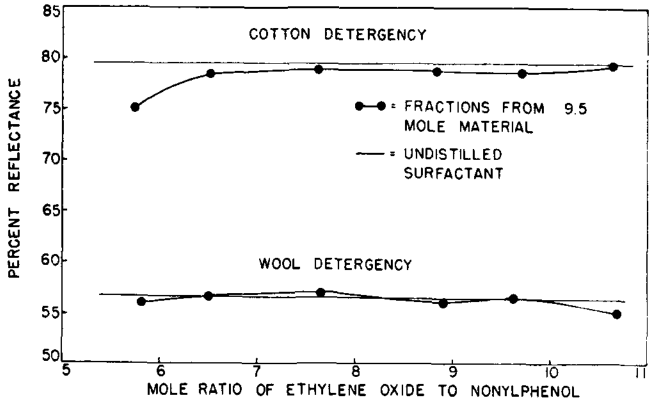

FIG. 7.

water containing 2.5 g. per liter of surfactant at 60° C. for 15 minutes. They were rinsed in the Terg-o-tometer in distilled water for two minutes and then dried in a hot-air oven at 50°C.

The wool swatches were soiled from a carbon tetrachloride suspension of carbon black and mineral oil to a reflectance also of approximately 40. These were also washed in the Terg-o-tometer, using distilled water which contained 2.5 g. per liter of surfactant.

The results (Figure 7) show that there is no significant difference between distilled and undistilled products with respect to both cotton and wool detergency.

Summary

It has been shown repeatedly (1, 2, 3) that for polyoxyethylated nonionic surfactants a certain hydrophobe-hydrophile balance (i.e., average mole ratio of ethylene oxide to hydrophobic material) is necessary to obtain maximum wetting, optimum detergency, etc. A study has been conducted to determine the effect of mole ratio distribution of ethylene oxide on the physical properties of a polyoxyethylated nonylphenol. This was accomplished by molecularly distilling two nonionics: a nonylphenol plus 6.0 moles of ethylene oxide and a nonylphenol plus 9.5 moles of ethylene oxide. The following conclusions have been reached concerning the effect of mole-ratio distribution on the physical properties of these surfactants.

1. The mole ratio distribution of ethylene oxide in a polyoxyethylated nonylphenol follows the Poisson formula and curve in a manner analogous to the polyoxyethylene glycols (Fig. 1).
2. The hydrophobe-hydrophile balance of the undistilled surfactant may be altered by molecular distillation. This is accomplished by narrowing the range of molecular species.
3. Wetting which is superior to the undistilled material may be effected by narrowing the distribution of molecular species (Figure 3).
4. Fractions from the distilled surfactant showed slight improvement in initial foam volume at certain mole ratios of ethylene oxide to base material over the undistilled material (Figure 6). No change in foam stability was noted.
5. Although there is an optimum ratio of ethylene oxide to the hydrophobic base at which maximum cotton or wool detergency is obtained, cotton and wool detergency are relatively unaffected by mole ratio distribution (Figure 7).
6. Surface and interfacial tension are also comparatively unaffected by mole ratio distribution change.
7. Emulsifying properties of these materials are adversely affected by narrowing the mole ratio distribution.

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Industrial Fat Splitting

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UNTIL quite recently fat hydrolysis had been considered as a heterogeneous reaction that occurs in the oil-water interface (3, 4, 10, 16). However Lascaray has shown (6, 7, 8, 9) that in the industrial Twitchell and autoclave splitting processes this reaction is essentially homogeneous and takes place in the oil phase, thanks to the dissolution of small quantities of water in it, continually renewed by stirring of the phases.

Later on Suen and Chien (15) deduced from their experiments by the sulfuric acid method that acid hydrolysis also occurs in the oil phase, being a reaction of the first order with respect to the unhydrolyzed oil. Mills (11) considers it obvious that the reaction takes place in the oil phase. Sturzenegger and Sturm (14), in a study of hydrolysis at high temperatures, agree with Lascaray's theory. Hartmann (2), on studying the kinetic order of splitting by the Twitchell process, reaches the conclusion that the resulting first-order reaction can be accounted for in the simplest way by assuming that the hydrolysis takes place in the oil phase. Bailey (1) considers the Lascaray theory today as generally admitted. Finally, Yanase (17) confirms the small importance of the heterogeneous reaction in Twitchell splitting by demonstrating that the addition of emulsifying agents gave no particular benefit.

