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

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INTRODUCTION.

§ 1. The saponification of esters of glycerine has been first experimentally studied by GEITEL.[1]) He determined the velocity of saponification of the three acetines in diluted acid solution, by titration of the split off acetic acid, and came to the result, that the ratio of the velocity constants of the reactions: triacetine → diacetine → monoacetine → glycerine is as 3 : 2 : 1, from which follows that the estergroups are all saponified with the same velocity, and that the velocity of saponification of a certain estergroup is independent of a neighbouring group being saponified or not.

ABEL[2]) advanced against this that good constants are likewise found when it is assumed that the saponification leads directly from triglyceride to glycerine, and that therefore GEITEL's measurements of velocity do not prove anything.

This is clear, as we arrive at the same equations of velocity in the two different cases as ABEL[3]) has proved in another paper for the general case of a reaction in n stages.

However with his *measurements of velocity* GEITEL has not proved that the saponification of triacetine proceeds in stages, but only that if it proceeds in stages the velocity constants of the three stages must be in the ratio of 3 : 2 : 1.[4]) This result on the contrary shows the impossibility to decide whether the process goes by stages or not from measurements of the velocity of the splitting off of fatty acid alone.[5])

GEITEL proved that the acid saponification of glycerine esters actually takes place in stages by demonstrating that rancid fats contain more

[1]) Z. f. pr. Chem. (2) **55** 429 (1897), **57** 113 (1898).

[2]) ULZER u. KLIMONT, Chemie der Fette 244 (1906).

[3]) Z. f. phys. Chem. **56** 558 (1906).

[4]) J. MEYER has proved (Z. f. Electrochem. **13** 485 (1907)), that this ratio only holds in approximation. For 18° C. the following ratio seems to hold more accurately: 3.10 : 2.00 : 1.14, for 25° C : 3.06 : 2 00 : 1.25.

[5]) Cf. also § 12.

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bound glycerine than agrees with an immediate splitting up into glycerine and three molecules of fatty acid. He could therefore assume analogous behaviour for the acetines.

JUL. MEYER [1]) has mathematically examined the course of the saponification in acid solution of esters of bivalent acids or alcohols, and has brought this into equation in a very lucid form. It is evident from his formulae that when the first stage passes twice as quickly as the second, the whole saponification becomes seemingly monomolecular. Measurements of velocity carried out by him for the acid saponification of the glycol acetates and of esters of different symmetrically built bi-basic acids, confirm this fully.

Also to J. MEYER's conclusions the objection might be made that a simply monomolecular saponification explains his results equally well. J. MEYER has, however, also determined the velocities of saponification of the methyl esters of the asymmetrical camphoric acid. Of the dimethyl camphorate one ester group now appeared to be much more quickly split off than another. Hence the velocity constants in the saponification of di- and mono-ester are not in the ratio of 2 : 1, so that here the results of the measurements of velocity lead us to conclude directly to the process in stages of the reaction. The assumption that also in the saponification of glycol esters etc. the reaction takes place in stages, is then perfectly justified. Besides JUL MEYER's experiments support GEITEL's view that the acetines in acid solution are saponified stagewise.

THE SAPONIFICATION IN EMULSION.

§ 2. Both GEITEL's papers and those of JUL. MEYER treat the saponification in solution. In the saponification of fat, however, always more or less fine emulsions of fat and an aqueous solution are worked with, and it is, therefore, now the question in what way the reaction takes place in this case.

In the first place it is the question: Where does the reaction take place? There are, namely, three possibilities:

1. Reaction takes place in the water phase.
2. Reaction takes place in the fat phase.
3. Reaction takes place on the boundary of the two phases.

Let us consider each of these possibilities separately.

1. *The reaction takes place in the water phase.*

In this case the velocity with which the triglyceride is converted, is determined by the number of molecules dissolved in the water

[1]) Z. f. phys. Chem. **66** 81 (1909).

phase. Now follows immediately another question, viz. may in this case an equation of velocity be applied which holds good for a solution? As NERNST [1]) has observed an equation of velocity holding for a homogeneous system leads to an entirely wrong conclusion in a heterogeneous system, when the velocity of reaction is dependent on the velocities of diffusion. This will always be the case where the velocity of reaction is great with respect to the velocity of diffusion.

When, however, on the contrary in a heterogeneous system the concentration equilibrium sets in rapidly, and the reaction proceeds comparatively slowly, the influence of the diffusion velocity is only slight, and can become quite imperceptible. This now is generally the case when both phases are liquid When a substance A dissolved in a solvent B is shaken with a solvent C, which does not mix with B, only a very short time is required to establish the equilibrium between the two solutions.

H. GOLDSCHMIDT [2]) has determined the velocity of saponification of ethyl acetate dissolved in benzine and shaken with about normal hydrochloric acid. Assuming that the reaction takes place in the aqueous solution he represented the velocity of saponification by the equation:

$$-\frac{dx}{dt} = K \cdot \frac{v_1 \cdot C}{v_2 + v_1 \cdot C} x \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which v_1 = volume of the aqueous solution, v_2 = volume of the benzolic solution, C = constant of partition of ethyl acetate between water and benzene. On the whole the reaction velocity appeared to be well represented by this equation.

Towards the end, the reaction in the opposite sense had to be taken into account.

It appears from this that when the velocity of reaction is not too great, the equations of velocity which hold in a homogeneous system may be applied in a heterogeneous system, consisting of two liquid phases.

Let us now return to the saponification of fat, and let us imagine the case that a triglyceride is saponified with diluted sulphuric acid according to the TWITCHELL process, in which fat and aqueous solution is held in emulsion by blowing in of steam, after addition of about $^1/_2$ % TWITCHELL reagent. GOLDSCHMIDT's formula may certainly not be used in this case for quantitative determinations. For

[1]) Z. f. phys. Chem. **47** 55 (1904).

[2]) Z. f. phys. Chem. **31** 235 (1899).

NERNST's law of partition cannot be applied here unreservedly, as the fat phase consists chiefly of triglyceride at the beginning of the saponification and chiefly of fatty acid at the end. The "constant" of partition C can, therefore, not be constant in this case. We can, however, draw a conclusion from equation (1) as to the probability or improbability of the supposition that the saponification takes place in the water phase. For at any rate there appears from it that if the said supposition is valid, the extent of the surface of contact between fat particles and water particles plays no part. But then the action of the TWITCHELL reagent must chiefly rest on this that it causes an increase of C, in other words, increases the solubility of the fat in the water phase. This is in itself very well possible, but seeing that the saponification without reagent practically does not take place, and obtains an efficient velocity on addition of not quite half a percentage to the emulsion, it is very improbable indeed, that increase of the solubility of the fat in the water phase should be the cause of it.

As will appear in § 4, the action of the TWITCHELL reagent can be quite plausibly accounted for by the supposition that the saponification takes place on the boundary of fat and water.

There is, however, another phenomenon that points to this. It appears namely, that, when triglycerides which contain little or no free fatty acid, are saponified, the reaction velocity is very small at first, then it increases and reaches a maximum. WEGSCHEIDER [1]), who assumes the reaction in the aqueous solution, wants to explain this by taking the concentration of the triglyceride in the water-phase constant. The increase of the reaction velocity would then be caused by the presence of lower glycerides in the waterphase. On this assumption WEGSCHEIDER comes to the following equation of velocity for the splitting off of fatty acid:

$$\frac{dx}{dt} = 9\,k\,.\,C - 6\,k\,.\,C\,.\,e^{-kt}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In this C represents the not changing concentration of the triglyceride in the aqueous solution, k is a constant of velocity.

