Butter Fat and Butter Fat Constants

By George Spitzer.

I.

When the greater portion of fat is removed from milk by skimming or separating, and the resulting cream subject to powerful mechanical treatment, the milk fat passes from the liquid into the solid state, by cooling the mixture below the melting point of butter fat. The fat globules thus collect and are formed into grains. By washing and working, the geater portion of buttermilk is removed and the substance called butter is left. Salt in suitable quantity is added according to the demands of the consumer. The analysis of butter, known as proximate analysis, consists in determining the per cent. of moisture, salt, proteids and fat.

The analysis of butter has reached a degree of great importance. The proximate analysis does not indicate whether the sample has been adulterated, but indicates its present condition, and may give some information as to the method of manufacture.

Since the enactment of the Pure Food Law, butter containing 16 per cent. or more moisture is held as adulterated butter. The composition of butter is a variable one, the proportion of different constituents, as fat, moisture, salt, etc., are variable, depending on methods of manufacture. Butter is then only a mixture of the above constituents, or properly speaking an emulsion of butter fat and water, containing salt, curd, and milk sugar. But when we treat of butter fat we have a substance of definite characteristic chemical composition. Both solid and liquid fats are formed by the combination of glycerol and fatty acids. Glycerol is a trihydric alcohol and consequently behaves as a trihydric base. It can then combine with the radicles of fatty acids expressed as follows:

$$C_3H_5 \begin{cases} OH\ HOO\ C(CH_2)n_1\ CH_3 \\ OH\ HOO\ C(CH_2)n_2\ CH_3 \\ OH\ HOO\ C(CH_2)n_3\ CH_3 \end{cases} = C_3H_5 \begin{cases} OO\ C(CH_2)n_1\ CH_3 \\ OO\ C(CH_2)n_2\ CH_3 + 3\ H_2O \\ OO\ C(CH_2)n_3\ CH_3 \end{cases}$$

forming an ester of mixed fatty acids, also called mixed triglyceride. From theoretical considerations, we can predict the existence of a simple triglycerides, where only one simple triglyceride can exist expressed as follows:

$$C_3H_5 \begin{cases} R \\ R \\ R \end{cases} \text{When } R = \text{the acid radicle,}$$

and this representation for each fatty acid. As glycerol is a trihydric alcohol, we might also expect mono and di-glycerides

$$C_3H_5 \begin{cases} OH \\ OH \\ R \end{cases} \qquad\qquad C_3H_5 \begin{cases} OH \\ R \\ R \end{cases}$$

Mono glyceride Di-glyceride

where R stands for any one fatty acid radicle and these are called mono or di-glycerids.

Wurtz, showed that it was inconsistent with the facts discovered. In nature only the triglycerids occur, while the mono and di-glycerids are as a rule rare, if they ever occur.

Butter fat consists of triglycerids of fatty acids, comprising butyric, caproic, caprylic, capric, lauric, myristic, palmitic, stearic, and oleic acids. All these fatty acids are mono basic and from theoretical consideration we might expect a mixture of simple triglycerids, such as tributyrin, triollein, etc. This combination of fatty acids with glyceral forming simple triglycerides in butter fat is disputed by Richmond and others.

If simple triglycerides existed as such in butter fat, we would expect a portion at least to be soluble in alcohol, at least the tributyrin which is quite soluble in alcohol. But when butter is dissolved in alcohol we find that only about 1% of fat goes into solution. And the portion soluble in alcohol consists of mixed triglycerides of fatty acids, indicated by the melting point and per cent of soluble acids. We conclude then that butter fat is a mixture of mixed triglycerides, expressed by the following formula,

$$C_3H_5 \begin{cases} R_1 \\ R_2 \\ R_3 \end{cases}$$

R_1, R_2, and R_3, represent different acid radicles. But as stated above butter fat consists of at least nine different fatty acids, we have then a mixture of mixed triglycerides, consisting of a combination of two or three different acid radicles to each glycerole residue.

II.

CHEMICAL ANALYSIS OF BUTTER FAT.

Since butter fat represents complex mixtures of glycerides of the different fatty acids, complete fat analysis should embrace the separation of each fatty acid quantitatively. An attempt to detect and identify the individual fatty acids, in a way as is done in inorganic chemistry in determining individual elements, must be abandoned as a hopeless undertaking in fat analysis. However, in fat analysis the results obtained are not accurate in strict scientific language, they are relative rather than absolute. Methods have been worked out which answer all technical purpose. These methods consist in obtaining certain "values" or numbers. These numbers are characteristic of the fats depending on the nature and properties of the fatty acids.