It thus appears that the main works of investigation on fat hydrolysis published in the last 10 years agree upon a homogeneous hydrolysis in the oil phase and that this theory is of general value since it is applicable with the same efficacy to the different industrial splitting processes, whether autoclave, Twitchell, high pressure, or sulfuric acid methods.

Therefore it seems desirable to review, under this new aspect, the different phases of the industrial fat splitting and to try to establish rules of general application.

Induction Period

An induction period, during which the rate of reaction, at first low, gradually increases up to its normal value, is observed whenever fats containing a low proportion of free fatty acids are hydrolyzed. The cause of the induction period is in relation with the small solubility of water in neutral fats, as opposed to higher solubility in fatty acids.

Mixtures of neutral tallow and its fatty acids were stirred with 10% water at 100°C. After a sedimentation period a well clarified sample of some 50 g. of fat was weighed, without loss of moisture, in a tared beaker, which was afterwards dried to constant weight. The results obtained are shown in Table I.

At 100°C. water is 4 to 5 times more soluble in fatty acids than in neutral fat since the solubility in fats increases proportionally to its fatty acid content.

TABLE I
Solubility of Water at 100°C. in Neutral Tallow and in Tallows With Different Free Fatty Acid Content

Free fatty acid %	Grams water dissolved in 100 g. fat
0	0.27
20	0.45
40	0.66
60	0.84
80	1.05
100	1.22

On hydrolyzing fats with low free fatty acid content, the concentration of water in the oil phase will therefore be low at first. When reagents or catalysts are employed, whether acid (Twitchell) or basic (autoclave), these hydrolytic agents are not soluble in neutral fats. At the beginning of the reaction the catalysts remain in the aqueous phase, being partially adsorbed in the interface and emulsifying fat and water. With fats of low free acid content, coinciding with the induction period, hydrolysis is then at first mainly heterogeneous. This induction period of hydrolysis in emulsion ends as soon as there exists 15 to 20% free fatty acids in the mixture since as the solubility of water in the fats increases, the reagents disappear in the aqueous phase and with these the emulsifying facility.

The length of the induction period depends mainly on the splitting temperature. Since the solubility of water in fats increases greatly as the temperature rises (10), the higher the reaction temperature, the shorter the induction period. At high temperatures (260 to 280°C.) Sturzenegger and Sturm (14) find very short induction periods, which are more pronounced at lower temperatures (240 to 225°C.). Mills (11) finds that no induction period is observed between 230 and 250°C. On the other hand, in Twitchell splitting, effected at 100°C., very long induction periods are observed, which may reach over 5 hours reaction time if much water is used (9). According to this, the longest induction periods must be observed in enzymatic splitting, which occurs at about 35°C.

The existence of an induction period in splitting fats with low free fatty acid content means a delay in the hydrolysis and a superfluous expenditure of steam. Two methods are advisable to reduce the induction period. The first consists in mixing the fat with a determined quantity of fatty acids, to obtain a mixture that will easily dissolve reagent and water. A variant for the autoclave splitting is to add the catalyst (metallic oxide), dissolved in an excess of fatty acid. The patent of the Société Générale Belge de Déglicerination, in 1906 (12), so much discussed at the time, that, in order to suppress the inductive period in autoclave splitting, added to the fat to split 5% of the mass from the preceding operation, now appears on an exact basis. With this simple expedient it was possible to begin the splitting in its rapid reaction phase, thus avoiding the delay produced by the induction period. The most advantageous proportion of fatty acid to be added is such as to have a percentage of free acid in the mixture of approximately 15%. The advantage thus obtained with a more rapid splitting may appear to be offset by the diminution of the installation's effective splitting capacity. But one appreciable benefit of a rapid reaction must be noted: the lesser darkening of the fatty acids, on account of their having been submitted for a shorter time to the action of high temperatures. In the case of fats with low free fatty acid content and therefore, in general, of good color, this advantage is well worth taking into account.