Equation (2) would really be able to explain the increase of the velocity of saponification, if it could be applied to the saponification of fat in this form. Now it is clear that (2) can only hold for the saponification by means of bases, as only in this case the fat phase which is in contact with the aqueous solution, consists practically exclusively of triglycerides, because of which the concentration of

[1]) Kais. Ak. d. Wissensch. Wien **116**, II b. 1325 (1907).

the triglyceride in the waterphase may be taken constant. As will appear in § 19 the saponification in alcalic surroundings takes place however practically directly from triglyceride to glycerine + fatty acid. Then the second term of the second member of (2) disappears, and we should have a velocity of saponification which does not change with the time. The facts, however, are different.

If the reaction takes place on the boundary of the two phases, the increase of reaction velocity is at once apparent. At the beginning we have namely a not very intimate emulsion of lye and triglyceride. As the saponification advances, the soap concentration in the waterphase increases, the surface tension between fat- and waterphase accordingly decreases; hence the emulsion becomes more intimate, and the surface where the reaction can take place, becomes greater.

After what precedes we may, therefore, put aside the first possibility as very improbable.

§ 3. 2. *The reaction takes place in the fat phase.*

This supposition is still less tenable, as a reaction which is catalytically accelerated by $H^{\cdot}$ or OH' ions, is very improbable in not aqueous surroundings.

§ 4. So the last possibility remains, namely:

3. *The reaction takes place on the boundary of the two phases.*

In the saponification in acid solution the velocity is a function of the number of collisions in the unity of time between an ester molecule and an $H^{\cdot}$ ion. For a given concentration and a definite temperature this number of collisions is fixed and therefore the velocity constant also.

If, however, as in the TWITCHELL process we have an emulsion of fat- and water particles, which move through one another in fine division, and if the reaction takes place on the boundary of the two phases, the velocity will be a function of the extent of the surface where the collisions can take place, i. e. of the fineness of the emulsion; hence the velocity constant will *not* be definite at a given temperature.

In the TWITCHELL process the accelerating influence of the reagent must chiefly, if not entirely, be found in the enlargement of the surface of contact between fat- and waterphase, in other words in the decrease of the surface tension between fat and water. That actually this surface tension is considerably decreased by traces of

reagent can be easily shown with DONNAN's pipette.[1]) (see § 7).

It may seem arbitrary that where it appears that already traces of TWITCHELL reagent considerably decrease the surface tension between fat and water, it has been assumed in § 2, that those traces cannot practically influence the solubility of the fat in water. Yet this is by no means the case. In order to increase the solubility of fat in water sufficiently a solvent for triglyceride would have to be added to the waterphase, which mixes with water. Further the waterphase would have to exhibit a certain (pretty considerable) concentration of this solvent throughout its volume. For a substance, however, which lowers the surface tension between fat and water this need not be the case. For the action of a substance to lower the surface tension is accompanied with adsorption at the surface common to the two phases, in consequence of which such a substance, though if calculated over the whole mass, it is present only in traces, can occur in pretty considerable concentration at the common surface. It is exactly this surface layer that counteracts the tendency of two colliding drops to join to one whole.[2])

The same considerations are also valid for the saponification in alcalic surroundings. Here the soap formed in the saponification acts so as to lower the surface tension between fat and water.

We arrive therefore at the conclusion that in the saponification in emulsion the reaction practically takes entirely place on the boundary of the fat and the water phase. We may then apply the equations of velocity holding in solution, when we take the fact into account that the constant of velocity depends on the fineness of the emulsion.

§ 5. Measurements of velocity have been carried out by M. NICLOUX[3]), who studied the saponification of cottonseed oil by the aid of the ferment found in ricinus seed. He found for:

$$k = \frac{1}{t} \log \frac{a}{a-x}$$

a good constant especially at low temperature (15°). From this it appears that in this case the fineness of the emulsion does not appreciably change during the saponification and that the ratio of the saponification velocities of the three glycerides is as 3 : 2 : 1 or as 1 : ∞ : ∞.[4])

[1]) Z. f. phys. Chem. **31**, 42 (1899).
[2]) DONNAN loc. cit.
[3]) Saponification des corps gras (1906).
[4]) See § 12.

As NICLOUX states [1]) that the quantity of glycerine split off after a certain time corresponds to the split off quantity of fatty acid, the latter ratio must be correct. In the experiments of M. NICLOUX triglyceride seems to have split off practically directly into fatty acid and glycerine.

In the saponification by means of bases the fineness of the emulsion does certainly not remain constant. For here the soap that is formed gives rise to a lowering of the surface tension between fat and aqueous solution, hence the fineness of the emulsion will increase during the saponification. The same thing holds, at least for the beginning of the reaction, for the autoclave saponification with zinc oxide and likewise for the saponification with lime. Nor does the fineness of the emulsion remain the same in the course of the TWITCHELL process. As can be shown with the aid of DONNAN's pipette the surface tension between e.g. linseed oil fatty acid and water is smaller than between linseed oil and water. Here too the surface - of contact between fat and water phase will therefore become larger in the course of the reaction.

It is clear that in these cases measurements of velocity are of little use. The constant of velocity will always present a course, and then there is no criterion whether the equations of velocity that have been drawn up, are correct or not. We shall have to adopt another course here.

When we draw up equations of velocity for the splitting off of fatty acid in the saponification of triglyceride, and when there occurs in them only one constant k, which is dependent on the extent of the surface of contact of fat- and waterphase, and which therefore from the beginning of the saponification may be considered really constant only during a small period Δt_1 we arrive after integration of the drawn up equations between the limits 0 and Δt_1 at a relation between the number of molecules of fatty acid (z) split off after the time Δt_1 and k and Δt_1. Let this function be:

$$z = f(k \times \Delta t_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For stagewise saponification a second equation denotes: the number of molecules of glycerine (s) split off after the time Δt_1 as function of k and Δt_1. Let this function be:

$$s = \varphi(k \times \Delta t_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If we now can eliminate $k \times \Delta t_1$ from the two equations (3) and (4), we find a relation:

$$\psi(z, s) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

[1]) l. c. 52.

which indicates the relation between the number of molecules of glycerine and fatty acid split off after the time Δt_1.

Let us now imagine that after the time Δt_1 has elapsed, the constant of velocity k changes into k', and let us now consider a following period Δt_2. At the beginning of this period the following equation holds:

$$z = f(k \times \Delta t_1)$$
$$s = \varphi(k \times \Delta t_1)$$

The same values z and s could, however, have been obtained with the constant of velocity k' in a certain period $\Delta t'_1$, so that:

$$\Delta t'_1 = \frac{k}{k'} \cdot \Delta t_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

At the beginning of this period we have, therefore, also:

$$z = f(k' \times \Delta t'_1)$$
$$s = \varphi(k' \times \Delta t'_1),$$

but then is after the lapse of the time t_2:

$$z = f\{k' \times (\Delta t'_1 + \Delta t_2)\}$$

and

$$s = \varphi\{k' \times (\Delta t'_1 + \Delta t_2)\}.$$

From these last equations $k' \times (\Delta t'_1 + \Delta t_2)$ can be eliminated in the same way as $k \times \Delta t_1$ from (3) and (4), which proves, therefore, that (5) also holds after Δt_2 has passed.

