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"ELECTROSYNTHESIS."

by

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Part 1: An Investigation of the Mechanism of Electrosynthetic and Allied Anode Reactions.
Introduction, and Brief Survey of Literature on the Mechanism of Electrosynthesis.

Since Kolbe's discovery in 1849 of the production at the anode of ethane during the electrolysis of a solution of potassium acetate, many investigations have been made with a view to determining the nature of the undoubtedly complex process at the anode surface. Kolbe himself had realised the exceptionally powerful character of electrolytic oxygen as an oxidising agent, and attributed the formation of "methyl" (i.e. ethane) to direct oxidation of acetic acid.

This theory of electrosynthesis has found supporters up to the present day. The substance oxidised is held to be the free acid or the anhydride, the former resulting from the action on water of the discharged anions:

$$2\text{CH}_3\text{COO} + \text{H}_2\text{O} = 2\text{CH}_3\text{COOH} + 0,$$

and the latter from their direct interaction, with loss of an atom of oxygen:

$$2\text{CH}_3\text{COO} = \text{CH}_3\text{CO.OCO.CH}_3 + 0.$$

Peroxides and peracids have also been suggested

Ann., 1849, 69, 279.
Schall, ibid., p. 83.
Fichter & Fritsch, ibid., 1923, 6, 329.
Robertson, ibid., p. 2057.
as intermediate products. Very little proof, however, seems to have been given for the formation of these intermediate substances, and Gibson, who found that the electrolytic oxidation of acetic anhydride does not produce even a trace of ethane, says "There is, in my opinion, no trustworthy foundation for the assumption that anhydrides, peracids, peroxides, or other intermediate compounds are formed". Muller also emphasises the fact that no proof whatever of the existence of these compounds at the anode has been brought forward.

The Oxidation Theory, then, may be said to rest upon the assumption that free acid is formed by the action of every ion liberated upon water, and that synthesis is due to the subsequent partial oxidation of this acid. For acetic acid the reaction is:

\[ 2\text{CH}_3\text{COOH} + \text{O} = \text{C}_2\text{H}_6 + 2\text{CO}_2 + \text{H}_2\text{O}. \]

In Gibson's own words: "The formation of ethane by electrolysis of potassium acetate with a platinum anode is, in reality, a very special case of oxidation, for the oxidising agent possesses three peculiar characteristics:

\((1)\) It is capable of creating and maintaining around itself, under suitable conditions, a large concentration of the appropriate oxidisable material. (This is done by the anode attracting and discharging

*loc. cit., p.486
acetate ions which thereafter react with water, regenerating the acid.)

"(2) It is capable of developing very high oxidising powers.

"(3) Its zone of action is extremely circumscribed, being limited to the comparatively small surface of the anode."

Gibson also finds that examination of the electromotive phenomena in connection with the formation of trichloromethyl trichloroacetate by electrolysis of trichloroacetic acid, indicates that this is an oxidation reaction:-

$$2\text{CCl}_3\text{COOH} + \text{O} = \text{CCl}_3\text{COOCCl}_3 + \text{CO}_2 + \text{H}_2\text{O}.$$  

Robertson,* applying Gibson's methods to the Crum Brown and Walker electrosynthesis of diethyl succinate from potassium ethyl malonate, arrives at a similar conclusion.

The alternative theory, which has been termed the Discharged Ion Theory, was first put forward by Crum Brown and Walker,† and has since been accepted as being the correct view by the majority of the writers of text books. It supposes that two discharged anions interact directly:

$$2\text{CH}_3\text{COO} = \text{CH}_3\cdot\text{CH}_3 + 2\text{CO}_2.$$  

It is to be noted that this theory assumes the momentary existence of free $\text{CH}_3$, the isolation

*loc. cit.
†Ann., 1891, 261, 107.
of which was Kolbe's original intention.

Murray investigated in great detail the conditions of ethane formation and, upon the evidence at his disposal, concluded that the oxidation theory could not be accepted. He, however, did not study the electromotive phenomena at the anode, and his results are in consequence of little assistance in arriving at a solution of the problem.