The second means of eliminating the induction period, especially applicable to the Twitchell process, is to increase the sulfuric acid concentration at the start, either strengthening its proportion, or, and this is more practical, reducing the initial quantity of water, which will be increased later up to its normal value. It is well known that sulfuric acid augments the activity of the Twitchell reagents. This effect, generally attributed to the increase of the H ions concentration, is in reality due (9) to the fact that the mineral acid lessens the solubility of the reagents in water, displacing them towards the oil phase, annulling their emulsifying action and thus suppressing the induction period. Hartmann (2) has confirmed the elimination of the induction period and the shortening of the hydrolysis time by this procedure and has pointed out its advantages in industrial practice.

Stirring

Although fat hydrolysis is a homogeneous reaction in the oil phase, as it takes place in a heterogeneous medium two material transfer processes of contrary sign must be established to and away from the interface between the two phases: a) diffusion of water molecules to the interior of the oil phase and b), in order to eliminate the glycerol as it is produced, diffusion of glycerol molecules to the water phase.

Since the net rate of the splitting reaction will be controlled by the slower process, depending on whether the chemical reaction or the diffusional process is the slower, the former or the latter will determine the real splitting rate. The diffusion coefficients are generally low so that transfer of water or glycerol through the interface will be effected slowly unless differences of concentration caused by hydrolysis are rapidly compensated by strong stirring. However, despite strongest agitation, a strongly adherent adsorption layer forms at the interface, which does not move with the rest and can advance only by diffusion. Thus the most intense stirring does not prevent the speed of diffusion from being decisive in the rate of hydrolysis.

Complete hydrolysis of 100 kg. neutral fat with a saponification value of 200, consumes 6.4 kg. water and produces 10.9 kg. glycerol. At 100°C. the quantity of water soluble in the oil phase is only a small fraction of the quantity necessary, and unless the water is renewed, the reaction will soon cease. At

185°C. the solubility of water in fat is from 2 to 3% so that there exists in the oil phase sufficient water for the reaction to advance up to 30 to 50%. At 230 to 250°C. the oil phase contains 10 to 20% dissolved water (10), that is, sufficient for the complete reaction.

Glycerol, which is practically insoluble in the dry fats, becomes somewhat soluble when the fats contain dissolved water. From data published by Mill and McClair (10) it may be deduced that a fat in equilibrium with a water-glycerol solution dissolves glycerol and water in such proportion that the glycerol: water relation is the same in both phases. A fat with 10% dissolved water, in contact with a solution of 15% glycerol, will contain 1.5% free glycerol in solution.

The retarding influence of glycerol on the progress of the reaction is noticeable only towards the end when the reaction approaches equilibrium. During the beginning and the greater part of the process, need of stirring will be determined only by the needs of water in the oil phase. Therefore the higher the splitting temperature, the less will be the importance of stirring. In the low temperature processes (fermentative and Twitchell) it will be necessary to employ a rather active stirring method. On the other hand, in the autoclave splitting process at medium temperature (185°C.), a simple mode of agitation will suffice, as, for instance, a slight escape of steam. At high temperatures (225 to 250°C.) stirring becomes unnecessary since from the beginning there exists sufficient water in the fat to complete the reaction. It will suffice to establish a counter-current of water to carry away the glycerol that forms.

Towards the end of the hydrolysis the velocity of the chemical reaction diminishes considerably and as the diffusion rates remain constant, the former controls the process. On account of the slow rate of reaction, the exchanges between the phases need to be little active and stirring loses importance.

Thus the conclusion of general application is that the higher the splitting temperature and the more advanced the stage of the process, the less will be the importance of stirring.

Kinetics of Splitting

If fat hydrolysis, as a slow reaction, progresses at a determined rate, as an incomplete reaction, it tends towards an equilibrium. Rate and equilibrium are two independent characteristics. Those factors influencing splitting rate have no action on the chemical equilibrium, and those capable of shifting the position of equilibrium do not influence its rate.

Whatever the process employed, the rate of hydrolysis is speeded by raising the temperature or by the use of catalysts but is not altered by the quantity of water employed. On the other hand, the degree of hydrolysis at equilibrium depends exclusively on the concentration reached by the glycerol, i.e., on the quantity of water used.