Since the same reasoning may be extended over the whole saponification, it appears that when the number of molecules of split off fatty acid in the saponification of fat can be represented by:

$$z = f(k \times t)$$

and the number of molecules of split off glycerine by

$$s = \varphi(k \times t),$$

in which equations k varies with the time, we must be able to derive a function:

$$\psi(z,s) = 0$$

by elimination of $k \times t$, the form of which does not change during the saponification, and which is independent of the change of k.

Since in the saponification of fat both split off glycerine and free fatty acid can be determined separately, we have a means in this to examine the mechanism of the reaction.

It may still be pointed out here that in the change of k with the time must also be included the decrease of concentration of the lye taking place in the saponification in alcalic surroundings. We shall, therefore, have to arrive at analogous equations for acid and alcalic saponification.

§ 6. Before proceeding to the derivation of an equation $\psi(z,s) = 0$, we must first discuss the question what is to be expected in the saponification of fats in which *different* fatty acids are present.

The natural fats are, namely, mixtures of different triglycerides and in a molecule of triglyceride there are often found two, sometimes three different groups of fatty acid. Now it is first of all conceivable that e. g. the oleic acid group is more easily separated from a molecule of oleo-dipalmitine than a palmitinic acid group. Secondly, however, the possibility exists e. g. for a mixture of trioleine and tripalmitine that the surface tension of one of these glycerides in contact with the water surroundings with which the saponification is carried out, is lower than that of the other. The consequence of this would be that the triglyceride, which has the lowest surface tension in contact with the water phase, was adsorbed at the common surface, and was consequently more rapidly saponified.

Of this, however, nothing has ever appeared.

It has been shown by THUM.[1]) that in the saponification with bases as well as when palm oil and olive oil become rancid, the iodine value of the split off fatty acids agrees with that of the fatty acids that are still combined to glycerine.

STIEPEL [2]) finds for autoclaved tallow fatty acids that the still combined fatty acids exhibit a somewhat higher iodine value than the split off ones; for the autoclavation of cocoanut oil and palm kernel oil he arrives, however, at the conclusion that the split off and the combined fatty acids have the same composition. STIEPEL finds a corroboration of this [3]) in the fact that on distillation of partially saponified cocoanut and palm kernel oil the distillate presents the same acid values as that on second distillation of the fat mass that had first remained behind in the kettle, after this mass had been saponified anew, and now entirely.

It follows from this that a difference in saponifiability between ester groups of different fatty acids may in general be neglected, and further that the surface tensions of the glycerides occurring in the fats examined by THUM and STIEPEL in contact with the saponifying surroundings can be only little divergent.

CONNSTEIN, HOYER and WARTENBERG [4]) have found that the fermentative saponification with the ricinus seed ferment proceeds more

[1]) Z. f angew. Chem. **3** 482 (1890).
[2]) Seifens. Ztg. **31** 937, 965, 986, 1006, 1026 (1904), **36**, 788, (1909).
[3]) Seifens. Ztg. **35** 1359 (1908).
[4]) Ber. **35**. 3988. (1902).

slowly as the molecular weight of the combined acids is lower. It is therefore not excluded that also when glycerides of fatty acids of different molecular weight occur side by side, they will present here a specific saponification velocity. Experiments of the same nature as have been made by THUM and STIEPEL are not mentioned by CONNSTEIN c. s.

§ 7. In order to be able to form an opinion about the surface tensions of fats in contact with different media, I made the following experiments:

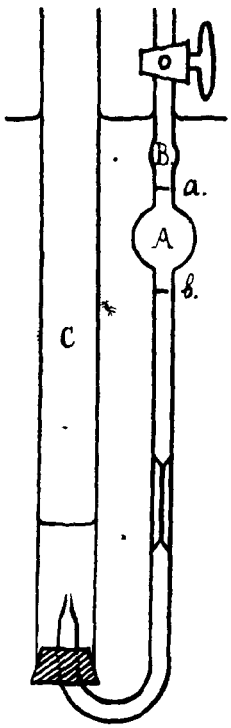


Fig. 1.

With the aid of DONNAN's pipette the number of drops were counted which, when a definite volume of different triglycerides flowed from a thin walled capillary, mounted up in water and some solutions, all this at 100° C. The arrangement of the experiments follows from fig. 1. The pipette with the tube *C* which contained the aqueous solution, was heated to 100° in a large glass beaker with water. During the outflow of the fat the beaker was not heated to avoid shaking through the boiling of the water. The filling took place by the fat being sucked up into the bulb *B*. The mouth of the capillary was then cleaned as well as possible with a cloth, and the tube *C* was fastened with a rubber stopper. The whole was now carefully heated in the beaker till the fat just appeared from the capillary mouth, then the solution (always a same quantity) was poured into *C* along the wall. When the whole had reached the temperature of 100°, then the level of the fat was reduced to *a* by opening of the cock, and then the number of drops was counted which mounted in the solution in *C* during the fall of the level of the fat from *a* to *b*. The diameter of the capillary mouth was about 1 mm. Trilaurine flowed out from *a* to *b* in about 4 minutes.

During the outflow of the fat every drop remains hanging at the capillary mouth till the upward pressure exceeds the tension of the surface. The greater, therefore, this surface tension is, the fewer drops will get detached when a definite volume of the fat substance flows out, and the smaller the number of drops that will mount in the aqueous liquid. When we disregard the difference in specific weight of the different triglycerides, the tension of the surface of

contact is roughly inversely proportional to the number of drops.

It it clear that the results obtained with the described apparatus give an indication only in rough approximation about the ratio of the surface tensions of different glycerides in contact with aqueous solutions. To determine this ratio quantitatively more accurate measurements are necessary than can be carried out with the DONNAN pipette. It will, however, appear in § 19 et seq. that the data obtained in the described way, can qualitatively entirely account for the phenomena that present themselves in the saponification of fats.

The obtained results are recorded in table I.

TABLE I.

1	2	3	4	5	6	7	8	9	10
Triglyceride	Acid value	Saponification value		Iodine value	Solidifying point of the fatty acids	Number of drops mounting at 100° C. in.			
		Calculated	Found			Water	1% solution of TWITCHELL reagent in H_2O	10% solution of potassium laurate in H_2O	12.3% solution of potassium palmitate in H_2O
Trilaurine	0.0	264.0	264.3	0.0	43°.7	10	44	53	190
Tripalmitine	<0 2	208.9	208.3	0.8	62.0	12	45	(110)	(370)
Tristearine	<0 2	189.2	190.0	0 0	68.7	13	50	(85)	—
Olive oil	1.43	—	191.0	83.9	22.5	11	50	(100)	(340)
Linseed oil	<0.2	—	191 3	182.3	20.6	15	48	(70)	(210)

Trilaurine was obtained by recrystallisation of Tangkallak fat from alcohol, then from ether, tripalmitine by recrystallisation of Chinese vegetable tallow from benzene, then washing of the obtained product with alcohol, and again recrystallisation from ether. Tristearine by recrystallisation of catalytically hardened linseed oil from benzene, then also washing with alcohol and recrystallisation from ether. The olive oil used was oil sold for consumption from French origin. The linseed oil had been freed from free fatty acid as well as possible by treatment with lye. From the constants recorded in

columns 2—6 the purity of the examined triglycerides appears sufficiently.

