$$p = 2 \qquad T = \tfrac{1}{3} \{ 2g^{2/3} + g^{1/3} \} \text{ ,, } \qquad g = \tfrac{1}{64} \{ \sqrt{1 + 24\,T} - 1 \}^3$$

When now the values found experimentally are compared with the values of column 8 of table 3 and with the curve $g = T^2$ of the figure, it appears that the experiment can be explained by the above reaction, if the initial value of p is $p \geq 1$.

The above should strictly speaking be completed with the determination of the quantity of "sulphate of glycerine mono sulphuric acid" formed when glycerine and sulphuric acid are mixed, which, however, will be exceedingly difficult to accomplish.

It is, therefore, only our intention to give a plausible explanation of the experimentally found curve B of the figure. Whether this explanation is perfectly correct may perhaps be decided by later experiments.

We see, therefore, that in the esterification of glycerine with fatty acid dissolved in strong sulphuric acid, complications are again met with, which cause a deviation from the ideal case.

Probably others than glycerine esters will be better adapted to realise this ideal case. It appears, however, from the above that it is exactly the deviations that often furnish valuable data about the mechanism of a reaction that takes place in stages.

In conclusion a few words about the second phase of the sulphuric acid saponification, viz. the boiling with water. When the reaction product of the first phase is made to flow into boiling water, a very fine emulsion is formed, the dispersity of which rapidly diminishes. The temporary fineness is caused by the presence of monolaurine, which greatly lowers the surface tension between water and fat.[1]) This is attended with adsorption of monolaurine at the surface of contact between fat and water (the place of reaction in saponification in emulsion), which causes it to be quickly saponified, and the dis-

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[1]) Treub l. c.

persity of the emulsion to decrease.[1]) A consequence of this is that in the initial stage of the second phase a considerable separation of glycerine takes place.

In the saponification in emulsion the relation between the relative concentrations of free fatty acid and free glycerine is now determined by the adsorption of the lower glycerides at the surface of contact between fat and water. In this case the three estergroups of the triglyceride may be taken as equivalent with very close approximation. The equation $T = \frac{1}{3}(g + g^{2/3} + g^{1/3})$, which is founded on this supposition, and which holds for the TWITCHELL-process, holds also at the end of the second phase of the sulphuric acid saponification, when the water contains but little sulphuric acid (from 1 to $2^0/_0$). If the acid content in the water is greater, then $T > \frac{1}{3}(g + g^{2/3} + g^{1/3})$.

SUMMARY.

The relation between the relative concentrations of free glycerine and free fatty acid was derived for the ideal case that tri-glyceride saponification takes place in solution, the ester groups are equivalent, and no complications present themselves.

It holds that the relative concentration of the free glycerine is at any moment equal to the third power of the relative concentration of the free fatty acid in case of stagewise saponification.

The same thing holds for the ideal case of esterification.

In the saponification of trilaurine with strong sulphuric acid only a very slight deviation was found, caused by the not perfect equivalence of the three ester groups. This is a direct and quantitative proof of the stagewise course of the reaction.

In the esterification of equivalent quantities of laurinic acid and glycerine dissolved in strong sulphuric acid deviations were found, which are probably caused by the action of the two-basic sulphuric acid.

Gouda, May 1917.   *Laboratory of the Royal Stearine*
Candle Works "Gouda".

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[1]) In treating fats, containing unsaturated acids, with strong sulphuric acid at high temperature, compounds are formed that keep up the dispersity of the emulsion during a longer time.