SECTION I

INTRODUCTION

§ **1.** THE OILS AND FATS INDUSTRY is essentially a **chemical industry**, i.e., it is based on certain fundamental chemical reactions. In order, therefore, to have an intelligent conception of the nature of the processes involved, and of the classes of materials which are made use of in this industry, it is absolutely essential to possess a knowledge of the **fundamental principles of chemistry** both theoretical and practical. To take only one example out of the hundreds that occur in practice, e.g., the product known technically as "DISTILLED GREASE STEARINE[1]"; in order that one may appreciate the properties of this substance, it is necessary to have a sufficient chemical knowledge to be able to answer, at least, the following questions:

(*a*) What is an acid?
(*b*) What is a base?
(*c*) How are these compounds distinguished?
(*d*) What combinations can each form?
(*e*) What laws govern such combinations?

Many other questions suggest themselves and unless equipped at the outset with the necessary knowledge to answer such queries it will be useless for the student to attempt to grasp the principles underlying works' processes and methods.

§ **2.** Compared however with many other industries, the chemistry of the operations in connection with oils, fats and waxes is remarkable for its simplicity. There are, in fact, three chemical elements only, which are concerned to any extent with the subject. These, in various conditions of combination, comprise all the different species of fatty and waxy bodies. Moreover these three chemical elements are perhaps the commonest and most familiar of all the elements. They are the non-metals :—

Hydrogen	(symbol)	H	(atomic weight)	1
Carbon	„	C	„	12
Oxygen	„	O	„	16

The atomic weights given are taken to the nearest whole number, and are correct to two places of decimals, rendering chemical calculations very easy.

[1] See § 168.

The **mineral oils and waxes** are, chemically speaking, simpler still, consisting mainly of the two elements CARBON and HYDROGEN in combination.

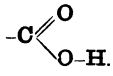
In the crude state most mineral oils contain small quantities of compounds of **oxygen** and **sulphur**, which are removed during the processes of refining.

§ **3.** The diversity of the compounds present in fatty bodies is attained chemically by the **varying number of carbon atoms** in the molecules of the different compounds, and also by the **different arrangement** of the atoms in the molecules. For example, the substance known as STEARIC ACID, which occurs in animal fats, contains 18 atoms of carbon linked to one another by chemical forces in the form of a chain, and diagrammatically represented thus :—

–C–C–C–C–C–C–C–C–C–C–C–C–C–C–C–C–C–C–[1]

whilst the compound known as Melissic[2] Acid, which occurs in beeswax, contains no less than 30 atoms of carbon linked in a similar manner.

Again, all the acids which occur in oils, fats, etc., contain a certain group of atoms arranged always in the same manner, and known as the "ACID" or "CARBOXYL" group graphically represented as follows:



Further, in all NATURAL OR FIXED OILS AND FATS (i.e., those derived from *animals* or *plants*), without a single exception, the base entering into combination with the numerous fatty-acid radicles, is, strangely enough, the same, viz., the **trihydric basic radicle** of **Glycerine**[3], e.g. $C_3H_5 \equiv$, glycerine being a trihydric alcohol[4], viz., $C_3H_5(OH)_3$.

§ **4.** Oils, fats and waxes consist of the following **natural groups** :

Products of animals and plants	(*a*)	Fixed oils, fats and waxes.
	(*b*)	Volatile or Essential oils.
Products of minerals	(*a*)	Petroleum[5] oils and waxes.
	(*b*)	Ozokerite[6] or Earth wax.
	(*c*)	Brown coal, bitumen, and peat oils and waxes.
	(*d*)	Shale oils and waxes.
	(*e*)	Coal tar oils.

Bones and rosin on dry distillation give "bone oil" (Dippel's oil) and "rosin oil."

[1] This chain of atoms is not necessarily straight, any more than would be a watch-chain when held in the palm of the hand.
[2] Gk. *melissa* = a bee.
[3] Gk. *glukus* = sweet.
[4] Arabic *al* = the, *Kohl* = stibium = sulphide of antimony.
[5] Lat. *petra* = a rock and *oleum* = oil.
[6] Gk. *ozo* = to smell and *kēros* = wax.