Bouveault states that the yield of dimethyl adipate is increased by electrolyzing sodium methyl succinate in anhydrous methyl alcoholic, instead of in aqueous solution. More recently Salauze has shown that when sodium acetate is electrolysed in anhydrous methyl alcoholic solution, very good yields of ethane are obtained. He states that no action of the discharged ions on the solvent occurs. An interesting point in this connection is that in methyl alcohol an anode of almost any conducting material (e.g. carbon, gold, platinised platinum) gives synthesis, although platinum and iridium are the only materials capable of withstanding the disintegrating action of the current for long periods. Now in aqueous solution, no synthesis occurs at anodes of any material other than polished platinum and iridium: this is recorded by several investigators.

† Jour. Chem. Soc., 1892, 61, 10.
§ ibid., 1925, 37, 522.
Preuner and Ludlam were the first to show the relation between electrosynthesis and the value of the anode potential, i.e. the potential difference between the anode and the solution in its immediate neighbourhood. These authors showed that a polished platinum anode in an acetate solution must acquire a potential of 2.54 volts before ethane formation commences. In the case of propionates this is 2.58 volts for ethylene formation, and 2.7 volts for butane, referred to a hydrogen electrode in the same solution as standard. They also observed that when the current passing through the solution was plotted against the anode potential, unmistakable bends ("knickpunkt") in the curves occurred at 2.54 volts with potassium acetate, and at 2.58 volts with potassium propionate. They concluded that reaction took place between the discharged ions to give an intermediate product.

Kaufler and Herzog adduce the following evidence in support of the Discharged Ion Theory:—When potassium acetate is electrolysed in presence of iodine or potassium iodide, methyl iodide is formed. They take this as indicating that free CH₃ is momentarily formed, since iodine has no action on any possible intermediate product such as acetic acid, acetic anhydride, or acetyl peroxide.

† loc. cit.
Similarly a mixture of potassium propionate and potassium iodide gives some ethyl iodide, and one of sodium propionate and sodium nitrite gives some nitroethane.

*Miller & Hofer, Ber., 1895, 28, 2430.*
Discussion of Previous Literature.

The really important contributions to the literature of this subject are clearly those of Gibson and Robertson, since they bring forward what they claim to be conclusive evidence in favour of the Oxidation Theory. It is proposed, therefore, to examine their papers in some detail before proceeding to an account of the author's own experimental work.

Following are the equations representing the electrosynthesis of ethane from an acetate (a) on the Discharged Ion Theory, and (b) and (b') on the Oxidation Theory:

(a) \[2\text{CH}_3\text{COO} = \text{CH}_3\cdot\text{CH}_3 + 2\text{CO}_2\]
(b) \[2\text{CH}_3\text{COO} + \text{H}_2\text{O} = 2\text{CH}_3\text{COOH} + \text{O}\]
(b') \[2\text{CH}_3\text{COOH} + \text{O} = \text{CH}_3\cdot\text{CH}_3 + 2\text{CO}_2 + \text{H}_2\text{O}\]

Equation (b) represents the reaction prevailing at low potentials, and undoubtedly this reaction takes place to some extent at least under all conditions.

It will be noticed at once that equations (b) and (b') when added together give equation (a). It would therefore appear that great care is needed in examining quantitatively the electrolytic products with a view to supporting either theory. Thus the amount of oxygen evolved during electrolysis must be independent of the mode of ethane formation; for, if equations (b) and (b') hold, an amount of oxygen equal to half the volume of ethane produced is used up for synthesis, whereas if equation (a) holds,
precisely this quantity of oxygen has never been formed at all, owing to the ions reacting with themselves instead of with water. Similar considerations apply to the amount of carbon dioxide liberated. Jahn bases his proof of the Oxidation Theory upon the fact that the amount of carbon dioxide found agrees with that calculated on this theory. The amount, however, would of necessity be the same on either theory.