Temperature. Fat hydrolysis possesses a positive temperature coefficient. An increase of temperature of 10°C. produces a rise of velocity of 1.2 to 1.5 times (8). The greater part of the homogeneous reactions have temperature coefficients of 2 to 4, and in some cases up to 7. The physical processes however, such as dissolution rate, diffusion, etc., have temperature coefficients of 1.3. The low coefficient of fat hydrolysis shows, as has already been said, that the process is governed principally by physical phenomena, as diffusion, which, when they are slower, control the rate of the reaction. It is therefore useless to try to deduce from the progress of hydrolysis the kinetic order to which the reaction belongs, as has recently been attempted (2, 15). As the diffusion equation has an identical form to that of a unimolecular reaction, the expression of an apparent first order reaction will always be obtained. Only if the temperature coefficient is determined, will it be possible to decide whether such observations constitute the kinetics of the physical process of diffusion or that of the chemical reaction of hydrolysis.

Table II shows (8) the relative rate of fat splitting at different temperatures, in the period of constant rate (7), taking the rate at 150°C. as unit.

TABLE II

Relative Rate of Hydrolysis at Different Temperatures

Temperature, °C.	Relative Rate
100	0.03
150	1
170	2.4
185	5.5
200	13.9
220	33.3

Nothing is known as to the influence of temperature on Twitchell hydrolysis since this is always carried out at 100°C. and would prove impracticable at the higher temperatures because the catalysts are destroyed.

Catalysts. The use in small amounts of certain hydrolytic agents, called "reagents" or "catalysts," considerably speeds the hydrolysis. The catalysts differ according to the splitting processes employed. In the autoclave and in some high temperature processes catalytic bases are used, consisting of some metallic oxides or hydroxides, which on combining with fats form metal soaps, which really act. In the Twitchell process acid catalysts are employed, formed of different sulfonated compounds of benzene or naphthalene with fatty acids, of composition not generally well known, obtained partially as by-products of mineral oil refining.

Despite such different composition both types of catalysts act in an analogous manner since they both possess the common property of difficult solubility in neutral fats and of easy solubility in fatty acids. At the beginning of the reaction, during the inductive period, the catalysts remain in the water phase, promoting emulsification and without favoring greatly the progress of hydrolysis. Only when there exists sufficient quantity of fatty acid, do the catalysts pass to the oil phase, the basic ones thanks to their transformation into metal soaps and the acid ones through their affinity with fatty acids. A proportion of 15 to 20% of free fatty acids is generally enough for all the catalyst to be found in the oil phase.

The catalytic action of the reagents is exercised fully in the oil phase. Experimental development has shown (7, 8) that this action is at last double: a) increase of solubility of water in the oil phase, and b) increase in the hydrolyzing activity of the dissolved water.

The reagents increase the solubility of water in the oil phase, thanks to the hydrophile groups they contain. In the metal soaps these are represented by the metal ions, and in the acid reagents by the SO_3H groups. Both possess a great affinity for water but, on being attached in their molecule to a hydrophobe rest, they must remain in solution in the oil phase. The result is that molecules of water are carried to that phase and are thus available for hydrolysis.

The activity of metallic oxides is ordered according to the hydrophile series (7), the divalent metals being, in terms of equal water dissolved, more active than the univalent. The series observed is as follows:

ZnO	MgO	CaO	LiOH	NaOH	KOH	NH_4OH	H_2O
6.0	3.1	2.3	2.0	1.7	1.4	1.1	1.0

The figures placed under the symbols represent the respective hydrolyzing activity, determined in the splitting of tallow at 185°C., with 60% water and 0.5% NaOH, or equivalent amount of the other catalysts, taking as a unit the splitting rate with pure water in equal conditions.

The preponderance of the divalent metals demonstrates that the molecules of water carried by these to the oil phase are more active than those carried by the univalent metals. From a kinetic point of view it may be supposed that for hydrolysis to be produced the molecule of water must collide with the molecule of glyceride. Of the numerous collisions that take place, only a few lead to an effective splitting, those which occur precisely in the point of union of the glyceryl and fatty acid radicals and also possess sufficient energy to break that union. Normally the molecules of water will need to be activated by the supply of a certain quantity of activation energy by the catalyst in order to overcome the energetic barrier that opposes the splitting.

It is known that the acids and bases appear to exercise a catalytic action in all the reactions produced with absorption or elimination of water. Their effect is proportional to the concentration of H and OH ions respectively. The ionization constant of water, namely the product of the concentrations of H and OH ions in pure water, possesses a very weak value at 25°C., about 10^{-14}, but at 250°C. it is almost 1,000 times greater. If, simultaneously with the raising of temperature, the level of energy opposing the hydrolysis is lowered, it is obvious that pure water at high temperatures may split fats without the help of catalysts.

