

Messrs. Blair and Dudley have pointed out that all the sulphur is not oxidized by the aqua regia method. The writer feels that too much stress cannot be brought to bear on the sulphur question in pig iron as no concordant results can be brought about from the pig iron to the steel.

One of the prominent eastern mills, to account for the error, uses a factor which is far ahead of reporting 100 per cent. of the results wrong as is the case with the evolution method. In conclusion, the writer earnestly invites any criticism if he has made misstatements. His motive has only been to help along the science.

Note.—Since writing the above more experimenting along this line with iron low in sulphur, say No. 1 Bessemer, has brought out the fact that the error between the gravimetric and volumetric methods is not so apparent until about a No. 2 grade is reached.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE AGRICULTURAL EXPERIMENT STATION.]

A CONTRIBUTION TO THE CHEMISTRY OF BUTTER-FAT.

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III. THE CHEMISTRY OF RANCIDITY IN BUTTER-FAT.

THE phenomena attending the development of rancidity in fats have attracted the attention of chemists for many years; even before the beginning of the present century, ere Chevreul had begun his classical "recherches chimiques sur les corps gras," and when the chemical constitution of fats was still unknown, it had been surmised that the physical changes which oils and fats underwent on long keeping were simply the results of oxidation; and this is the view most generally accepted at the present time, notwithstanding the fact that many eminent chemists in the past have sought to explain the development of rancidity in other ways.

From the very complexity of its composition we would suppose butter-fat to be a rather unstable body; if butter-fat is sealed up and preserved in a cold, dark place, it will retain its normal character and appearance for many months, but if kept in a

warm locality with free exposure to the air and light, it will very speedily undergo chemical and physical changes and become, as we say, rancid.

By the term "rancidity" is meant not simply, as is generally supposed, a development of free acid (though this is the general concomitant of rancidity), but any chemical or physical change in the character of a fat from the normal. Fats can be rancid without necessarily being very acid;¹ rancidity, according to the present most commonly accepted understanding of the term, is simply oxidation, and in the early stages of the process butter-fat may lose its characteristic color and smell, and develop an abnormal lardy taste, and still not show an excessive degree of acidity.

That rancidity in butter, as many authorities aver, is primarily the result of the activity of bacteria, is no doubt partly true of whole butter with its lactose, casein, and other constituents to serve as bacterial food, but it is certainly not the case with pure butter-fat which is unable to support micro-organic life. The independent researches of both Duclaux² and Ritsert³ prove beyond question that bacteria cannot thrive in a medium of pure fat, and that all changes which take place in fats on keeping are wholly the results of an oxidation, conditioned to a great extent by exposure to light. The distinction between rancid butter and rancid butter-fat should be borne in mind, since the former condition may prevail without the latter. We have paid but little attention to the development of rancidity in whole butter,⁴ and will make this a subject for future study. The present work is confined entirely to those changes which the pure fat undergoes after its separation from all impurities.

¹ We believe v. Klecki was the first to distinguish between the terms rancidity and acidity. *Ztschr. anal. Chem.*, 34, 633 (1895).

² *Annal. de l'Institut Pasteur*, 1888.

³ *Untersuchungen über das Ranzigwerden der Fette*.

⁴ Lactic acid is always found in both fresh and rancid butter, but never in rancid butter-fat. We have found 0.03 per cent. of lactic acid in fresh butter made from ripened cream, and 0.12 per cent. in a rancid butter. The latter sample also contained 0.23 per cent. of free volatile acids, having a mean molecular weight of 94, to which acids the rancid odor and taste of the butter were no doubt largely due.

The statement frequently met with that rancidity in butter is produced by the action of a butyric ferment upon the fat with the formation of butyric acid, is not warranted. It is a well-known fact that milk sugar may pass by fermentation through lactic into butyric acid, and there is every probability that, under favorable conditions, much of the lactose in butter is converted in this way into volatile acid products.

The part which bacteria play in the spoiling of butter has been studied but little up to the present time; the question is one well worth the attention of bacteriologists.

The three factors most active in the production of rancidity in fats are openness to air, exposure to light, and degree of warmth. Given sufficient time, decomposition may occur with the suppression of any one or even two of these elements, but it is of course most rapid when all three conditions are favorable.

In the development of rancidity in butter-fat, under the usual conditions named above, there are observed first of all several changes as regards color, odor, taste, and general appearance. The sample examined begins first to acquire a lighter color; this change appears first on the surface, and the parts most exposed to the light, from which points the action spreads slowly downward until finally the whole mass has become bleached.¹

With this loss of color we notice also the development of a lardy odor and taste; as the period of rancidity advances the odor increases in pungency, while the taste, which at first was not markedly acid, becomes exceedingly burning and unpleasant. In addition to the above we observe some changes in consistency; the sample, which originally was firm and solid in texture, begins to take on a granular look and finally turns, after many months, into a semisolid pasty mass.

If we determine the various constants of a butter-fat at different periods of rancidity, we notice still other important changes, as can be seen from the following table :

TABLE XII.