§ **5.** Many plants, as stated above, yield **two kinds of oil**.

(*a*) **Non-volatile**, contained mostly in the *seeds* and *fruits* of plants.

(*b*) **Volatile**, contained mainly in the *leaves*, *stems* and *flowers* of the plant.

The first group are the so-called "**fixed oils**." They are obtained by means of expression from the seeds, etc., or by extraction with solvents. The second group are known as the "**volatile**" or "**essential oils**." They are obtained by distillation with steam and are mainly used in perfumery, being all characteristically odorous[1].

§ **6.** Animal and Vegetable oils are in nature produced by a process of **synthesis**, that is, they are built up from simpler substances by means of the activity of the living protoplasm of animal and plant cells. The oil appears as minute spherical globules embedded in the protoplasm of the cell. These globules increase in size and coalesce, frequently constituting the largest portion of the tissue in which they are found.

The **natural function** of oils in plants appears to be to act as a reserve food supply for the young embryo during its development. In animals, the fat forms a warm protective coat around the abdominal viscera and probably also forms a food reserve to some degree.

Beeswax is secreted by the bee as a building material for the honey-comb.

§ **7.** **Considered chemically**, all fixed oils and fats are compounds of **glycerine** with a **fatty acid**, termed **glycerides**, which form one of the classes of a large number of compounds known as "**esters**" or "**ethereal**[2] **salts**."

They are recognized by the fact that when they are split up by suitable treatment they yield glycerine and a fatty acid. The **animal and vegetable waxes** are also esters, but the base contained in these is an alcohol *other* than glycerine, and consequently no glycerine is obtainable from them.

§ **8.** **Mineral oils and waxes** may be divided into the **three groups**:

A. Oils and waxes obtained in a more or less pure condition from the earth, e.g.:

(*a*) Petroleum;

(*b*) Ozokerite.

B. Oils and waxes obtained by extraction of mineral products with suitable solvents, e.g.:

(*a*) Montan Wax from Brown Coal;

(*b*) Bitumen Wax from Bitumen;

(*c*) Peat Wax from Peat.

[1] These form a class of compounds outside the scope of this book and constitute an industry to themselves.

[2] Lat. *æther* = Gk. *aither* = the sky, from Gk. *aitho* = to burn.

C. Oils and waxes obtained only by destructive distillation of mineral products, e.g. :

(*a*) Shale oil and waxes from Shale ;
(*b*) Coal tar oils from Coal tar.

Chemically considered the mineral oils and waxes are mainly mixtures of compounds known as **hydrocarbons**. As previously stated, hydrocarbons are compounds consisting of carbon and hydrogen only, and, as will be shown in a later section, there are many types of hydrocarbons whose differences in properties are mainly due, not to different proportions of carbon and hydrogen, but to the different arrangement of the carbon and hydrogen atoms in the molecule, i.e., to the constitution or structure of the molecule.

SECTION II

CHEMISTRY OF THE OILS, FATS AND WAXES

CHAPTER I

FATTY OILS, FATS AND NATURAL WAXES

§ **9.** Oils and fats are not simple substances. They are substances consisting of more or less definite mixtures of **two or more glycerides**[1], simple or mixed. According to the character of the glycerides they contain—whether solid or liquid, etc.—and the amounts of each, so the properties of the various oils and fats differ one from the other.

§ **10.** Glycerides are **colourless, odourless and tasteless substances**, whilst the oils and fats as obtained in commerce are all more or less distinguished by differences of colour, odour and taste. These properties serve to give in many cases an easily recognisable character to the oils and are produced by small quantities of extraneous substances dissolved in the oil or fat.