These "numbers" or "values" have been termed quantitative reactions. When the methods are strictly followed, uniform results are obtained, and for that reason the "number" or "values" are called "constants," specific for each kind of fat. The "constants" in fat analysis are divided into

Physical	Solidifying point,	
	Melting Point,	
	Refractive index,	
	Sp. gravity.	
Chemical	Reichert-Meissl	value.
	Saponification	value.
	Iodine	value.
	Hener	value.
	Thermal or	
	Maumené	value.

III.

THE RELATION OF BUTTER FAT CONSTANTS AND CALCULATED DATA FROM THE CHEMICAL ANALYSIS.

In chemical analysis of butter fat it is often desirable to obtain data of relations other than the relations obtained directly by the determination of the chemical constants. From these data we are able to account and interpret some of the variation in the physical constants, where, owing to the complexity of the glycerides the chemical constants do not indicate in themselves the variation of the physical properties.

9—33213

Three samples of butter fat were analyzed. The constants determined, both of the fat and fatty acids. In order to secure butter fat of extreme variation in the chemical and physical properties. Use was made of the fact that when fats are placed where the temperature is below the melting point of the softer glycerides crystalization takes place, the harder glycerides separating from the softer. By filtration, separating the soft portion and the process repeated, fractions of hard and soft fats are obtained whose constants differ widely. The three samples thus secured, i. e., the original butter fat and the soft and hard glycerides when analyzed gave the constants as enumerated in Table I.

TABLE I.

	Butter fat.	*Soft Portion.*	*Hard Portion.*
Reuchert-Meissl	30.00	33.85	24.66
Iodine Value	39.82	43.55	33.08
Saponification Value	230.1	232.78	226.4
Mean Molecular Wt. Calc	732.	723.	744.9
Refractive Index[1]	44.	44.8	43.
	1.4552	1.4558	1.4545
Melting Point	32.5	13.2	38.1
Insoluble Acid[2]	87.54	86.67	88.64
Soluble or Volatile Acids[3]	6.9	6.90	5.17
Constants of the Insoluble Acids of the Samples in Table I.			
Iodine Value	42.14	46.2	35.66
Saponification Value	220.53	221.6	218.7
Melting Point	39.2	35.3	42.4
Refraction Index[1]	33.75	34.2	32.7
	1.4479	1.4482	1.4471
Mean Molecular Wt. Calc	254.8	253.2	256.6

IV.

VOLATILE ACIDS.

The high per cent. of volatile acid in butter fat is one of its chief characteristics. By means of this fact it is possible to differentiate it from all other animal and vegetable fats, and it is natural that great importance is attached to the determination of volatile acids or Reichert-Meissl value.

[1]Butyrofactemeter reading at 40°C.
[2]Or Hehner value.
[3]Calculated as butyric acid.

The Reichert-Meissl value does not represent the total volatile or soluble acids, but only a reasonably constant fraction, provided the operation is conducted uniformally according to the prescribed method.

From the Reichert-Meissl value the total volatile acids can be calculated, with considerable degree of accuracy. By the Reichert-Meissl process of distillation from 85 to 89 per cent. of the total volatile acids are distilled. (See Richmond's Dairy Chemistry, p. 264; Lewkowitsch, Fats, oils and waxes Vol. 1, p. 332.) Then to calculate the total volatile or soluble acids[4] we make use of the number of cubic centimeters of NaOH N/10 required to neutralize the volatile acids obtained from five grams of fat. Then for the per cent. of total volatile or soluble acids in the butter fat as recorded in Table I, calculated as butyric acid, we have $30.00 \times .0088 \div 5 \times 100/87 = 6.10$ per cent. of volatile acid as butyric acid, a result which agrees with the chemical analysis of the butter fat Table I. For the soft portion of fat the total volatile acids calculated from the Reichert-Meissl numbers gave 6.82 per cent., while that obtained by direct determinations was 6.90 per cent., a difference of .08 per cent.

For the hard portion the total volatile acids calculated from the Reichert-Meissl number gave 4.98 per cent., that found by direct determination 5.17, a difference of .19 per cent.

In the three analyses the total volatile acids calculated from the Reichert-Meissl number is a close approximation to that found by direct determination, assuming that 87 per cent. of the volatile acids are distilled.