Age of sample.	Degrees rancidity.	Acid number.	Saponification number.	Ether number.	Reichert number.	Iodine number.	Oleic acid. Percent.
Fresh	0.9	0.48	228.1	227.6	15.63	34.95	38.79
1 week	2.3	1.28	230.3	229.0	15.80	34.55	38.35
1 month	19.4	10.90	241.0	230.1	17.00	28.40	31.52
2 months	51.5	28.84	260.0	231.2	18.75	14.35	15.93
4 months	53.5	30.00	262.1	232.1	19.80	11.15	12.38
8 months	63.2	35.38	269.3	233.9	21.13	8.55	9.49

We observe with the development of rancidity, a decided increase in the acid, saponification, and Reichert numbers, a slight increase in the ether number, and a very marked decrease in the iodine absorption.

“Degrees rancidity” is a constant employed by many chem-

¹ This observation pertains only to samples of natural color; with butters artificially colored the bleaching is not always evident, showing that certain butter colors are not affected by the development of rancidity.

ists as another way of expressing the free acid in fats, and is placed in this and succeeding tables only for the purpose of comparison. It was introduced into fat analysis by Stockmeier¹ and represents the number of cubic centimeters of normal alkali required to neutralize the free acid in 100 grams of fat: the number of cubic centimeters of tenth normal alkali necessary to neutralize the free acid in ten grams of fat would also give "degrees rancidity;" one degree rancidity would correspond to an acid number of 0.56.

The effects of rancidity upon the composition of butter-fat are also shown by Table XIII, where the chemical constants of four different samples are given in both the fresh and rancid conditions.

TABLE XIII.

Butter-fat.	Condition.	Degrees rancidity.	Acid number.	Saponification number.	Ether number.	Iodine number.	Oleic acid. Per cent.	Acetyl number.	Insoluble acids. Per cent.	Glycerol. Per cent.
1a	Fresh	0.80	0.45	229.9	229.5	33.93	37.66	4.8	87.20	12.54
1b	Rancid	2.18	1.22	232.3	231.1	29.96	33.26	7.6	86.80	12.40
2a	Fresh	0.89	0.50	223.9	223.4	34.49	38.28	3.5	88.96	12.21
2b	{ Rancid, } 1 month	12.66	7.09	233.7	226.6	28.69	31.85	10.9	85.06	12.02
3a	Fresh	0.98	0.55	232.6	232.1	29.56	32.81	4.1	86.41	12.69
3b	{ Rancid, } 2 months	20.95	11.73	247.7	236.0	19.76	21.93	15.1	80.42	12.35
4a	Fresh	0.93	0.51	225.6	225.1	34.92	38.76	3.8	88.46	12.33
4b	{ Rancid, } 3 months	26.43	14.80	245.3	230.5	22.55	25.03	18.0	81.15	11.67

Sample 1 was exposed for three months to air and light in a cold room during winter; *a* represents the unoxidized bottom layer, and was unchanged; *b* represents the upper oxidized part which was bleached and had an abnormal taste and smell. Samples 2*b*, 3*b* and 4*b* were allowed to become rancid in a warm place, with free exposure to air and light.

In addition to the facts previously observed we note from the above table that with the advancement of rancidity there is an increase in the acetyl number and a decrease in the percentages of insoluble acids and glycerol. Other changes produced in the

¹ *Vierteljahrsschrift Nahr. und Genussmittel* (1889), 428. According to Stockmeier, a butter-fat showing more than eight degrees rancidity should be condemned as unfit for use. Chemists have recognized the impossibility of fixing any such arbitrary standard as this: a butter-fat may show only two or three degrees rancidity and still be offensive to our organs of sense, which latter, we may say, are far superior to any chemical methods in forming judgments as to the palatability of foods.

chemical and physical constants of butter-fat by rancidity will be presented in the course of the article.

EFFECTS OF RANCIDITY UPON THE ACIDS OF BUTTER-FAT.

It is a well-known fact, and one wholly confirmed by the preceding tables, that the oleic acid is the constituent of butter-fat most susceptible to chemical change; being an unsaturated compound it absorbs oxygen with great avidity at the points of unsaturation, yielding either oxy-compounds or decomposing into simpler bodies of lower molecular weight. It is impossible to express by chemical equations either of these changes, owing to the complexity of the reaction and the great variety of products formed.

By means of oxidizing agents oleic acid has been found to yield not only all the members of the homologous series from formic to capric acid, but also certain dibasic and oxy-acids.¹ While the oxidation process itself, which takes place with oleic acid in the development of rancidity, is less violent than that produced by artificial means, we may say that the character of the decomposition products is to a considerable extent the same.

A. Scala² detected in a strongly rancid olive-oil formic, acetic, butyric, and oenanthylic acids, also several dibasic acids of the type $C_nH_{2n-2}O_4$, among others azelaic and sebacic acids; besides these another acid was isolated which, from the analysis of its barium salt, was identified as dioxystearic acid. The same authority also shows that the saturated acids could take no part in the formation of these decomposition products, since they offer a complete resistance to oxidation; small portions of stearic and palmitic acid, on long standing, were found to suffer under ordinary conditions no change in weight; oleic acid, on the other hand, after ten months' exposure to the air and light, increased in weight over eight per cent. As an additional confirmation of this, it was found that the increase in weight, which different fats underwent on becoming rancid, was in direct proportion to their content in oleic acid.