Concerning the intrinsic probability of the Oxidation Theory, it must be admitted that it would be somewhat surprising to find that the carboxyl hydrogen of a fatty acid is attacked by an oxidising agent in preference to the hydrogen atoms of the hydrocarbon portion of the molecule. One is accustomed to regard a carboxyl group as being very stable towards oxidising agents. The Oxidation Theory, in fact, could scarcely have been considered seriously had it not been shown by Gordon* that comparatively large quantities of ethane and methane are formed when acetic acid is oxidised with sodium persulphate. His work shows that the best ethane yield is obtained by heating the following solution to 75-80°: sodium persulphate (70%) 96 grams, sodium acetate (cryst.) 7 grams, glacial acetic acid 5 c.c., water 1000 c.c. In view of the gentleness of the oxidation under these conditions of dilution and

* Jour. Phys. Chem., 1914, 18, 55.
temperature, it is curious that the acetic acid should be attacked. Gordon accounts for the methane by assuming catalytic action of the persulphate in eliminating carbon dioxide from the acetic acid:

\[ \text{CH}_3\text{COOH} = \text{CO}_2 + \text{CH}_4. \]

It is possible that the persulphate may also have a catalytic effect in the production of ethane.

Referring to the facts ascertained by Preuner and Ludlam that an anode of polished platinum must acquire a potential of 2.54 volts before any appreciable quantity of ethane is formed, and that also at this potential there occurs a break in the current - anode potential curve, Gibson deduces two alternatives:

1. that at 2.54 volts the acetate ion is first discharged at the anode, in which case strong evidence in favour of the Discharged Ion Theory would be obtained, or
2. that at 2.54 volts the anode has acquired an oxidising potential high enough to allow the reaction,

\[ 2\text{CH}_3\text{COOH} + \text{O} = \text{CH}_3\text{CO} + 2\text{CO}_2 + \text{H}_2\text{O}, \]

to proceed; or in other words, that at anode potentials above 2.54 volts acetic acid acts as a depolariser.

In order to examine this assertion, we must enquire what is meant by the notion of "discharging potential" when applied to composite anions such as \( \text{CH}_3\text{COO}, \text{SO}_4 \), etc. When a solution of a zinc salt

*loc. cit., p. 477.*
is electrolysed between platinum electrodes, it is clear that the cathode becomes covered with zinc, and so functions as a zinc electrode. The value for the discharging potential of 0.5 volt for a normal zinc ion concentration, then, has the definite meaning that the back electromotive force due to the electrolytic solution pressure of the zinc is 0.5 volt, which must be exceeded by the electrolysis current before any further deposition of zinc can take place. The value of 2.2 volts for $\text{SO}_4^{2-}$, however, can have no such definite meaning, because here we are dealing with an unstable residue which takes part in secondary reactions. In the former case the back electromotive force reaches its maximum value as soon as an appreciable quantity of zinc has been deposited, but in the latter it is dependent upon the concentration of the accumulated products of electrolysis at the electrode. This concentration is itself dependent upon the velocity of the reaction of reactions by which the accumulated material is removed. Thus 2.2 volts, at which a bend occurs in the current - anode potential curve for an approximately normal solution of sulphuric acid, is more accurately described as a depolarisation potential. Polarisation is here used in the sense of the accumulation of products of electrolysis at an electrode faster than they can be removed.

Let us consider, therefore, what these accumulated products are when a solution of an acetate is being
electrolysed. It may be assumed that the first reaction at the anode, which consists in the neutralisation of the electric charge on the ion, takes place instantaneously as soon as the ion reaches the electrode, i.e. it takes place with infinite velocity. Any subsequent chemical reactions in which the discharged ion may be involved will take place with a finite velocity dependent upon the concentration of the reacting substances and upon the temperature. Thus no matter what views may be held as to the mechanism of ethane formation, there must necessarily exist in the neighbourhood of the anode an accumulation of the unstable substance CH₃COO. The first reaction may then be written reversibly:

\[
\text{CH}_3\text{COO}^* \rightleftharpoons \text{CH}_3\text{COO} + \text{O}^.
\]

Some at least of these discharged ions take part in reaction (b) giving atomic oxygen, which causes an additional back electromotive force due to the reaction:

\[
0 + \text{H}_2\text{O} + 2\text{O} \rightleftharpoons 2\text{OH}^*.
\]

We thus have two unstable products at the anode, which is accordingly polarised. The point in the anode potential - current curve at which a bend occurs is therefore the point at which these substances have attained concentrations sufficiently high to allow of their being removed with appreciable rapidity. This depolarisation may conceivably be effected in five ways:
Reactions (3) and (4) represent the complete oxidation to carbon dioxide and water of acetic acid and discharged acetate ion respectively.