The per cent. of volatile acids distilled vary with the rate of distillation, size of distilling flasks, etc. But when the relation of the Reichert-Meissl value and the total volatile acids are once determined, close approximations can be made in the calculation of total volatile or soluble acids.

The Reichert-Meissl value furnishes means to calculate the mean molecular weight of the volatile acids, and by the use of the mean molecular weight the relative proportion of the different volatile acids entering into the glycerides of butter are indicated. In Table I, in case of butter fat, we found the Reichert-Meissl value to be 30.00, i. e., it required 30 cubic centimeters of N/10 potassium hydrate to neutralize the volatile acids obtained from five grams of butter fat as determined by the Reichert-Meissl process. Since the 30 cubic centimeters represent only 87 per cent. of the total volatile acid, then for the total volatile acids present in five grams of fat it would require 34.48 cubic centimeters of N/10 potassium hydrate. Then to find the number

[4]For the purpose of calculating the total volatile acids, the factor 87 was used; this being in agreement with Richmond and the work done at the Purdue Dairy Chemistry Laboratory.

of grams of potassium hydrate to neutralize the volatile acids in 100 grams of butter fat, we have the following proportion:

$$.005612 \times 34.48 \times 20 = 3.86 \text{ grams of KOH}$$

In order to calculate the molecular weight of the volatile acids, we first calculate the weight of the soluble acids. To do this we make use of the amount of insoluble acid or Hehner Value. The per cent. of insoluble acid was found to be 87.54, mean molecular weight 254.8. The molecular weight of the glycerides of the insoluble acids would be $(254.8)3 + 38 = 802.4$ mean molecular weight of the insoluble acids as triglycerides.[5]

Then from the following proportion we obtain the per cent., or parts per hundred of the triglycerides of the insoluble acids. 764.4 : 802.3 :: 87.54: x, x = 91.87 grams per hundred of glycerides of the insoluble acids.

Now 100 — 91.87 = 8.13 glycerides of the soluble acids. Since 3KOH = 92 parts of glycerol or 38 parts of C_3H_2, then from the quantity of KOH required to neutralize the soluble acids in 100 grams of fat, which was found to be equal to 3.86 grams, we can calculate the per cent. of C_3H_2 combined with the soluble acids by means of the following proportion; 186.36:3.86::38:x, x = .87 per cent. of C_3H_2. If we subtract this from the glycerides of the soluble acid we have then the amount of soluble acids in 100 grams of butter fat.

$$8.13 - .87 = 7.26$$

and therefore the molecular weight is determined from the following proportion:

x:56.12::7.26:3.86, x = 104.5 mean molecular of the volatile acids in this sample of butter fat.

The mean molecular weight of the volatile acids of butter varies from 96 to 130 as recorded by Richmond and Lewkowitsch. This is quite natural and from the molecular weight of the different volatile acids entering into the glycerids we can expect a variation in the mean molecular weight. A slight variation of the different acids would cause a marked increase or decrease in the mean molecular weight. The molecular weights of the different volatile acids entering into the glycerids we can expect a variation in the mean molecular weight. This fact adds weight to the assumption that the proportion of volatile acids are not constant. A slight variation of the different acids would cause a marked increase or decrease in the mean molecular weight. The molecular weights of the different volatile acids entering into the triglycerides of butter fat are as follows:

[5]For the saponification of a triglyceride by K OH is expressed by the following equation.

$$C_3H_5\begin{cases}R_1\\R_2\\R_3\end{cases} + 3\,K\,OH = C_3\,H_5(OH)_3 + K\,(R_1\,R_2\,R_3)$$

M. W. of $C_3H_5 = 41 \therefore 41 - 3 = 38$ since the 3 hydrogen atoms are taken by the acids.

Butyric acid	88
Capraic acid	116
Caprylic acid	146
Capric acid	172

V.

CALCULATION OF MIXED GLYCERIDES.

To calculate the mean molecular weight of the mixed glycerides of the butter fat we make use of the saponification value. This value represents the number of milligrams of potassium hydrate required to saponify one gram of fat. By use of the following equation for the saponification of any triglycerides.

$$C_3H_5 \begin{cases} R_1 \\ R_2 + 3\,K(OH) = C_3H_5(OH)_3 + K\,(R_1\,R_2\,R_3) \quad (I) \\ R_3 \end{cases}$$

Then it follows directly that

$$x : 3(56.12) :: 1 : \text{Sap. Val. or } x \frac{3(56.12) \text{ x } 100}{\text{Sap. Val.}}$$ mean molecular of the glyceride. Likewise we obtain the mean molecular weight of the mixed insoluble acid $x = \frac{56.12 \text{ x } 100}{\text{Sap. Val.}^{6}}$ Mean molecular weight.