The amount of oxygen which butter-fats absorb on becoming rancid we have found to vary somewhat with the conditions. A

¹ Watts' Dictionary of Chemistry, Edition of 1892, 3, 637.

² Staz. sperim. agr. ital., p. 613 (1897). Abstract in Biedermann's *Centrbl. für Agriculturchemie*, March, 1899, p. 196.

thin layer of butter-fat, exposed in a melted state to the action of air and light, gained at the end of two weeks 1.54 per cent. of the original weight; it then began to lose, and at the end of two months had lost 1.94 per cent. of the weight of the sample when fresh. Chemical change proceeds much faster with fats if melted, so that the preceding example can not be taken as a fair illustration of what takes place under ordinary conditions.

The following elementary analysis of two butter-fats, one fresh and the other rancid, gives some information as regards the amount of oxygen absorbed during rancidity.

TABLE XIV.

Butter-fat.	Condition.	Carbon. Per cent.	Hydrogen. Per cent.	Oxygen. Per cent.
I	Fresh	75.17	11.72	13.11
2 ¹	Rancid, 2 years old	73.88	11.57	14.55

These results show that the effect of rancidity is to cause a decrease in the percentages of carbon and hydrogen, with a corresponding increase in the percentage of oxygen. Similar results were secured by Lenz² in the case of fresh and rancid horse-fat.

Inasmuch as the iodine number is dependent upon the amount of oleic acid, it is obvious enough that this constant should show a decrease as the period of rancidity advances. We have given in Tables XII and XIII the percentages of oleic acid corresponding to the various iodine numbers. There is some uncertainty among chemists as to the accuracy of calculating the per cent. of oleic acid from the iodine absorption;³ this uncertainty would be still greater in the case of rancid fats, where there is the possibility that other unsaturated compounds besides oleic acid may for the time exist.⁴

The increase in the saponification number as the period of rancidity advances, can be explained only by the breaking up of higher acids into acids of lower molecular weight,—an explanation which is confirmed by the decrease observed in the per-

¹ This sample, which was badly decomposed, stood during the time indicated in a cool place near a window, where the light could have its full effect.

² *Ztschr. anal. Chem.*, p. 441 (1889).

³ For a discussion of this point consult Wiley's *Agricultural Analysis*, 3, 367. See also this *Journal*, 21, p. 811.

⁴ Such an error would not alter the main facts of the case, however, as the effect would be to magnify rather than diminish the actual percentage of oleic acid.

centage of insoluble acids, and by the increase which takes place in the Reichert number.

It was thought that a determination of the mean molecular weight of the volatile acids from rancid butter-fats would throw some light upon the character of the lower acids formed by decomposition, but the results were in some ways disappointing. The majority of the experiments showed but little difference between the molecular weights of the volatile acids from the fresh and rancid samples, the general tendency seeming to be towards a slight decrease in this constant, as the butter-fat became rancid. The mean molecular weight of the volatile acids formed by decomposition would appear from this to have nearly the same value as that of the volatile acids in the fresh sample; this would bear out the view that, in the breaking up of the oleic acid, several different soluble acids are formed, the lower members of the series apparently being produced in the largest quantity.

The free acid, which soon makes its appearance in all rancid fats, is due not simply to oleic acid and its decomposition products, but to other acids as well. In the development of rancidity there seems to be a gradual breaking up of all the glycerids. Samples of tripalmitin which we have prepared from butter-fat, while much more stable than the parent substance, show after long standing the same tendency to become rancid and develop free acid. This is true of other glycerids as well, the acid part of the molecule splitting off from the glycerol base with the probable disruption of the latter. In the case of complex oleins (oleobutyryl, oleopalmitin, etc.), the changes which so soon effect the oleic acid would no doubt hasten the disintegration of the entire glycerid. The first change which manifests itself in fats on becoming rancid is apparently an oxidation of some oleic acid within the molecule, as changes appear in physical and chemical properties before any considerable development of free acid. Butter-fat No. 1 in Table XIII affords us a good illustration of this; the upper oxidized layer of this sample, when compared with the lower unchanged part, shows a decrease of over four per cent. in oleic acid, and an increase of nearly three units in the acetyl number, while the acid number of the

rancid portion appears but eight-tenths higher than that of the unchanged fat.

A determination of the iodine absorption of the free insoluble acids throws some light upon the proportion of free oleic to other acids. 100 grams of a rancid butter-fat were shaken with an equal quantity of hot ninety-five per cent. alcohol. After cooling completely in ice-water, the alcoholic solution was poured through a filter and exactly neutralized with a dilute solution of potassium hydroxide, using phenolphthalein. The solution was then heated on the steam-bath until all alcohol was evaporated, when the residue was treated with 100 cc. of hot water. The soapy solution, after standing on the bath for a little while to allow any fat which may have been removed by the alcohol to rise, was filtered, cooled and thoroughly extracted with ether to remove all traces of unsaponified matter. An excess of dilute hydrochloric acid was then added to decompose the soaps, and the insoluble acids collected in the usual way.