It now appears from columns 7 and 8 that the surface tensions of the examined triglycerides in contact with water and a 1 °/₀ solution of TWITCHELL reagent diverge but little *inter se*, and it is clearly visible that in the presence of reagent the drops get sooner detached, the surface tension between fat and water phase has therefore decreased.

In alcalic surroundings greater divergencies were found between the different triglycerides inter se (see columns 9 and 10). It is, however, very much the question if they are essential. In triglycerides which cannot, like trilaurine, be purified by recrystallisation from alcohol, it is exceedingly difficult to remove the last traces of free fatty acid. In alcalic surroundings these traces cause a lowering of the surface tension, and give moreover rise to irregular moistening of the capillary mouth, which is the cause that often great deviations are found in repeated determinations. The values which are little reliable for this reason, have been placed between ( ). The lowest number of drops (rounded off to tens) that was found on repeated determination, has always been given. These values are of importance in so far, that they show clearly the influence of the molecular weight of the soap which is dissolved in the water.

As appears from THUM and STIEPEL's observations and from the results with DONNAN's pipette described in this §, no difference need in general be made in the derivation of an equation $\psi(z, s) = 0$ between natural fats and simple triglycerides. A function derived on this supposition must, however first be tested by different fats in the fermentative saponification, before further conclusions are drawn from it.

DERIVATION OF AN EQUATION $\psi(z, s) = 0$.

§ 8. As the reaction takes place on the boundary of fat and water phase, the velocity with which each of the stages of saponification proceeds, will be governed by the surface tension of tri-, di- and monoglycerides against saponifying surroundings. For if e. g. the surface tension of the diglyceride against the water phase is smaller than that of the tri-glyceride, the diglyceride will directly after its formation be adsorbed at the surface of contact, and therefore reach a greater concentration in the surface layer than when no adsorption took place. The consequence of this will be that an estergroup of a molecule of diglyceride has on an average a greater

chance to be saponified than an estergroup of a molecule of triglyceride.

To be able to form an opinion about the surface tensions of tri-, di-, and monoglycerides against saponifying surroundings the behaviour of the laurines was examined by the aid of the apparatus described in the preceding §. The results are found in table 2.

TABLE 2.

1	2	3	4	5	6	7
Fat substance	Saponification value		Melting point	Number of drops flowing out at 100° C. into:		
	Calculated	Found		Water	1% solution of TWITCHELL reagent in H_2O	10% solution of potassium laurate in H_2O
Trilaurine	264.0	264.3	46°	10	44	53
Dilaurine	246.3	246.3	54	13.5	42	470
Monolaurine	205.0	204.4	62.8	—	—	—
90 Trilaurine + 10 Dilaurine	—	—	—	12	44	90
90 „ + 10 Monolaurine	—	—	—	80	280	flows!
Laurinic acid	280.7	280.4	43°.7 [1])	38	70	—

The laurinic acid was prepared by saponification of trilaurine, obtained from Tangkallak fat, followed by distillation in vacuo. The lower laurines were obtained by esterification of laurinic acid with excess of glycerine at about 200° in the way indicated by VAN ELDIK THIEME [2]). To purify the dilaurine it was first recrystallized from alcohol (to remove monolaurine), then from benzene (to remove trilaurine). The monolaurine was first recrystallized from petroleum-ether (to remove di- and trilaurine), then from alcohol (to remove monolauryldiglycerine). All the glycerides were perfectly free from oleic acid and free fatty acid. For the rest the constants mentioned in columns 2—4 sufficiently express the purity of the substances used.

The number of drops of monolaurine rising in aqueous solutions could not be determined, as a skin is formed on the boundary of

[1]) Solidifying point.

[2]) Thesis for the doctorate. Delft (1911).

monolaurine and water, so that there is no question of "drops". To be able to form in spite of this an opinion about the surface tension of monolaurine against aqueous solutions, the number of drops that mounted of a mixture of 90 % trilaurine and 10 % monolaurine, has been given in table 2, while for a comparison the thus obtained values of dilaurine have been given.

From table 2 the following conclusions can be drawn:

1. In acid and neutral surroundings the surface tensions of tri- and dilaurine in contact with the saponifying medium differ little, that of monolaurine is much less. We must therefore expect that in case of saponification in non alcalic surroundings the monoglyceride will be adsorbed at the boundary of fat- and water phase, and will, therefore, be saponified with a velocity greater than that with which it has been formed.

2. In alcalic surroundings both the surface tensions of di- and of monolaurine in contact with the saponifying medium are much smaller than that of trilaurine. Both di- and monoglycerides will, therefore, be absorbed here at the boundary layer; hence they are saponified with velocities greater than that with which they have been formed.

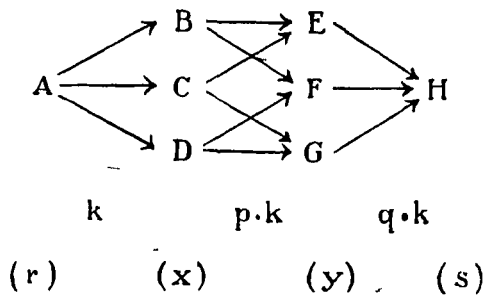
As appears from what precedes the increase of concentration of the lower glycerides at the surface of contact between fat and water phase must be taken into account in the derivation of an equation $\psi(z, s) = 0$. We now put:

p resp. q = the number of times that the concentration of the diglyceride, resp. monoglyceride at the boundary layer is greater in consequence of the adsorption than if no adsorption had taken place, and we put p and q both constant.

This assumption is an approximation, because the adsorption is *not* proportional to the total concentration of the adsorbed substance. [1]) This approximation will be the closer as the concentration of the lower glycerides will vary between a narrower margin during the saponification.

§ 9. Since the difference in velocity of saponification between esters of primary and secondary alcohols is only slight, and the isomeric di- and monoglycerides can therefore be considered here as equivalent with close approximation (which also follows from GEITEL's and J. MEYER's results), we come to the following scheme for the saponification of fat:

[1]) See FREUNDLICH, Z. f. phys. Chem. **57**, 385 (1907).



In this A represents a molecule of triglyceride, which can be converted into a molecule of diglyceride (B, C, or D) in three ways with a constant of velocity k. A molecule of diglyceride, e.g. B can give a molecule of monoglyceride (E or F) in two ways with a constant of velocity $p.k$, while finally every molecule of monoglyceride forms glycerine (H) with a velocity constant $q.k$. The number of molecules of A present after a time t will be expressed by r, the number of molecules of B, C, and D each by x, of E, F, and G each by y, and of H by s.

It is clear, that when there is no difference in saponifiability of the different ester groups, the concentrations of B, C, and D, and of E, F, and G are equal inter se at any moment.

Let us now suppose a molecules of triglyceride A to be present at the beginning of the reaction.

The velocity of saponification of A is now denoted by the equation:

$$-\frac{dr}{dt} = 3\,k\,.\,r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

When we integrate (7) and consider that for $t = 0$, $r = a$, then follows:

$$r = a\,.\,e^{-3kt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The variation of the number of molecules B (hence also of C and D) is represented by:

$$\frac{dx}{dt} = k\,.\,r - 2pk\,.\,x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

When the value of r from (8) is substituted in (9), then follows:

$$\frac{dx}{dt} + 2pk\,.\,x = a\;\;k\,.\,e^{-3kt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This equation can be solved by putting:

$$x = m \times n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

in which, therefore, an arbitrary value can be given e.g. to m; n is then fixed.