It will therefore be realised that Gibson's second alternative is capable of extension, and that his conclusion that the particular reaction studied, namely the formation of trichloromethyl trichloroacetate, is an oxidation reaction, can scarcely be held as valid, since it is largely based on the fact that the potential at which this ester was observed to be first formed (2.35 volts) is not the discharging potential of the trichloroacetate ion.

Both Gibson and Robertson record a sharp fall in the amount of oxygen evolved at or about the synthetic potential, and Robertson bases his conclusion that the synthesis of diethyl succinate from potassium ethyl malonate is an oxidation reaction, entirely upon this evidence. His argument is as follows:- The Faraday reaction, which takes place exclusively at low potentials, may be regarded as being maintained during rise of potential, and any other reaction as being superimposed upon it. Since the union of discharged ions uses no oxygen, the oxygen
curve (oxygen evolved per unit time - anode potential) would in this case reach a maximum at the synthetic point and remain at that value. But if oxidation reactions occur, some of the oxygen produced by the Faraday reaction would be used up, and so the curve would fall.

It has already been indicated that no evidence upon the one side or the other can be obtained from a consideration of the amount of evolved oxygen: on the same experimental evidence it might equally well be argued in favour of the discharged ion theory that since at the point where synthesis commences, some ions, instead of reacting with water to produce oxygen, are now reacting with themselves, the amount of oxygen evolved in unit time will begin to fall. Both arguments are quite inconsistent with the hypothesis, which seems to be a reasonable one, that the Faraday reaction is maintained during rise of potential.

If this matter be regarded from another point of view, it will be seen that the amount of evolved oxygen is dependent upon the concentration of active oxygen at the anode, since it is produced by the reaction \( O + O = O_2 \). If, with rising anode potential, the amount of \( O_2 \) evolved in unit time decreases, then the concentration of atomic oxygen must also be decreasing. But since the anode potential is

*Robertson, loc. cit., p. 2063.*
simultaneously rising, it cannot be the atomic oxygen alone which is responsible for the back electromotive force observed. This confirms the previous statement that the discharged ions themselves cause a back electromotive force.

Since the Oxidation Theory involves the partial oxidation of the acid, it is of interest to enquire to what extent complete oxidation to carbon dioxide and water takes place. From Robertson's figures for bright platinum, it can be calculated readily that from 30 to 40 per cent. of all the active oxygen liberated at the anode is used for complete oxidation between the potentials of 2.02 and 2.30 volts, i.e. before any synthesis commences. This theory therefore requires the extremely unlikely assumption that partial oxidation necessitates a higher potential (i.e. greater concentrations of reacting materials) than complete oxidation.

No positive evidence whatever would therefore appear to have been put forward in support of the Oxidation Theory.

On the other hand, the work of Bouveault and of Salauze, already cited, proves that under suitable conditions the discharged anions do indeed interact directly with one another.
EXPERIMENTAL.

The Electrolysis of Potassium Propionate.*

With a view to the collection of further data bearing upon reactions at the anode during electrolysis, it was decided to investigate the conditions attending the formation of ethylene and butane from a solution of potassium propionate. The various factors which were taken into consideration were anode potential, current density, material of anode, and temperature and concentration of solution. Potassium propionate is very suitable for such an investigation, as all the electrolytic products are gaseous, and can therefore be estimated quantitatively. Propionic acid of ascertained purity was used throughout.

Apparatus. The cell in which the electrolysis was conducted was similar to that used by Gibson and by Robertson; the electrodes were not placed in separate compartments. Current was passed through the cell from a battery of accumulators through a potentiometer system capable of fine adjustment over its whole range. In series with the cell was placed an ammeter with suitable shunts; this instrument, when unshunted, was sensitive to 0.01 milliampere.

The potential difference between the anode and a calomel electrode was measured on a second

potentiometer system by the compensation method, a cadmium cell being taken as the standard. From the value obtained for this potential difference, the potential of the anode on the hydrogen standard was calculated. A galvanometer giving a readable deflection with a current of 0.1 microampere was used to determine the point of balance.

Gas analysis. Owing to the solubility of ethylene in water, it was necessary to analyse the evolved gases over mercury. The Bone and Wheeler apparatus, in which the gas is expanded to constant volume and the pressure changes after the absorption of each constituent are read, was found to give rapid and accurate results with small quantities of gas. This apparatus has the advantages that it is entirely self-contained, and that small quantities of fresh reagents are used in each estimation. An apparatus for the production of electrolytic oxygen was kept permanently attached, so that a supply of the pure gas was always available for the combustion of the butane - hydrogen mixture.