The iodine number of the free insoluble acids obtained from a rancid butter by this process was 18.47, corresponding to 20.50 per cent. of oleic acid. Thum¹ found in experiments with palm- and olive-oil that the free fatty acids in rancid oils contained oleic acid in almost exactly the same proportions as in the neutral fat. Similar results were obtained by Spaeth² in the case of rancid lards. Such experiments show that the method, so commonly practiced, of calculating the total acidity of rancid fats to oleic acid alone is by no means accurate.

The amount of free volatile or soluble acids in rancid butter-fats is much smaller than might be expected. A comparison of the acid numbers, and the acid numbers for the water-soluble acids alone, indicates that in the early stages of rancidity at least, the free soluble acids bear to the total free acids a relation smaller than that existing between the soluble acids and total acids of normal butter-fat. The following table will make this clearer :

¹ *Ztschr. angew. Chem.*, 482 (1890).

² *Ztschr. anal. Chem.*, 471 (1896).

TABLE XV.

Butter-fat.	Character of sample.	Total acid number (<i>t</i>).	Water soluble acid number (<i>s</i>).	Relation ($\frac{s}{t}$)
1.....	Rancid, 1 month	7.09	0.84	0.1184
2.....	" 2 months	11.73	1.57	0.1338
3.....	" 8 "	35.38	5.99	0.1664
	Total acids of butter-fat,	228.5 ¹	40.5 ²	0.1772

The determination of the value *t*, or ordinary acid number, has already been described³ and need not be mentioned here. The value *s*, or water-soluble acid number, represents the milligrams of potassium hydroxide necessary to neutralize the free water-soluble acids in one gram of fat, and is found by washing about ten grams of the rancid fat with successive portions of boiling distilled water until all acid is removed, and then titrating the filtrate with tenth-normal alkali.

It is seen from the preceding table that the value $\frac{s}{t}$ increases with the period of rancidity, and approaches the relation existing between the total and soluble acids of normal butter-fat; this relation would no doubt be equaled or even exceeded by fats in a very advanced stage of rancidity. The results in Table XV confirm the statement of Bondzynski⁴ and Rufi that rancidity in butter-fat is due principally to the formation of free insoluble acids, and that free volatile or soluble acids are not found to any extent except in a very advanced stage of decomposition.⁵ This would not only indicate that the glycerides of the soluble acids in butter-fat are the most stable, but also leads to the following very pertinent question. If the statement previously made in regard to the breaking up of oleic acid into lower soluble acids be correct, *why is it that these acids do not appear to any great extent in the free condition?* That such acids are apparently formed was shown in Table XII by the increase in the Reichert number which fats undergo on becoming rancid, and that they are formed to a considerable extent, seems evident from the decrease which takes place in the percentage of insoluble acids, as is seen from Table XIII.

¹ The average saponification number of butter-fat. This Journal, 21, 613. Table I.

² The milligrams potassium hydroxide required to saponify the soluble acids in one gram average butter-fat. *Ibid.*, p. 628.

³ This Journal, 21, 614.

⁴ *Zischr. anal. Chem.*, 1 (1890).

⁵ Spaeth found the same true of rancid lard. *Ibid.*, 479 (1896).

There are several possible ways of explaining this non-appearance of the soluble acids formed by decomposition. There is the possibility that the oleic acid, when in the glyceride form, may split up into a soluble and an insoluble acid, the soluble acid remaining in combination with the glycerol base; this hypothesis, however, does not seem a tenable one since a large amount of free oleic acid is found in rancid fats, as was shown by a preceding experiment.¹ There is also the possibility that esters of the soluble acids may in some way be formed, but this view seems no more plausible than the other; such esters have been found in whole butter,² but we have not been able to detect their presence in rancid fats.

The best explanation of this difficulty which we have been able to arrive at is the following: the first products formed by the decomposition of oleic acid are not of an *acid* but of an *aldehyde* nature; these aldehyde bodies are further changed by oxidation into soluble acids, but this takes place only in a very advanced stage of rancidity, which would explain the fact, already referred to, that free soluble acids are not formed to any great extent except in rancid fats of considerable age. By the action of alcoholic potash, aldehydes are decomposed into acids, and small quantities of dark resinous compounds;³ this would account for the fact that the soluble acids of decomposition do not appear until after saponification, and would also explain the brown coloration which all rancid fats undergo when treated with alkalis.

The presence of aldehydes in rancid fats is indicated on other than theoretical grounds. The cocoanut-like odor, so peculiar to butter-fat in the early stages of rancidity, and the very pungent smell developed later, are probably due to aldehyde products. Spaeth⁴ has called attention to the reducing action which all rancid fats have on Becchi's silver solution as an evidence of these bodies, while E. von Raumer⁵ has detected their presence by the aid of Schiff's reagent. The latter test we have found to be one of extreme delicacy.