As

$$\frac{dx}{dt} = m \cdot \frac{dn}{dt} + n \cdot \frac{dm}{dt},$$

(10) passes into:

$$m \frac{dn}{dt} + n \left\{ \frac{dm}{dt} + 2pk \cdot m \right\} = a \cdot k \cdot e^{-3kt} \quad . \quad . \quad . \quad (12)$$

Let us now take m so that

$$\frac{dm}{dt} + 2pk \cdot m = 0.$$

On integration of this last equation we then find for m:

$$m = e^{-2pkt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)\ ^{1)}$$

Introducing this value into (12), we get:

$$e^{-2pkt} \cdot \frac{dn}{dt} = a \cdot k \cdot e^{-3kt},$$

from which by integration:

$$n = \frac{a}{2p-3} \cdot e^{(2p-3)kt} + C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Now follows from equations (11), (13), and (14):

$$x = m \cdot n = \frac{a}{2p-3} e^{-3kt} + C \cdot e^{-2pkt} \quad . \quad . \quad . \quad . \quad (15)$$

Bearing in mind that for $t = 0$ also $x = 0$, we find for the integration constant C:

$$C = -\frac{a}{2p-3},$$

through which (15) passes into:

$$x = \frac{a}{2p-3} \cdot \{e^{-3kt} - e^{-2pkt}\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

The change of the number of molecules E (hence also of F and G) is represented by:

$$\frac{dy}{dt} = 2pk \cdot x - qk \cdot y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

If the value of x from (16) is substituted in (17), then follows:

$$\frac{dy}{dt} + qk \cdot y = a \cdot \frac{2pk}{2p-3} \cdot \{e^{-3kt} - e^{-2pkt}\} \quad . \quad . \quad . \quad (18)$$

This differential equation can be solved in the same way as (10). We then find:

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1) A constant of integration can of course be omitted here

$$y = a \,.\, 2p \,.\, \left\{ \frac{e^{-3kt}}{(2p-3)(q-3)} - \frac{e^{-2pkt}}{(2p-3)(q-2p)} + \frac{e^{-qkt}}{(q-3)(q-2p)} \right\}. \quad (19)$$

At last the number of molecules of split off glycerine (s) can be calculated from:

$$\frac{ds}{dt} = 3\, qk \,.\, y,$$

or from:

$$s = a - r - 3(x + y).$$

We then find·

$$s = a \left\{ 1 - \frac{2pq}{(2p-3)(q-3)} e^{-3kt} + \frac{3q}{(2p-3)(q-2p)} e^{-2pkt} - \frac{6p}{(q-3)(q-2p)} e^{-qkt} \right\}. \quad (20)$$

The number of molecules of split off fatty acid is, as appears from the scheme at the beginning of this §.

$$z = 3x + 3 \,.\, 2y + 3s.$$

When we substitute in this the equations (16), (19), and (20), we get:

$$z = 3a \,.\left\{ 1 - \frac{1 + (2p-1)(q-2)}{(2p-3)(q-3)} e^{-3kt} + \frac{2(q-p)}{(2p-3)(q-2p)} e^{-2pkt} - \frac{2p}{(q-3)(q-2p)} e^{-qkt} \right. \quad (21)$$

Now we can eliminate $k.t$ from the formulae (20) and (21) for definite values of p and q, which gives us a relation between s and z. It is however, more practicable to substitute two other quantities for s and z.

The total number of molecules of glycerine is a. If we now call that part of the total quantity of molecules of glycerine that is split off g, then

$$g = \frac{s}{a}.$$

The total number of molecules of fatty acid is $3a$. If we now call that part of the total quantity of molecules of fatty acid that is split off T, then:

$$T = \frac{z}{3a}.$$

Now follows from the equations (20) and (21):

$$g = 1 - \frac{2pq}{(2p-3)(q-3)} e^{-3kt} + \frac{3q}{(2p-3)(q-2p)} e^{-2pkt} - \frac{6p}{(q-3)(q-2p)} e^{-qkt} \quad (22)$$

and

$$T = 1 - \frac{1 + (2p-1)(q-2)}{(2p-3)(q-3)} e^{-3kt} + \frac{2(q-p)}{(2p-3)(q-2p)} e^{-2pkt} - \frac{2p}{(q-3)(q-2p)} e^{-qkt} \quad (23)$$

If now p and q are successively given different values, we obtain

4*

equations for g and T, from which $k \cdot t$ are more or less easy to eliminate in accordance with the values assumed for p and q.

§ 10 Before proceeding to substitute for p and q numerical values, we point out that the equations (22) and (23) do not allow us to substitute the following values:

$$p = {}^2/_3 \ , \ q = 3 \text{ and } q = 2p.$$

It is easy to see that in the derivation of (22) and (23) operations have been performed, which it is not allowed to execute with the above mentioned values of p and q. If we yet wish to introduce these values, we must proceed as in § 9, and substitute the assumed values for p and q from the very first. We then get transcendental equations for the function:

$$\psi(T,g) = 0.$$

§ 11. Let us now first define the limits between which all the curves represented by the functions $\psi(T,g) = 0$, for different values of p and q, must lie. It is clear that the extreme values, which p and q can have, are ∞ and $\frac{1}{\infty}$.

Let us first put $p = \infty$ and $q = \infty$. The physical meaning of this is, that the increase of concentration of the lower glycerides at the surface of contact in consequence of the adsorption is so great that their velocity of saponfication compared with that of the triglyceride, is ∞.

The equations (22) and (23) pass in this case into:

$$g = 1 - e^{-3kt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$T = 1 - e^{-3kt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

from which

$$g = T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

This result can of course at once be understood. In fig. 2, where g and T are both given in percentages, A represents this limit.

The equation $g = T$ will be more fully discussed in § 19.

Let us now put $q = \frac{1}{\infty}$. The physical meaning of this would be that the monoglyceride reaches only a concentration of $\frac{1}{\infty}$ in consequence of negative adsorption in the boundary layer. This limit has only mathematical signification. (See Fig. 2 p. 53.)

The equations (22) and (23) pass in this case after finite time, into:

$$g = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

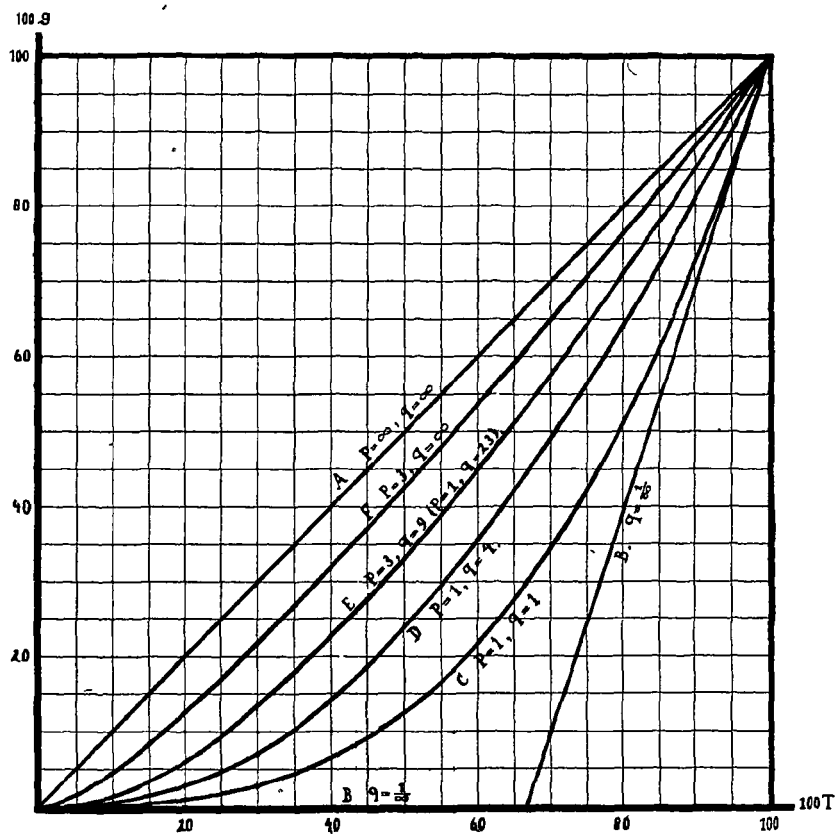

Fig. 2.