VI.

CALCULATION OF GLYCEROL.

By making use of the saponification equation (I) in our calculation we can calculate the per cent. of glycerole in mixed triglycerides. From equation (I), 3 K OH = 92 parts of glycerole, i. e., $3(56.12) = C_3H_5(OH)_3 = 92$,-molecular weight of glycerole or 56.12 grams of K OH correspond to 30.667 grams of glycerole, and from the saponification value we have the amount of K OH necessary to saponify one gram of fat. The amount of glycerole in one gram of fat is determined by use of the following proportion

$$56.12 : 30.667 :: \text{Sap. Val.} : x,\ x = \frac{30.667 \text{ x Sap. Val.}}{56.12}$$

amount of glycerole in one gram of fat and multiplying this by 100 gives the

[6]Saponifications values are expressed in milligrams in the calculations.

amount in 100 grams or the per cent. If in the above we substitute the saponification value as found in table I, for pure butter fat, we have

$$\frac{30.667 \times 230.1 \times 100}{56.12} = 12.57 \text{ per cent. of glycerole.}$$

The per cent. found by chemical determination was 12.58.

If we calculate the per cent. of C_3H_2 from the above relations (eq. I) and subtract this from 100 the difference give the total per cent. of both soluble and insoluble acids. This is apparent from the following equation by rearranging the molecule of the triglyceride.

$$C_3H_5 \begin{cases} R_1 \\ R_2 \\ R_3 \end{cases} = C_3H_2\ H\ (R_1\ R_2\ R_3)$$

Referring to equation (I) we see that 3 (K OH) = C_3H_2 where C_3H_2 = 38 therefore 56.12 grams of K OH corresponds to 12.667 grams of C_3H_2 and from the following relation we can calculate then the amount of C_3H_2 in one gram of fat. $56.12 : 12.667 :: \text{Sap. Val.} : x,\ x = \frac{12.667 \times \text{Sap. Val.}}{56.12}$ = grams of C_3H_2

and multiplying this by 100 gives the amount per 100 grams or per cent. By using the saponification value as used in calculating the glycerole we have

$$\frac{12.667 \times 230.1 \times 100}{56.12} = 5.19$$

per cent. of C_3H_2. This amount when subtracted from 100 gives the per cent. of mixed fatty acids

$$100 - 5.19 = 94.81$$

By chemical analysis the insoluble acids of pure butter fat (Table I) was 87.54, and from the method of calculation (p. 130) the soluble acids were found to be 7.26 per cent. The total acids then would be 94.80 per cent., while the total acids calculated from the value obtained for C_3H_2 would be 94.81 involving an error of .01 per cent.

VII.

THE RELATION OF THE MAUMENE VALUE TO THE IODINE VALUE.

From numerous determinations of the Maumené value and its relation to the unsaturated fatty acids, there undoubtedly exists a relation between the rise of temperature and the iodine value when adding concentrated sulphuric acid to oils. The higher the iodine value the higher the rise of temperature. To obviate small variations of the strength of sulphuric acid, Thompson and Ballentyne (Chem. Zeit. 1909) proposed to refer the rise of temperature with fifty grams of fat and ten c.c. of sulphuric acid to the rise of temperature with fifty grams of water under exactly the same conditions and in the same vessel. The ratio of the rise of temperature of the fat to the rise of temperature of water, they express as the "specific temperature reaction" that is[7]

$$\frac{\text{Rise of temperature of fat x 100}}{\text{Rise of temperature of water}} = \text{Specific temperature reaction.}$$

The following table gives the rise of the temperature of butter fat (Maumené value), specific temperature reaction, iodine value and ratio of the Sp. T. R. to the iodine value.

TABLE II.

No.	Rise of Temp.	Specific Temp. Reaction.	Iodine Value.	Ratio of Specific Temp. Reaction to Iodine Value.
1	34.7° C	83.6	46.36	1.8
2	39.5° C	95.2	56.00	1.74
3	30.8° C	74.2	39.43	1.88
4	32.0° C	77.1	36.29	2.1
5	30.5° C	73.5	39.22	1.84
6	27.0° C	65.1	31.21	2.08
7	23.5° C	56.6	30.00	1.88
8	23.4° C	56.6	28.54	1.98
9	25.8° C	62.2	32.73	1.9

Rise of temperature of water 41.5° C.