¹ This article, p. 982. Indications are that most of the changes which affect the oleic acid take place after the latter has been set free.

² Author: *Ztschr. anal. Chem.*, 10 (1899).

³ Watts' Dictionary of Chemistry, second edition, 1, 111.

⁴ *Ztschr. anal. Chem.*, 487 (1896).

⁵ *Ibid.*, p. 487.

Schiff's reagent is prepared by saturating a solution of rosaniline acetate with sulphur dioxide gas, and allowing it to stand in a stoppered bottle until completely decolorized. In making the test about one cc. of the melted fat is placed in a test-tube with ten cc. of hot water and thoroughly shaken; one cc. of the reagent is then added and the contents of the tube shaken up a second time. If aldehydes are present the fat and liquid underneath will be colored a splendid violet,—the intensity of the coloration being proportional to the rancidity of the sample. Fresh butter-fat gives no test with Schiff's reagent, even after many hours' standing; with fats of moderate rancidity the coloration varies from a pink to a bright cherry-red, while with very old and rancid specimens the layer of melted fat is colored a very dark purple, the liquid underneath being a deep violet. The fact that both fat and liquid were colored would show that aldehydes were present in both soluble and insoluble forms. After saponifying a rancid fat and decomposing the soap solution with an excess of hydrochloric acid, the Schiff test was applied with negative results,¹ thus proving beyond all doubt that the action of alkalies is to completely destroy all compounds of an aldehyde nature.

The existence of aldehydes in rancid fats, and their behavior with saponifying agents, explains another point which we have not yet referred to in connection with Tables XII and XIII. It will be seen from these tables that with the development of rancidity there is a noticeable, but not excessive, increase in the ether number. The true ether number of a rancid fat, representing as it does the milligrams of potassium hydroxide necessary to saponify the neutral fat in one gram of substance, would naturally be lower than that of a fresh sample, since with the breaking up of the glycerides the quantity of neutral fat becomes steadily less.² The presence of aldehydes, however, causes a vitiation in the true ether number; these bodies are not affected in the determination of the acid number, but when the alcoholic potash is added in excess for the determination of the saponification number, the aldehydes, as has been shown, are decom-

¹ The insoluble acids were slightly tinged, but strange to say the coloration was not as pronounced as with the acids from fresh butter-fat. We attribute this reaction in the insoluble acids to a slight decomposition of the oleic acid subsequent to the saponification.

² This supposition is confirmed by the decrease which takes place in the percentage of glycerol.

posed into acids, to neutralize which an excess of potassium hydroxide is required greater than that necessary to saponify the neutral fat alone. This vitiation of the ether number is much greater than the tables indicate, owing to the fact just mentioned that the true ether number of a fat steadily decreases with the advancement of rancidity.

We have already alluded to the fact that oxy-acids are found in all butter-fats irrespective of age, and the statement was made in a previous article that the low acetyl number, which fresh butter-fat shows, and the steady increase of this constant with age, suggest that these compounds are entirely after-products, and do not exist in the milk-fat before secretion. Experiments already mentioned¹ indicate that the oxy-acids are derived entirely from oleic acid, dioxystearic acid being principally formed.

The following table, compiled from results given in Tables XII and XIII, offers a few interesting comparisons, and gives some idea of the probable manner in which the oleic acid of butter-fat is decomposed.

TABLE XVI.

Butter-fat.	Condition.	Oleic acid. Per cent.	Insoluble acids. Per cent.	Loss in oleic acid. Per cent.	Loss in insoluble acids. Per cent.	Acetyl number.	Increase in acetyl number.	Increase in oxy- acids. Per cent. ²
No. 1..	Fresh	38.28	88.96			3.5		
No. 1..	Rancid	31.85	85.06	6.43	3.90	10.9	7.4	1.78
No. 2..	Fresh	32.81	86.41			4.1		
No. 2..	Rancid	21.93	80.42	10.88	5.99	15.1	11.0	2.51
No. 3..	Fresh	38.76	88.46			3.8		
No. 3..	Rancid	25.03	81.15	13.73	7.31	18.0	14.2	3.28
No. 4..	Fresh	38.79	87.72					
No. 4..	Rancid	9.49	72.03	29.30	15.69			

We observe from the above table that the loss in insoluble acids accounts for but little more than half the loss in oleic acid ; the ratio seems to be a fairly constant one, and averages about fifty-five per cent. This figure, then, may be taken to represent approximately the amount of oleic acid in the loss which is con-

¹ By Scala, this article, p. 979.

² Calculated as dioxystearic acid by the formula, $x = \frac{100 \text{ cm.}}{a(56100 - 42x)}$. This Journal, 21, 817.

verted into lower soluble acids.¹ Calculating the increase in the acetyl numbers to dioxystearic acid will make up about twenty-five per cent. more of this loss in oleic acid, thus leaving about twenty per cent. still unaccounted for; the formation of insoluble aldehyde products² during the saponification may explain this discrepancy.

Owing to the formation of oxy-acids the chemical and physical characteristics of the insoluble acids from butter-fat suffer marked changes with the development of rancidity. The following constants were determined on the insoluble acids of butter-fat No. 4 in the preceding table.