§ **11.** A pure glyceride is a compound of **glycerine with a fatty acid**. Consider for a moment the base caustic potash [KOH]; this is capable of combining with an acid to produce a salt and water, e.g. a solution of KOH and a solution of HCl when mixed till the resulting hydrochloric acid solution is neutral, gives a solution of a salt KCl (potassium chloride) and more water H_2O: this reaction is quantitatively represented by the chemical equation

$$\text{Solution of KOH} + \text{solution of HCl} = \text{a solution of KCl} + H_2O.$$

Similarly a solution of KOH can form a solution of a salt when mixed with a solution of a fatty acid, e.g. stearic acid $C_{17}H_{35}.CO.OH$, viz.

$$KOH + C_{17}H_{35}.CO.OH = C_{17}H_{35}.CO.OK + H_2O.$$

Now glycerine is a **trihydric alcohol** and is thus a **triacid base**, so that **one molecule** of glycerine $C_3H_5(OH)_3$ is capable of combining with **three molecules** of a monobasic acid, e.g. a fatty acid. The

[1] One or two fats are known which appear to consist practically of one glyceride only.

reaction between glycerine and stearic acid is represented by the chemical equation[1]

$$\begin{matrix} C_{17}H_{35}.CO.OH \\ C_{17}H_{35}.CO.OH \\ C_{17}H_{35}.CO.OH \end{matrix} + C_3H_5\begin{matrix}\diagup OH \\ -OH \\ \diagdown OH\end{matrix} = \begin{matrix} C_{17}H_{35}.CO.O \\ C_{17}H_{35}.CO.O- \\ C_{17}H_{35}.CO.O \end{matrix}\diagdown\!\!\diagup C_3H_5 + 3H.OH.$$

Since glycerine is a triacid base it is theoretically possible for **one molecule** of glycerine to react with either **one**, **two**, or **three molecules** of a monobasic acid; hence the following types of glycerides are possible with stearic acid, viz.

1. **Mono-glycerides.**

$$\underset{\text{1 molecule of stearic}^2\text{ acid}}{C_{17}H_{35}CO.OH} + \underset{\text{1 molecule of glycerine}}{C_3H_5(OH)_3} = \underset{\text{1 molecule of monostearin}}{C_{17}H_{35}CO.O.C_3H_5(OH)_2.} + \underset{\text{1 molecule of water}}{H_2O}$$

2. **Di-glycerides.**

$$\underset{\text{2 molecules of stearic acid}}{2C_{17}H_{35}CO.OH} + \underset{\text{1 molecule of glycerine}}{C_3H_5(OH)_3} = \underset{\text{1 molecule of distearin}}{(C_{17}H_{35}CO.O)_2 : C_3H_5.OH} + \underset{\text{2 molecules of water}}{2H_2O}$$

3. **Tri-glycerides.**

$$\underset{\text{3 molecules of stearic acid}}{C_{17}H_{35}CO.OH} + \underset{\text{1 molecule of glycerine}}{C_3H_5(OH)_3} = \underset{\text{1 molecule of tristearin}}{(C_{17}H_{35}CO.O)_3 : C_3H_5.} + \underset{\text{3 molecules of water}}{3H_2O}$$

The structural or constitutional formula for glycerine is represented by the plane formula

$$\begin{matrix} CH_2.OH\ (1) & \text{or} & (\alpha) \\ | & & \\ CH.OH\ (2) & & (\beta) \\ | & & \\ CH_2.OH\ (3) & & (\gamma) \end{matrix}$$

in which it is seen that the three hydroxyl groups OH are attached to different carbon atoms and are numbered (1), (2) and (3) or (α), (β) and (γ) in order to indicate the position of each group in the molecule. It has been previously stated that the property of a carbon compound depends not only upon its composition by weight of each of the constituent elements but also upon the **structure** or **constitution** of the molecule. On referring to the monoglycerides given above it will be seen that *one* hydroxyl-group of the glycerine molecule has been replaced by *one* acid radicle of the stearic acid molecule and hence at first sight there appear to be *three* possible structures for the monoglyceride, viz.