The acid catalysts activate the molecules of water, considerably increasing the H ions concentration. They are 15 to 20 times more active than the best basic catalists since they effect hydrolysis at 100°C., which cannot be done to an appreciable degree with any basic catalyst.

It has been customary to ascribe the action of basic catalysts to the OH ions, but in the presence of free fatty acid such ions cannot exist in appreciable amount. On the other hand, the OH ions are catalysts some 1,400 times more active than the H ions, and yet in fat hydrolysis the basic catalysts are much less active than the acid. One must thus dismiss the influence of OH ions. The basic catalysts appear to act through their metal ions since the activity they show is in relation to the ionizing potential of the respective metal atoms, whether these ions act directly or, and this is more probable, they "activate" the molecules of water by increase of their degree of ionization.

'Since the rate of hydrolysis depends on the quantity of water dissolved in the oil phase and on the degree of activation of this water, the increase of the quantity of catalytic agent will produce a proportional increase in the rate of hydrolysis. In practice it is often interesting to obtain a rapid hydrolysis, not only for the increase of output of the installation, but chiefly on account of the lesser darkening produced in the fatty acids during a short reaction. The most rational method of obtaining this result is to increase the proportion of catalyst up to the economic limit admissible. There generally exists a prejudice against using small amounts of catalysts of about 0.5%. However as the expense in respect of catalyst is usually low, there should be no hesitation in using much larger proportions when for various reasons a quick reaction is desired.

In modern processes of continuous hydrolysis at high temperatures there is a tendency to suppress the use of catalysts, owing to the complication of their subsequent separation and doubtless to the fact that the reaction without them is considered already sufficiently rapid. Temperature and catalyst being two independent variables that raise the hydrolysis rate, it is illogical to dispense with the advantages offered by the use of catalysts, with which the same speed of reaction may be obtained at a lower temperature and the consequent simplification and economy in the installation.

Chemical equilibrium. As already stated, fat hydrolysis is limited by the reverse reaction of esterification. The position of equilibrium is independent of temperature. The hydrolysis of glycerides proceeds without detectable heat of reaction (5, 7). The degree of hydrolysis at equilibrium is also independent of the presence or absence of catalysts, of their nature or quantity, because catalysts, taking no part in the reaction, can have no influence on the chemical affinity of the fatty esters to water but merely on the resistance opposing the progress of the reaction.

In accordance with the law of mass action the position of equilibrium depends on the concentration acquired by the glycerol in the oil phase. As, according to the results of Mills and McClair (10),

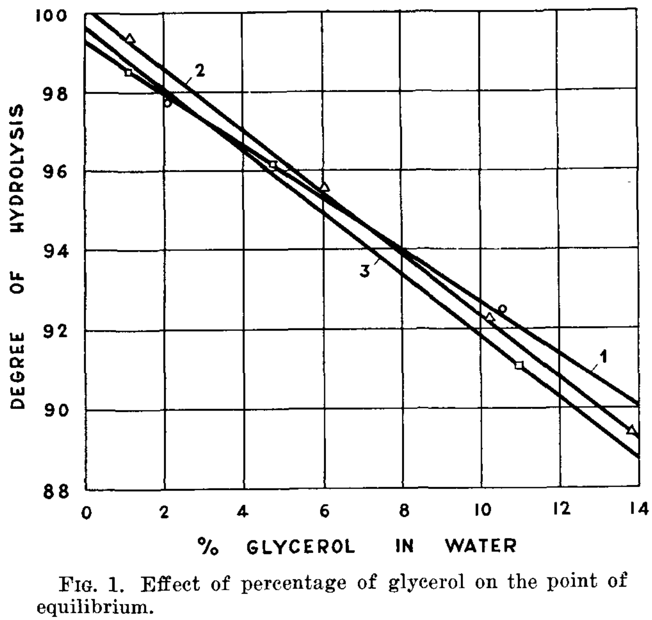

FIG. 1. Effect of percentage of glycerol on the point of equilibrium.