TABLE XVII.

Condition of butter-fat.	Mean molecular weight of insoluble acids.	Melting-point of insoluble acids.
Fresh.....	260.2	40.2° C.
Rancid.....	273.7	44.7° C.

These differences are such as one would expect; the increase in the mean molecular weight and melting-point of the insoluble acids, both being the results of the formation of oxy-acids.

EFFECTS OF RANCIDITY UPON THE GLYCEROL OF BUTTER-FAT.

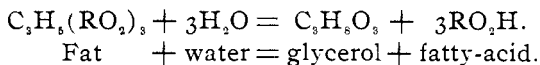
One of the most disputed points in connection with the rancidity of fats is that concerning glycerol. A large number of chemists hold that, as fats become rancid, glycerol is liberated in the free state, and cite the instance of palm-oil, which seems to split up almost quantitatively into its fatty acids and glycerol; in contradistinction to this many chemists, having tested rancid fats for free glycerol with totally negative results, claim that no free glycerol is formed; other chemists, attempting to reconcile these conflicting views, take the somewhat intermediary position, that fats on becoming rancid are decomposed into free acid, and free glycerol, but that the latter is almost immediately destroyed by oxidation.

A quantitative decomposition of a perfectly pure and dry neutral fat into its glycerol and acids, is manifestly impossible, as

¹ Including those already existing and those formed by the action of alkali on the aldehydes.

² The presence of aldehyde condensation products, resin, etc., which are always formed by alcoholic potash, would produce an error in the determination of the insoluble acids. The insoluble acids from rancid butter-fats are invariably colored by these bodies, the coloration varying from a yellow to a dark brown according to the rancidity of the sample.

such a reaction would require the presence of a large amount of water.



To reason from the analogy of palm-oil is not permissible; this oil is abnormal in many ways, containing, as it does, some twelve per cent. of free acid, even when fresh, with a considerable amount of moisture and other impurities.¹

The percentage of glycerol in rancid fats cannot be calculated from the ether number, owing to the vitiation in this constant previously referred to. The process of separating the glycerol from other bodies, and determining its percentage by direct weighing, is never accurate and would be still less applicable with rancid fats, where the glycerol would be contaminated with various impurities. A statement made by some chemists that fats undergo an increase in the percentage of glycerol on becoming rancid, is undoubtedly due to some such faulty method of analysis as the above.

The determinations of glycerol in rancid fat made by us were all performed according to the method of Benedikt and Zsigmondy, as previously described.¹ The results, which are tabulated in Table XIII, all show a decrease in the percentage of glycerol as the butter-fat became rancid, the decrease being proportional to the rancidity of the sample.

It is impossible to say just how this loss of glycerol is incurred; it no doubt takes place in the separation of the various fatty acids, and there is good reason to suppose that these acids, since they do not occur as anhydrides, have seized upon the glycerol radical for the elements of water necessary to their formation. If this theory be correct, very little if any glycerol would appear in the free condition; we have examined rancid butter-fats for free glycerol by washing with large quantities of boiling water, and testing the filtrate by the Benedikt and Zsigmondy method. Small quantities of oxalic acid were formed, equivalent to from one-tenth to two-tenths per cent. glycerol; this may have been derived, however, from the oxidation of water-soluble aldehydes, as well as from glycerol. We believe a small amount of acrolein

¹ According to Benedikt the percentage of impurities with different grades of palm-oil ranges from 0.50 to 17.00 per cent. *Analyse der Fette*, third edition, p. 525.

² This Journal, 21, 621.

is formed from glycerol in the development of rancidity and attribute the pungent irritable odor which all rancid fats give off—especially on being warmed—to the presence of this compound.

EFFECTS OF RANCIDITY UPON THE PHYSICAL CONSTANTS OF BUTTER-FAT.

The alterations in chemical composition, which butter-fats undergo with age, produce very decided changes upon the physical constants.

It is a well-recognized fact that as rancidity is developed the specific gravity of fats increase. The specific gravity $\frac{40}{15.5}^{\circ}$ C. of fresh butter-fat was found to range from 0.9050 to 0.9102; the values of this constant for rancid butter-fats, at the same temperatures of comparison, were considerably higher, and varied between 0.9195 and 0.9252. This increase is easily explained by the fact that in the development of rancidity the oleic acid, of low specific gravity, is changed by oxidation into compounds of greater density. This is in full agreement with the statement of Brühl¹ that "by the addition of oxygen the specific gravity of bodies always exhibits a marked increase, no matter what the product of oxidation may be, whether acid, alcohol, oxy-acid, or other in character." It is owing to this increase in specific gravity that the viscosity of fats becomes greater, as the period of rancidity advances.