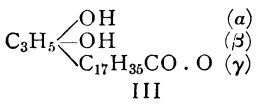
$$C_3H_5\begin{matrix}\diagup C_{17}H_{35}.CO.O & (\alpha) \\ -OH & (\beta) \\ \diagdown OH & (\gamma)\end{matrix} \qquad \text{I}$$

$$C_3H_5\begin{matrix}\diagup OH & (\alpha) \\ -C_{17}H_{35}.CO.O & (\beta) \\ \diagdown OH & (\gamma)\end{matrix} \qquad \text{II}$$

[1] This reaction does not take place completely on mixing the acid and glycerine; the conditions for such reaction are indicated later.

[2] Gk. *stear* = fat.

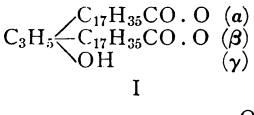
and



III

Now the positions (*a*) and (*γ*) in the glycerine molecule are identical, since on inverting the formula the same structure is obtained, i.e. to say the positions (*a*) and (*γ*) are symmetrical about the molecule. Since then, the monoglycerides I and III are identical but are different from II, **two monoglycerides are possible.**

On examining the possible structures of the diglycerides, e.g.



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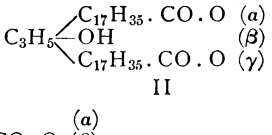

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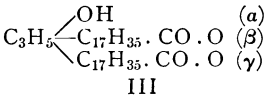

III

it will be seen that structures I and III are identical but different from structure II, hence there are **two possible diglycerides**.

From the above it is also evident that there is only **one possible triglyceride** (in the case of a simple glyceride).

§ **12.** As previously stated the terms "**fatty oils, fats and natural waxes**" are used to designate those oils, fats and waxes which are the products of animals and plants as distinguished from those oils and waxes which result from the treatment of certain mineral products.

All fatty oils and solid fats yield glycerine on suitable treatment. This capacity of yielding glycerine is the ultimate test for distinguishing between fatty oils or fats and those substances which in many respects are similar to them.

§ **13. The natural waxes** (i.e. those derived from animal and vegetable sources) resemble fats very closely in most of their properties. They, however, contain no glycerides and thus can yield no glycerine on being subjected to the same treatment that causes fats to yield glycerine.

The popular names for some of these substances are misnomers, e.g. **Japan wax** and **myrtle wax** are both **true fats**, yielding glycerine when split up, whilst **sperm oil** is not a fatty oil but a liquid wax, since no glycerine is obtainable from it.

The natural waxes, however, agree with the fatty oils, in this respect, that they are compounds of fatty acids with alcohols, i.e. they are esters; the alcohols obtained from waxes being monohydric. whilst glycerine is trihydric.

§ **14. Glycerides**, on treatment with water in the form of high pressure steam, are split up or decomposed into two parts, which, combining with the elements of water, produce a **fatty acid** and **glycerine.** Taking, for example, the triglyceride stearin, the reaction is represented by the following chemical equation:

$$\begin{matrix} C_{17}H_{35}.CO.O \\ C_{17}H_{35}.CO.O \\ C_{17}H_{35}.CO.O \end{matrix}\Big\rangle C_3H_5 + \begin{matrix} H.OH \\ H.OH \\ H.OH \end{matrix} = \begin{matrix} C_{17}H_{35}CO.OH \\ C_{17}H_{35}CO.OH \\ C_{17}H_{35}CO.OH \end{matrix} + C_3H_5\Big\langle \begin{matrix} OH \\ OH \\ OH \end{matrix}$$

1 molecule of tristearin — 3 molecules of water — 3 molecules of stearic acid — 1 molecule of glycerine

or written in contracted form,

$$(R.CO.O)_3 : C_3H_5 + 3H_2O = 3R.CO.OH + C_3H_5(OH)_3$$

where R represents a monovalent hydrocarbon radicle, known as an **alkyl group**.

It will thus be observed that it is incorrect to speak of a fat *containing* glycerine since this body is only produced on the fat being *split up* and the glyceryl radicle $C_3H_5\equiv$ combining with three $-OH$ radicles of water.