$$T = 1 - \frac{4p-3}{6p-9}\, e^{-3kt} + \frac{1}{2p-3}\, e^{-2pkt} - {}^1/_3 \quad . \quad . \quad . \quad (28)$$

i.e. in finite time no glycerine is split off, the reaction goes no further than monoglyceride. In finite time T approaches $^2/_3$.

If $t = \infty$, (22) and (23) passes for $q = \frac{1}{\infty}$ into:

$$g = 1 - e^{-qkt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

$$T = 1 - \tfrac{1}{3}\, e^{-qkt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

from which:

$$T = {}^2/_3 + {}^1/_3 g \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

For $q = \frac{1}{\infty}$ we find therefore the two boundary lines

$$g = 0 \text{ and } T = {}^2/_3 + {}^1/_3 g;$$

both are indicated by B in fig. 2.

All the curves $\psi(T,g) = 0$ which are possible for different values of p and q, must therefore lie within the limits:

$$g = T,\ g = 0,\ \text{and}\ T\ {}^2/_3 + {}^1/_3 g$$

§ 12. Let us now put $p = 1$, $q = 1$. The physical meaning of this is that there is no question of adsorption, because the surface tensions of all the glycerides in contact with the saponifying surroundings are the same. The velocity of saponification of an ester group is now independent of whether or no a neighbouring group is saponified.

For this case we find from (22) and (23):

$$g = (1 - e^{-kt})^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

$$T = 1 - e^{-kt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

from which:

$$g = T^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

This curve is indicated by C in fig. 2. It touches the boundary lines B at $g = T = 0$ and at $g = T = 1$.

Equation (34) is valid for the saponification in solution. From GEITEL's [1]) and J. MEYER's [1]) measurements follows that it holds for the saponification of triacetine, at least with close approximation. If it is possible to measure the split off quantity of glycerine in this

TABLE 3.

1	2	3	4	5	6	7	8
	Value of 100 T for:						
100 g	$p=1$ $q=1$	$p=2$ $q=2$	$p=1$ $q=4$	$p=3$ $q=9$ of ($p=1$) ($q=23$)	$p=1$ $q=\infty$	$p=3$ $q=\infty$	$p=\infty$ $q=\infty$
0	0	0	0	0	0	0	0
10	46.42	39.03	34.29	25.99	22.66	17.20	10
20	58.48	51.90	45.99	37.56	34.59	28.24	20
30	66.94	61.45	55.20	47 25	44 73	38.26	30
40	73.68	69.27	63.17	55.99	53.92	47.75	40
50	79.37	75.98	70.37	64.12	62.50	56.90	50
60	84.43	81.89	77 02	71.83	70.63	65.82	60
70	88.79	87.17	83.24	79.21	78.41	74.55	70
80	92.83	91.94	89.15	86.34	85.88	83.15	80
90	96.55	96.22	94.73	93.26	93.10	91.62	90
100	100	100	100	100	100	100	100

[1]) loc. cit.

case, then the saponification of triacetine in stages can be *directly* proved by this way.

When the equations (25) and (33) are compared it appears[1]) that measurement of the velocity of fatty acid separation can never be conclusive with respect to the question whether or no the saponification of triacetine in acid solution takes place in stages[2]).

In column 2 of table 3 (see p. 54) we find the values of $100\,T$ corresponding to the given values of $100\,g$ for the case that $p = q = 1$.

§ 13. Let us now put $p = 1$, $q = 4$, i.e. in consequence of the adsorption the concentration of the monoglyceride in the boundary layer is 4 times as great as it would be if no adsorption had taken place.

For this case equations (22) and (23) become:

$$g = 1 + 8e^{-3kt} - 6e^{-2kt} - 3e^{-4kt} \quad . \quad . \quad . \quad . \quad . \quad (35)$$

$$T = 1 + 3e^{-3kt} - 3e^{-2kt} - e^{-4kt} = 1 - e^{-kt}\{1 - (1 - e^{-kt})^3\} \quad (36)$$

From these two equations e^{-kt} can be eliminated by solving the fourth power equation (35) and substituting the found value in (36).

From (35) we find:

$$\left.\begin{array}{l} e^{-kt} = {}^1/_6\ \{4 - \sqrt{16-9z} + \sqrt{9z-4-8\sqrt{16-9z}+18\sqrt{(2-z)^2}+{}^4/_3(1-g)}\} \\ \text{in which:} \\ z = {}^2/_3 \cdot \{2 - \sqrt[3]{g(1-\sqrt{1-g})} - \sqrt[3]{g(1+\sqrt{1-g})}\}. \end{array}\right\} \quad (37)$$

In column 4 of table 3 are found the values of $100\,T$ calculated by the aid of these equations.

These equations will be more fully discussed in § 22. The curve D of fig. 2 represents the corresponding values of $100\,T$ and $100\,g$ graphically. It touches the boundary line B at $g = T = 0$.

§ 14. If we put $p = 2$, $q = 2$, then:

$$g = 1 + 8e^{-3kt} - 3e^{-4kt} - 6e^{-2kt} \quad . \quad . \quad . \quad . \quad . \quad (35)$$

$$T = 1 + e^{-3kt} - 2e^{-2kt} = 1 - e^{-2kt}(2 - e^{-kt}) \quad . \quad . \quad . \quad (38)$$

It appears that the split off quantity of glycerine is a same function of the time as in the case that $p = 1$, $q = 4$. This is a general property. If $p = 2m$ and $q = 2m$, or $p = m$ and $q = 4m$, in both cases we have:

$$g = 1 - \frac{8m^2}{(4m-3)(2m-3)}e^{-3kt} - \frac{3}{4m-3}e^{-4mkt} + \frac{6}{2m-3}e^{-2mkt}$$

[1]) In the acid saponification in solution k is invariable.

[2]) Cf. § 1 The fatty acid splitting off likewise becomes seemingly monomolecular for $p = {}^1/_2$, $q = \infty$ and for $p = \infty$, $q = 2$.

Hence in order to calculate T for a definite value of g, for the case $p = 2$, $q = 2$, we can make use of the equations (37) and (38). The thus obtained value is found in column 3 of table 3.