In regard to melting-point rancid butter-fats exhibit the greatest irregularity, and we have finally come to the conclusion that it is impossible to make a satisfactory determination of the melting-point of butter-fats in a very advanced stage of decomposition. In the early period of rancidity the melting-point is somewhat higher than that of the fresh butter-fat; the increase, which is probably due to the formation of oxy-compounds of higher melting-point, is not a marked one, however, the differences ranging from 0.1° to 1.5° C. A quite characteristic phenomenon, observed with some rancid butter-fats, was that of double melting-point. As an example a rancid butter-fat, by the capillary tube method,² melted at 24.2° C.; after keeping the

¹ *Ann. Chem.* (Liebig), 211, 128. See note 2, p. 992 of this article.

² The official method could not be used with any degree of success, owing to the solubility of decomposition products in alcohol.

temperature at this point for a few minutes the fat solidified again and, on increasing the heat, remelted at $33.4^{\circ}\text{C}.$ ¹ Samples of excessive rancidity do not exhibit this trait; such fats will usually begin to liquefy at from 22° to $24^{\circ}\text{C}.$, but will remain turbid from insoluble particles, and will not become perfectly clear until the temperature reaches 35° to $40^{\circ}\text{C}.$ This behavior is probably due to the presence of two classes of decomposition products; those of low melting-point, such as fatty aldehydes and lower acids, and those of high melting-point, such as oxy-acids. In this way too would be explained the peculiar semi-fluid consistency, which very rancid fats acquire, fresh butter-fat, under the same conditions, remaining firm and solid.

The development of free acid, which takes place in rancid fats, has a very marked effect upon the critical temperature of dissolution. This simple test devised by Crismer² is especially valuable in testing fats and merits a brief description in this connection. About one-half cc. of melted butter-fat is placed in a slender test-tube with twice its volume of absolute alcohol. The tube is closed with a cork, through which a thermometer is passed so that its bulb is entirely covered with the solution and does not touch the walls of the tube. The tube and thermometer thus prepared are passed through a tightly fitting cork into a larger tube partly filled with water; the whole is then gently heated, with constant shaking, until the mixture of alcohol and butter-fat becomes perfectly clear. The temperature at which turbidity appears, after allowing the apparatus to cool, is noted as the critical temperature.

Crismer has observed that with rancid butter-fats the critical temperature is materially lowered, and that this lowering is proportional to the acidity of the fat. By neutralizing such products with weak alkali and washing the fat with hot water, the normal critical temperature was found to be restored; we have secured the same result by washing the rancid fat with alcohol.

The near critical temperature of several fresh butter-fats, examined by us according to the above method, was $57^{\circ}\text{C}.$ ³

¹ Other instances are known of fatty bodies showing double melting-point. Palmitin melts at $50.5^{\circ}\text{C}.$ and again at $66.5^{\circ}\text{C}.$ *Analyse der Fette*, third edition, p. 44.

² *Bull. Assoc. belge*, 10, 312 (1896). Abstract in *Analyt.*, 22, 252, 71.

³ Of the various rapid tests for adulterated butters this is one of the most reliable. Crismer found for pure butter-fat critical temperatures ranging from 50° to $57^{\circ}\text{C}.$, and for margarine and mixtures results between 64° and $78^{\circ}\text{C}.$

rancid butter-fats gave results ranging from 45° to 50° C. according to the degree of acidity.

It is very interesting to note the effect which rancidity has upon the refractive power of fats. All observers¹ agree in this that the refractive index of a fat increases with the development of rancidity, but differ as to the explanation of the phenomenon.

Unfortunately we had no refractometer in the early stages of our work, and so no comparative readings could be made on the various rancid butter-fats used in these experiments. Recently, however, we have been able to make a large number of refractometer readings on various fresh and rancid butter-fats, and in all cases found that the rancid samples gave a higher refractive index. The readings were made on a Pulfrich instrument, the yellow sodium ray (*D*) being used.

TABLE XVIII.

	Range in refractive indices, 30°C.		Mean.
Fresh butter-fats.....	1.45872	1.45922	1.45897
Rancid " "	1.45982	1.45992	1.45987

Instead of using the refractive index as a means of comparison, we have preferred to use the specific refractive power. The coefficient of refraction varies greatly with the specific gravity, so that a determination simply of the refractive index leaves one very much in doubt as to whether or not any changes observed may not be due wholly to differences in density.

The specific refractive power is calculated from the formula² $\frac{N-1}{D}$, in which *N* equals the refractive index of the substance and *D* its specific gravity.

TABLE XIX.

	Specific gravity $\frac{30^\circ \text{C}}{15.5^\circ} (D)$.	Refractive index $30^\circ \text{C} (N)$.	Specific refractive power $\left(\frac{N-1}{D}\right)$.
Fresh butter-fat.....	0.91260	1.45897	0.50292
Rancid " "	0.92571	1.45987	0.49677

It is seen that the specific gravity and refractive index of rancid butter-fats is higher, but that the specific refractive power is lower. These results are in perfect accordance with the

¹ See articles by Spaeth and Scala already referred to.

² Landolt : *Ber. d. chem. Ges.*, 15, 1031.

observations of Brühl,¹ that by the addition of oxygen the specific gravity of bodies shows a marked increase and that the same change takes place but to a less degree with the refractive index, but that the specific refractive power is always *smaller* in the body richer in oxygen.²

In view of this, since the percentage of oxygen increases in fats as they become rancid, the changes which affect the refractive power find an adequate explanation.