From the foregoing equation it will be seen that one molecule of a triglyceride on being split up combines with the elements of water producing **one molecule** of **glycerine** and **three molecules** of a **fatty acid**.

In the case of **waxes** which are decomposed on treatment with a strong base, such as caustic soda or caustic potash, only **one molecule** of a **fatty acid** or one molecule of a salt of the fatty acid is obtained for one molecule of the ester split up. Thus Spermaceti[1] consists largely of the ester composed of Palmitic acid and Cetyl alcohol $C_{15}H_{31}CO.O.C_{16}H_{33}$, and is decomposed by caustic potash as represented by the following equation

$$C_{15}H_{31}.CO.O.C_{16}H_{33} + KOH = C_{15}H_{31}.CO.OK + C_{16}H_{33}OH$$

Cetyl palmitate — Potassium hydrate — Potassium palmitate — Cetyl alcohol

i.e. **one molecule** of the ester yields **one molecule** of a salt of a fatty acid.

§ **15. Carnaüba wax** contains an ester, amongst others, composed of **two molecules** of a fatty acid combined with one molecule of a dihydric alcohol, which it yields on treatment with caustic potash; such alcohols are termed glycols, the one obtained from Carnaüba wax having the formula $C_{25}H_{50}(OH)_2$.

[1] Gk. *sperma* = seed, *ketos* = a whale.

§ **16.** It has already been shewn that there are three classes of glycerides, viz.

A. Monoglycerides of general formula $R.CO.O.C_3H_5(OH)_2$,
B. Diglycerides „ „ $(R.CO.O)_2C_3H_5.OH$,
C. Triglycerides „ „ $(R.CO.O)_3C_3H_5$,

where R represents an alkyl group (see § 14).

Apparently **only the triglycerides occur in nature.**

Reimer and Will found in an old sample of rape-oil the **diglyceride** of Erucic[1] acid, viz. $(C_{21}H_{41}.CO.O)_2C_3H_5.OH$. This however was probably formed by the loss of a molecule of Erucic acid from the triglyceride, on rancidity taking place.

§ **17.** A. **Monoglycerides.** These were first obtained synthetically by Berthelot who heated fatty acids with excess of glycerine in a sealed tube; both mono- and diglycerides were obtained.

The modern method is to mix equivalent proportions of mono-chlor-hydrin and finely powdered sodium salts of the fatty acids and heat. Sodium chloride separates and the glyceride is extracted with ether and filtered through charcoal. The reaction that takes place is represented thus:

$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.Cl \end{array} + R.CO.O.Na = \begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.R.CO.O \end{array} + NaCl$$

mono-chlor-hydrin — sodium salt of fatty acid — mono-glyceride — sodium chloride

As before stated (see § 11) there are **two possible** monoglycerides of a fatty acid. The following are a few of the monoglycerides:

(i) α Monoformin[2] $C_3H_5\begin{cases} H.CO.O\,\alpha \\ (OH)_2 \end{cases}$ B.P. in vacuo 165° C.

(ii) α Monoacetin[3] $C_3H_5\begin{cases} CH_3.CO.O\,\alpha \\ (OH)_2 \end{cases}$ a thick liquid, soluble in water: B.P. at 2 mm. 130° C.; S.G. at 15° C. 1·2212.

(iii) α Monobutyrin[4] $C_3H_5\begin{cases} C_3H_7.CO.O\,\alpha \\ (OH)_2 \end{cases}$ an oily liquid; B.P. 270° C. S.G. at 17° C. 1·008; 8 volumes of ester mix with three volumes of water.

(iv) α Monolaurin[5] $C_3H_5\begin{cases} C_{11}H_{23}.CO.O\,\alpha \\ (OH)_2 \end{cases}$ M.P. 59° C.

(v) α Monomyristin[6] $C_3H_5\begin{cases} C_{13}H_{27}CO.O\,\alpha \\ (OH)_2 \end{cases}$ M.P. 68° C.