1) Palm kernel oil, Twitchell, 100°C. (9).
2) Tallow, autoclave, 235 and 250°C. (10).
3) Coconut oil, autoclave,, 235 and 250°C. (10).

the concentrations of glycerol in the oil and aqueous phases are in a relation of simple proportionality, the equilibrium can be characterized by the concentration of glycerol in water, which is more convenient for control of the reaction.

Experimental study shows that the nature of the fat has very little influence on the degree of hydrolysis at equilibrium. In Figure 1, from data obtained by Lascaray (9) and by Mills and McClair (10), curves are reproduced for different fats, split by Twitchell or the high temperature autoclave method, by plotting the maximum degree of hydrolysis attainable against the concentration of glycerol in the water phase. In the zone under consideration, namely that affecting industrial practice, the curves almost coincide, the divergencies do not amount to 1% of split fat. From these curves it may be deduced that the influence exercised by the concentration of glycerol on the degree of hydrolysis at equilibrium may be expressed by the following simple equation:

$$H = 100 - 0.8\,G$$

where H is the degree of hydrolysis at equilibrium and G the percentage of glycerol in the "sweet waters." This empirical formula claims validity only up to concentration of 20% glycerol, that is, in the zone of industrial interest. Despite its simplicity it turns out to be more exact than that proposed by Sturm and Frei (13). Table III has been so calculated. As the curve of hydrolysis versus time approaches asymptotically the abscissa, equilibrium is reached only after infinite time. The values indicated in the last column of Table III represent the degree of hydrolysis at which practically the reaction is to be interrupted, with relation to the concentration acquired by the sweet waters.

TABLE III

Influence of the Concentration of Glycerol on the Degree of Hydrolysis at Equilibrium

Glycerol	Degree of hydrolysis at equilibrium	Maximum attainable. Degree of splitting in practice
%	%	%
1	99.2	97.5
2	98.4	96.0
4	96.8	94.5
6	95.2	93.0
8	93.6	91.5
10	92.0	90.0
12	90.4	88.5
14	88.8	87.0
16	87.2	85.5
18	85.6	84.0
20	84.0	82.5

The above considerations lead to the following important conclusion: within the limits used industrially, to every concentration of glycerol there corresponds a maximum degree of hydrolysis attainable, which is independent of the temperature, the method of splitting, the presence or absence of catalysts and even of the nature of the fat.

Splitting in Several Stages

The two conditions demanded by industry, namely, high degree of splitting and maximum concentration of sweet waters, are, according to Table III, incompatible. A high degree of splitting is possible only with a very low concentration of glycerol. This difficulty is overcome in practice by means of hydrolysis in two or more stages, interrupting the reaction when the glycerol has reached an acceptable concentration and replacing it by pure water. It is unnecessary to add more reagent as this latter is conserved entirely in the oil phase. Only in the Twitchell process is it customary to add a little sulfuric acid. Its action consists in lowering the solubility of the catalyst in water, preventing its passing again from the oil to the aqueous phase, where its action would be almost nil.

To reach a very high degree of splitting the use of three or four stages is indispensable since the concentration of glycerol of the sweet waters must be below 1%. It is furthermore necessary to extract completely the liquors resulting from each boiling since all the remaining glycerol will act as a brake upon the following stage and will reduce the limit attainable. Some glycerol is in every way soluble in the hydrated fat. In general, the autoclaves, on account of their form, offer the possibility of an easy separation of the phases. This does not usually occur with the vats of the Twitchell process, which generally have a flat bottom which makes it inevitable that, on separating the phases, appreciable quantities of glycerol will remain in the vat. Constructors should bear in mind this requirement, varying the design of the Twitchell vats in the sense of giving them conical or inclined bottoms that will permit a perfect separation of the phases.

Summary

The reaction of fat splitting, whatever the process employed, obeys the following general rules:

a) The greater the proportion of free fatty acids in the fat to be hydrolyzed, the shorter will be the induction period.

b) The higher the reaction temperature and the more advanced the process, the less necessary the stirring.

c) The rate of hydrolysis is augmented by the raising of temperature and by the use of catalysts, proportionally to its quantity. The most active catalysts are those which most increase the solubility of water in the oil phase and which at the same time most activate that water, raising its degree of dissociation.

d) The degree of hydrolysis at equilibrium, whatever the fat to be split, depends exclusively on the glycerol concentration of the sweet waters.

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