§ 15. If we put $p = 3$, $q = 9$, (22) and (23) change into:

$$g = (1 - e^{-3kt})^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

$$T = {}^1/_3 \{(1 - e^{-3kt})^3 + (1 - e^{-3kt})^2 + 1 - e^{-3kt}\} \quad . \quad . \quad (40)$$

from which:

$$T = {}^1/_3 \cdot \{g + g^{2/3} + g^{1/3}\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

In column 5 of table 3 are found the values of 100 T calculated by the aid of this equation. The curve E of fig. 2 represents the corresponding values of 100 T and 100 g for this case graphically. It touches the boundary line B at $g = T = 0$.

With a deviation $< 0{,}3\,^0/_0$ equation (41) holds also for the case $p = 1$, $q = 23$. This will be more fully discussed in § 21.

§ 16. For $p = 1$, $q = \infty$ (22) and (23) change into:

$$g = 1 + 2\,e^{-3kt} - 3\,e^{-2kt} \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

$$T = 1 + e^{-3kt} - 2\,e^{-2kt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

from which

$$(1 + g - 2\,T)^3 = (1 + 2\,g - 3\,T)^2 \quad . \quad . \quad . \quad . \quad (44)$$

If T is solved from this, we find:

$$\left.\begin{aligned} T &= {}^1/_8 \{1 + 4g + 2\sqrt{1 + 8g} \cdot \cos(120^\circ - {}^1/_3\,\varphi)\}, \\ &\text{in which:} \\ \cos\varphi &= -\frac{8g^2 + 20g - 1}{\sqrt{(1 + 8g)^3}} \end{aligned}\right\} \quad . \quad . \quad (45)$$

The values of 100 T calculated from this are found in column 6 of table 3.

§ 17. If we put $p = 3$, $q = \infty$, (22) and (23) become:

$$g = 1 - 2\,e^{-3kt} + e^{-6kt} \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

$$T = 1 - {}^5/_3\,e^{-3kt} + {}^2/_3\,e^{-6kt} \quad . \quad . \quad . \quad . \quad . \quad (47)$$

from which:

$$T = {}^1/_3\,(2g + \sqrt{g}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

In column 7 of table 3 are found the values of 100 T calculated from this. The curve F of fig. 2 represents the corresponding values of 100 T and 100 g for this case graphically. It touches the boundary line B at $g = T = 0$. Equation (48) will be more fully discussed in § 20.

Testing of the Derived Formulae.

§ 18. Measurements for the purpose of a comparison of the split off quantity of glycerine with the split off quantity of fatty acid have been carried out by KELLNER[1]), who determined free fatty acid and combined glycerine[2]) of partially saponified palmkernel oil by different methods of saponification.

Let us first examine how T and g are to be found from KELLNER's observations. For the calculation of the percentage of split off fatty acid the procedure is always as follows: The acid value is determined of a sample of the fat (which has first been washed with water and then dried), this is divided by the acid value of the esterfree fatty acid, and multiplied by 100. The value obtained (we shall call this 100 T') now indicates how much free fatty acid the sample contains in percentages, but only in approximation what percentage of the total fatty acid present occurs as free fatty acid (100 T). The acid value of the esterfree fatty acid indicates how many mgr. KOH is required to neutralize 1 gramme of this fatty acid. If of a sample of partially saponified fat we want to determine what percentage of total fatty acid present occurs as free fatty acid, we must know, *not* the number of mgr. KOH (a), required to neutralise the free fatty acid of 1 gramme of fat, but the number of mgr. KOH (b) required for a quantity of fat which contains the same quantity of total fatty acid as 1 gramme of esterfree fatty acid. The value of saponification being a measure for the total fatty acid present, we get:

$$\frac{b}{a} = \frac{\text{saponification value of the esterfree fatty acid}}{\text{saponification value of the fat to be examined}} \quad . \quad . \quad (49)$$

It is clear that in consequence of the glycerine content of the partially saponified fat, always $b > a$. To find, therefore, T from T', we multiply by b/a.

To calculate g we multiply the glycerine content of every sample again by b/a, and thus find the number of grammes of glycerine present in a quantity of the sample, which contains 100 grammes of total fatty acid. If we now also know the glycerine content of the triglyceride, hence also the quantity of glycerine present in so much triglyceride as contains 100 grammes of fatty acid, g can be directly determined.

§ 19. Let us now discuss KELLNER's results.

[1]) Chemiker Ztg. **33**, 453, 661, 993. (1909).

[2]) According to the oxidationmethod.

We calculate from the given acid values and fatty acid contents (table 4—8):

Acid value esterfree fatty acid . . . . . = 258.0, from this:
Mol. weight „ „ „ . . . . . = 217.8
„ „ triglyceride , ... = 691.4
grammes of glycerine in 100 gr. triglyceride . . = 13.31
„ „ „ „ triglyceride of 100 gr. fatty acid = 14.08.

For the saponification of palmkernel oil with aqueous KOH KELLNER now gives the values of columns 1, 2, 3, and 6 of table 4.

TABLE 4.

1	2	3	4	5	6	7
Acid value	Saponification value	% glyc. in the fat	% glyc. with resp. to total fatty acid	100 g	% free fatty acid in the fat	100 T
96.3	249	8.26	8.56	39.20	37.32	38.67
193.3	253.8	3.41	3.47	75.35	74.92	76.16

It appears from columns 5 and 7 that $g = T$, hence practically $p = q = \infty$ (cf. § 11 and fig. 2 line A), in other words, there practically directly takes place splitting up into fatty acid and glycerine.

The values found by KELLNER for the saponification of palm kernel oil with lime are found in columns 1, 2, 3, and 6 of table 5,

TABLE 5.

1	2	3	4	5	6	7
Acid value	Saponification value	% glyc. in the fat	% glyc. with resp. to total fatty acid	100 g	% free fatty acid in the fat	100 T
101.65	248.8	7.80	8.09	42.54	39.39	40.85
169.5	251.0	4.31	4.43	68.54	65.69	67.52

Here too it appears on comparison of columns 5 and 7 that $g = T$, and therefore $p = q = \infty$ must be practically valid also here. It follows therefore from KELLNER's experiments that in the saponification of palmkernel oil with aqueous lye, as well as with

lime, the triglyceride splits up practically directly into glycerine and fatty acid.[1])

This result is in conflict with the results of LEWKOWITCH [2]), who in the alcalic saponification of tallow and cottonseed oil concluded to a saponification in measurable stages from the increase of the acetyl value. It is, indeed, not probable that tallow and cottonseed oil would have a stagewise saponification in alcalic surroundings, and palmkernel oil practically not.

As in the saponification of olive oil, tallow and tristearine with normal KOH R. FANTO [3]) has found that here too the separated quantity of glycerine agrees with direct splitting up of the triglyceride into glycerine and fatty acid, in LEWKOWITCH's experiments, the increase of the acetyl value must be explained by other causes than the presence of lower glycerides. MARCUSSON [4]) has shown that this is really the case. The increased acetyl value is as well caused by the *fatty acids,* as by the fat that has remained unsaponified. Probably the oxidation of the unsaturate fatty acids plays a part here, which also explains the irregularity of increasing and decreasing of LEWKOWITCH's acetyl values.

The results obtained by FANTO and KELLNER, perfectly confirm the conclusion drawn at the end of § 8. In alcalic surroundings the adsorption of the lower glycerides at the surface of contact between fat and water phase is so great that the chance to collision between an OH′ ion and a molecule of di- and monoglyceride is practically ∞ compared with the chance to collision between an OH′ ion and a molecule of triglyceride.