[1] Gk. *ereugomai* = to vomit. Erucic is derived from the Eruca a genus of Cruciferae whose seeds applied to the skin produce blisters.
[2] Lat. *forma* = an ant.
[3] Lat. *acetum* = vinegar.
[4] Lat. *butyrum* = butter.
[5] Lat. *laurus* = laurel.
[6] Lat. *myristica* = a nutmeg.

(vi) α Monopalmitin $C_3H_5\begin{cases}C_{15}H_{31}\cdot CO\cdot O\,\alpha\\(OH)_2\end{cases}$ M.P. 72° C. soluble to extent of 5 % in absolute alcohol.

(vii) α Monostearin $C_3H_5\begin{cases}C_{17}H_{35}CO\cdot O\,\alpha\\(OH)_2\end{cases}$ M.P. 73° C.; crystallizes in microscopic needles.

(viii) α Monocerotin[1] $C_3H_5\begin{cases}C_{25}H_{51}\cdot CO\cdot O\,\alpha\\(OH)_2\end{cases}$ M.P. 78·8° C.

(ix) α Monomelissin $C_3H_5\begin{cases}C_{29}H_{59}CO\cdot O\,\alpha\\(OH)_2\end{cases}$ M.P. 92° C.

(x) α Monoolein[2] $C_3H_5\begin{cases}C_{17}H_{33}CO\cdot O\,\alpha\\(OH)_2\end{cases}$ a yellowish liquid: S.G. at 21° C. 0·947; solidifies at 0° C.

Gruss[3] has recently prepared β monoglycerides by using dichlorhydrin and removing chloro-derivatives by the action of silver nitrite.

(xi) β Monolaurin $C_3H_5\begin{cases}OH\quad\alpha\\C_{11}H_{23}\cdot CO\cdot O\,\beta\\OH\quad\gamma\end{cases}$ small white crystals. M.P. 61° C.

(xii) β Monopalmitin $C_3H_5\begin{cases}OH\quad\alpha\\C_{15}H_{31}\cdot CO\cdot O\,\beta\\OH\quad\gamma\end{cases}$ white leaflets. M.P. 74° C.

B. **Diglycerides.** These are prepared by similar methods to the foregoing, viz. the heating of a mixture of one molecule of dichlorhydrin and two molecules of the sodium salt of a fatty acid. There are two possible structural forms of a diglyceride (see § 11), viz. :

$$C_3H_5\begin{cases}R\cdot CO\cdot O\,\alpha\\OH\\R\cdot CO\cdot O\,\alpha\end{cases} \quad + \quad C_3H_5\begin{cases}R\cdot CO\cdot O\,\alpha\\R\cdot CO\cdot O\,\beta\\OH\end{cases}$$

termed αα or symmetrical diglycerides and αβ or asymmetric diglycerides.

The following are some of those which have been prepared :

(i) Diformin $C_3H_5\begin{cases}(H\cdot CO\cdot O)_2\\OH\end{cases}$ prepared commercially by heating 10 parts of pure formic acid H . CO . OH with 4 parts of 95 % glycerine to 140° C. Dilute formic acid distils over and diformin is left.

S.G. at 15° C. 1·304. B.P. at 20–30 mm. 163°–166° C.

(ii) Diacetin $C_3H_5\begin{cases}(CH_3CO\cdot O)_2\\OH\end{cases}$ formed together with monoacetin on heating anhydrous glycerine with acetic acid. It is a commercial product and used to adulterate essential oils ; S.G. at 15° 1·178 ; B.P. at 40 mm. 175° C.

(iii) αα Dibutyrin $C_3H_5\begin{cases}C_3H_7\cdot CO\cdot O\,\alpha\\OH\\C_3H_7\cdot CO\cdot O\,\alpha\end{cases}$ S.G. at 17° 1·083 B.P. at 19 mm. 173–176° C.

[1] Lat. *cerotum* = wax.
[2] Lat. *oleum* = oil.
[3] *Ber.* 1910. 43. 1288, 1291.