Another important effect of rancidity upon fats is the marked decrease in the calories of combustion. This is a fact which requires but little explanation. Rancidity is in reality only a slow process of combustion, like other forms of oxidation; it is therefore plain that a certain amount of heat is given off by fats in the development of rancidity and that in consequence thereof the original heat-producing power must suffer a decrease.³ The following experiments performed on a fresh and rancid butter-fat will illustrate this. A Hempel-Atwater bomb calorimeter⁴ was used in the work.

TABLE XX.

	Chemical composition.			Calories.
	C. Per cent.	H. Per cent.	O. Per cent.	
Fresh butter-fat.....	75.17	11.72	13.11	9366.
Rancid " "	73.88	11.57	14.55	9095.

CONCLUSION.

We have attempted to give in the preceding pages a few of the main facts in connection with the subject of rancidity. The point was made in the beginning of this paper that the nature of the chemical and physical changes, which take place in the decomposition of fats, is one largely dependent upon conditions.

¹ Die chemische Constitution organischer Körper in Beziehung zu deren physikalischen Eigenschaften. By J. W. Brühl. *Ann. Chem.* (Liebig), 211, 121.

² More fully expressed in the language of the original. *Ibid.*, p. 128. "Aus dieser Tabelle ergibt sich, dass durch die Addition von Sauerstoff die Dichte der Körper stets sehr bedeutend zunimmt, gleichgiltig, welche Art von Verbindung, ob Säure, Alkohol, Oxysäure, u. s. W., hierdurch gebildet wird. Gleichzeitig, aber weit schwächer, wächst auch der Brechungsindex. Dagegen ist die auf gleiche Dichte reducirte brechende Kraft, oder das Brechungsvermögen, bei dem an Sauerstoff reicheren Körper stets kleiner."

³ Brühl: *Op. cit. supra*, p. 126. "Die Verbrennungswärme der Körper sinkt sowohl durch Vereinigung derselben mit Sauerstoff, * * * * *, oder durch Ersetzung von Wasserstoff durch Sauerstoff."

⁴ Seventh report of the Storrs Agricultural Experiment Station, Conn., p. 135.

The results of the present article were obtained under only one particular set of conditions; *viz.*, those most favorable to the production of chemical change. Had the conditions of warmth, light, and exposure to the air been varied, a difference no doubt would have been observed in the degree and character of some of the changes produced. Further investigations as to these points are greatly to be desired.

As we found it difficult to make the distinction between normal and abnormal butter-fats a sharp one, so are we perplexed if we try to draw the line between the qualities fresh and rancid. Butter-fat, as fresh as it can possibly be obtained, gives distinct acid and acetyl numbers, and these changes were no doubt initiated before the cream was separated and churned; we may say therefore that, in a certain chemical sense, fresh butter-fat itself is rancid. If chemical changes begin thus early, we naturally ask ourselves, to what limits can this process of decomposition in fats go? This is a difficult question to answer for we know of no instances where fats were kept a sufficient length of time to enable any conclusions as to this point being formed. The ultimate products of oxidation would of course be water and carbon dioxide, but under ordinary conditions this result would hardly be reached; we are probably safe in saying that chemical change will not cease until all the glycerides are decomposed and the oleic acid is completely changed; whether or not other changes of a different order, such as the formation of paraffin bodies, may set in, is wholly a matter of conjecture.

Owing to lack of time we were unable to make a closer study of the various decomposition products formed in butter-fat by rancidity; nothing whatever was done toward the separation and identification of the various aldehydes, acids and other bodies produced in rancid fats, and this we feel to be a serious omission to completeness. As we stated at the beginning, these studies upon butter-fat were conducted in a very desultory manner, being pursued only as other laboratory duties permitted; this we offer as an excuse for the very general and fragmentary character of much of our work. We hope if possible in the future to make further studies in this most fascinating field of chemical research.

In conclusion the writer desires to acknowledge the help and encouragement received from various friends. Our thanks are

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SOME BOILING-POINT CURVES.

PAPER II.

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In a recent paper on boiling-point curves¹ I presented the results of my work on mixtures of organic liquids in which alcohol, acetone and chloroform respectively was one of the constituents. In the following paper I have worked out the curves for mixtures in which benzene and methyl alcohol, respectively, is one of the constituents.

The apparatus and thermometer used were the same as those employed in my previous work and, therefore, need no description. All of the chemicals used were purified as I have already described, with the addition of benzene, which was first allowed to stand over sulphuric acid to both dry and remove any possible traces of thiophene and then decanted and distilled through a high column. None of the purified materials varied more than 0.5° C. in their boiling-point and nearly all not more than 0.1° C.

All readings were made at the prevailing atmospheric pressure and in no case was the variation great enough to seriously affect the accuracy of the results. For purposes of comparison the curve for benzene and alcohol by Thayer,² for benzene and carbon

¹ *J. Phys. Chem.*, 3, 317 (1899).

² *Ibid.*, 2, 382 (1898).