§ 20. For the fermentative saponification of palmkernel oil KELLNER found the values given in columns 1, 2, 3, and 6 of table 6. (See p. 60).

On comparison of columns 5 and 7 it appears that here $g \neq T$. In column 8 are recorded the values found for $100\,T$, when T is calculated from g by the aid of formula (48), i. e. on the assumption that $p = 3$ and $q = \infty$. (See § 17 and fig. 2 curve F).

It appears that the calculated and observed values of $100\,T$ agree sufficiently, especially when we consider that g cannot be determined

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1) KELLNER draws this conclusion by comparison of the found glycerine content of the partially saponified fat with that calculated on the assumption of a direct complete splitting up.

2) Ber. **33**, 89 (1900); **36**, 175, 3766 (1903); **37**, 884 (1904); **39**, 4095 (1906).

3) Monatshefte f. Chemie **25** 919 (1904).

4) Ber, **39** 3466 (1906), **40** 2905 (1907).

TABLE 6.

1	2	3	4	5	6	7	8
Acid value	Saponification value	% glycerine in the fat	% glyc. with respect to total fatty acid	100 g	% free fatty acid in the fat	100 T	100 T calc. from (48)
66.7	241 5	10.63	11.36	19.32	25.86	27 63	27.53
78.4	243.3	9.95	10.55	25.07	30.39	32.23	33.40
84.27	243.6	9.63	10.20	27.56	32.66	34.59	35 87
116.10	247 2	7.92	8.27	41.26	44.99	46.96	48.92
165.15	250 8	5.38	5.53	60.72	64.01	65 85	66.45
234.22	252.7	1.41	1.44	89.77	90.78	92.68	91.43

more accurately than to about 1 % (for smaller values of g a much greater error is even inevitable).

Of course the conclusion may *not* be drawn that in the said saponification $p = 3$ and $q = \infty$. Also by assuming other values of p and q equations can be drawn up (which however in general do not enable us to express T explicitly as function of g), which more or less accord with the values found experimentally [1]). Accordingly equation (48) and likewise the equations discussed in the following §§ must be considered as formulae of approximation, which roughly give an insight into the relations of the surface tensions of the three glycerides against the saponifying surroundings. When the relation between p and q on one side and the surface tensions between aqueous solutions and the three glycerides on the other side are quantitatively known, then we shall be able to decide in how far the here assumed values of p and q are conformable to the truth.

With regard to table 6 it may still be pointed out that the results obtained by KELLNER do not agree with what was found by M. NICLOUX for the fermentative saponification of cottonseed oil. From NICLOUX's values follows a practically direct splitting up into glycerine and fatty acid. (See § 5). Possibly the difference lies in this that KELLNER kept the emulsion in motion by blowing in air, NICLOUX on the other hand brought about the emulsion by stirring, and left it undisturbed after that.

[1]) It is the question whether p and q are *here* only functions of the surface tensions between glycerides and the *aqueous solution*, as the enzym is not in solution according to NICLOUX (loc. cit.). (See also § 7).

In conclusion it may still be pointed out here that the relation existing between free fatty acid and separated glycerine offers a chance to throw light on the mechanism of the splitting up of fat in germinating seeds. It is still an open question whether the reaction takes place there analogously to the saponification by the aid of the ferment from ricinus seed.

§ 21. In the saponification according to the TWITCHELL process KELLNER found for palmkernel oil the values from columns 1, 2, 3, and 6 of table 7.

TABLE 7.

1	2	3	4	5	6	7	8
Acid value	Saponification value	% glycerine in the fat	% glyc. with respect to the total fatty acid	100 g	% free fatty acid in the fat	100 T	100 T calc. from (41)
56.9	241.7	(11.36)	(12.13)	(13.85)	22.05	23.54	(30.79)
91.9	242.0	10.32	11.00	21.88	35.63	37.99	39.48
122.4	244.8	8.72	9.19	34.73	47.43	49.99	51.48
177.5	248.9	5.15	5.34	62.07	68.81	71.33	73.38
210.3	252.0	2.87	2.94	79.12	81.54	83.48	85.72

In column 8 are found the values of 100 T calculated from g by the aid of formula (41), which has been derived for the case that $p = 3$ and $q = 9$, but which with a deviation smaller than 0.3 % is also valid for the case that $p = 1$, $q = 23$ (cf. § 15 and fig. 2 curve E).

In the first row the found and the calculated values of 100 T diverge greatly. This, however, says little, as this great difference already disappears if the glycerine content of the fat is 12.1% instead of 11.36%. When little glycerine has as yet been separated, a small error in the glycerine content of the concerned sample or of the triglyceride, on which the calculation of g is based, has a very great influence on the calculated value of T. The agreement between the other values of column 7 and 8 is satisfactory.

As it now appears from the experiments described in § 7 and § 8 that $p = 1$ in general in the TWITCHELL saponification, q must have a value in this case, which, as appears from the agreement

of columns 7 and 8 in table 7, differs little from the value $q = 23$ at the lower limit. [1])

§ 22. The values found by KELLNER in the autoclave process of palmkernel oil are found in columns 1. 2, 3 and 6 of table 8.

TABLE 8.

1	2	3	4	5	6	7	8
Acid value	Saponification value	% glycerine in the fat	% glyc. with respect to total fatty acid	100 g	% free fatty acid in the fat	100 T	100 T calc. from (36) and (37)
55	242	(12.16)	(12.96)	(7.95)	21.30	22.71	(31.24)
131.5	247.5	9.84	10.26	27.13	50.96	53.12	52.72
193	251	5.28	5.43	61.43	74.80	76.89	77.94
212	252	3.75	3.84	72.23	82.17	84.13	84.89
218	253	2 83	2.89	79.47	84.48	86.15	88.85
229.5	254.7	2.11	2.14	84.80	88.94	90.09	91.86

In column 8 are found the values of 100 T calculated from g by the aid of the equations (36) and (37), i.e. on the assumption that $p = 1$ and $q = 4$ (see § 13 and fig. 2 curve D).

In the first row the deviation between the found and the calculated values of 100 T is again greatest. Much importance should not be attached to this here either, as this deviation already disappears when the glycerine content of the fat is 12.6% instead of 12,16%. The other values of columns 7 and 8 agree sufficiently.

It is not improbable that also in the autoclave saponification, where the saponification takes place in feebly acid surroundings, $p = 1$. Nothing can be said of this, however, with any certainty, as the influence of zinc soap has not been examined in the experiments of §§ 7 and 8. If really $p = 1$ also here, q must have a value which differs little from $q = 4$ in virtue of the agreement of columns 7 and 8 of table 1.

SUMMARY.

It has been shown in this paper that in the saponification in emulsion the reaction takes chiefly place on the boundary of the

[1]) A deviation upward has little influence. (See table 3 columns 5 and 6).

two phases and that in this case the process of the saponification is governed by the value of the surface tensions between the glycerides and the saponifying medium.

As velocities of saponification do not give an insight here in the mechanism of the reaction, because they are influenced by the variable fineness of the emulsion, equations were derived which give the relation between separated fatty acid and separated glycerine.

The equations, in which the increase of concentration of the lower glycerides at the surface of contact between fat and water-phase were taken into acount, appeared to be able to account for the different course of the saponification in different surroundings.

In conclusion I gladly avail myself of the opportunity to express my thanks to Dr. GEITEL for the kind interest he has taken in my work.

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