From results recorded in Table II the ratio is quite uniform except Nos. 4 and 6. If no other factors would influence the rise of temperature except the unsaturated fatty acids it would seem possible to determine a factor

[7]This ratio is multiplied by 100 to avoid decimals.

such that when the Sp. T. R. is divided by this factor the quotient would express the iodine value, this seems possible with fresh oils or fats, but when fats are exposed to air, partial oxidation takes place and this increases the rise of temperature. The values in Table II, were determined from butter fat of different degree of freshness, which had not been exposed to the air.

In considering other constants both physical and chemical no fixed relation exists. While it is true that the per cent. of olein influences the refractive index, no quantitative relation exists between the refractive index and the per cent. of olein or oleic acid. This shows that oleic acid is not the only varying factor in butter fat influencing the refractive index. Since each acid entering into the glycerids of butter fat has its own specific refractive index, and from what has been said with reference to the mean molecular weights of the volatile acids, we must expect the physical properties to vary as the proportion of acids vary, which enter into the formation of a molecule of the triglyceride. The same reasoning applies to the insoluble acids. This variation of the proportion of the different fatty acids entering into the glycerides of butter fat, must also exert a varying influence on the physical properties, such as the refractive index, melting point, congealing point, specific gravity, etc.

DESCRIPTION OF CHEMICAL AND PHYSICAL CONSTANTS.

Solidifying Point.—The solidifying point indicates the temperature at which butter fat solidifies. When butter fat is heated to 40° C. or 50° C., then allowed to cool slowly, a point is reached when the temperature remains stationary. This depends on the property, that when substances solidify on cooling, the latent heat of fusion, is liberated and the rise of temperature due to the latent heat equals the lowering of the temperature of the fat. When the temperature reaches this stationary point, the reading of the thermometer is taken and is called the *solidifying point*.

Melting Point.—The melting point indicates the temperature at which butter fat melts. Various methods are used in determining t e melting point. To obtain comparable results the same method must be used. It must also be borne in mind that fats do not show their normal melting point shortly after being melted and then cooled. After butter fat has been melted it should be allowed to cool at least twelve hours before the melting point is determined.

Refractive Index.—The refractive index expresses the ratio of the velocity of light in vacuum to that of the velocity of light in the medium under investigation. When light passes from a rarer medium into one of greater optical density the rays of light on entering the denser medium deviate towards the normal, the ratio of this deviation from the normal for the two media is constant and is called the refractive index with reference to the two media.

Specific Gravity.—Specific gravity expresses the ratio between masses of equal volumes of a substance and that of water taken as a standard. The masses of two bodies are proportional to their weights, the specific gravity of a substance can be expressed thus: Specific gravity $= \frac{X}{Y}$, where X and Y represent the weights respectively of equal volumes of the substance and water.

Reichert-Meissl Value.—The Reichert-Meissl value expresses the number of cubic centimeters of decinormal solution of Sodium or Potassium hydrate required to neutralize the volatile acids obtained from five grams of butter fat by the Reichert-Meissl distillation Process. The Reichert-Meissl value does not represent the absolute amount of volatile soluble acids, but only indicates the relative amount of the volatile acids.

Saponification Value.—The saponification value expresses the number of miligrams of potassium hydrate required to saponify one gram of fat, its value depends on the molecular weight of the fatty acids. The lower the molecular weight the higher the saponification value.

Iodine Value.—The iodine value indicates the per cent. of iodine or iodine chloride absorbed by the fat. All unsaturated fatty acids have the property of absorbing iodine forming substitution compounds. In butter fats the oleic acid is the only unsaturated acid.

Insoluble Acids or Hehner Value.—This value represents the insoluble acids in fats. Inasmuch as fats are composed of mixed glycerides of fatty acids both soluble and insoluble, on saponification of the mixed glycerides, the fatty acids form salts with the liberation of glycerol. When the salts thus formed are decomposed by some mineral acid, the insoluble acids can be separated from the soluble acids and the per cent. of insoluble acids is called the *Hehner value.*

Maumene Value.—When mixing sulphuric acid with oils the temperature rises and varies with the source of the oils and their chemical composition, the rise being also greater for the drying oils than for the nondrying oils.

The rise of temperature for different oils is called the *Maumene value* of the oils.

Purdue University.