The following gases were estimated in each sample: carbon dioxide, ethylene, oxygen, carbon monoxide, butane, and hydrogen. Bromine water was used for the absorption of the ethylene, alkaline pyrogallol for the oxygen, and ammoniacal cuprous chloride for the carbon monoxide. The residue of butane and hydrogen

* For a description and illustration of this apparatus, see "Analysis of Coal and Its By-Products," Illingworth, p.264 et seq.
was mixed with excess of oxygen and exploded. From the total contraction, and the amount of carbon dioxide found after combustion, the quantities of these constituents were calculated.

**General method.** Unless otherwise stated, all propionate solutions were normal with respect to free propionic acid: this concentration of acid was found to be necessary in order to avoid the solution becoming alkaline during the course of an experiment.

The cell was filled with solution, the current switched on, and the potentiometer adjusted so that the current passing was of the order of a few milliamperes. After an interval of at least 18 hours the current, now fallen to a fraction of a milliampere, was read and the anode potential calculated. The gas being evolved was then collected until sufficient for an analysis was obtained, the values of the current and anode potential being noted at intervals. These were found to vary very slightly with room temperature; large variations were not experienced provided sufficient time had been allowed for the system to reach equilibrium. After a gas sample had been secured, the potential applied to the terminals of the cell was raised, and the process repeated. Great care was taken to ensure constancy of current and anode potential before sampling the gas, and sufficient time was always allowed for the solution to come into equilibrium with the gaseous mixture above it. The size of the anode used was such as to
enable the range of anode potentials desired for any one experiment to be obtained at convenient current values, i.e. between 0.5 and 150 milliamperes. The time required for collecting the gas varied from a few minutes to several days, according to the current passing. The gas was withdrawn from the cell by means of a Dittmar pipette filled with mercury, and was transferred directly from this to the analysis apparatus.

Method of expressing results. All gas analysis figures, unless it is stated otherwise, refer to samples freed from carbon dioxide. Graphs have been drawn showing the relation between anode potential and the quantities of the various constituent gases. In this way the progress of the reactions producing these gases can be most readily studied. The significance of the curves so obtained depends upon the way in which these quantities are expressed. The actual percentage of gas in the mixture is never used, except in the case of butane which never exceeds 5 per cent. of the total gas, since this is dependent upon the amount of other constituents. The figures are expressed (1) as volume of gas evolved per hour, which involves the actual current passing in the cell, or (2) as the ratio of the volume of gas to that of hydrogen, which is equivalent to the amount of gas per unit of current.

General results. At low anode potentials, the mixture consisted chiefly of oxygen and hydrogen,
with a little ethylene, but no butane. As the potential was raised, the ethylene increased rapidly, reaching a maximum, after which butane made its appearance. Simultaneously with the increase of ethylene, the oxygen began to decrease, finally reaching a minimum. About one per cent. of carbon monoxide was always present.

Formation of ethylene.

(a) N solution of potassium propionate at 10°. Electrodes - platinum foil 1 cm. apart. Size of anode 15 x 24 mm. = 0.072 sq. dec. (counting both sides of the foil). In the following table the first column shows the anode potential in volts (V), the second the amount of ethylene evolved in c.c. per hour (E), and the third the ratio of ethylene to hydrogen (R):-

<table>
<thead>
<tr>
<th>V</th>
<th>E</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.36</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>2.475</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>2.535</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>2.60</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>2.66</td>
<td>0.14</td>
<td>0.07</td>
</tr>
<tr>
<td>2.705</td>
<td>0.37</td>
<td>0.13</td>
</tr>
<tr>
<td>2.75</td>
<td>1.87</td>
<td>0.24</td>
</tr>
<tr>
<td>2.775</td>
<td>8.08</td>
<td>0.33</td>
</tr>
<tr>
<td>2.79</td>
<td>16.95</td>
<td>0.41</td>
</tr>
<tr>
<td>2.83</td>
<td>39.0</td>
<td>0.47</td>
</tr>
<tr>
<td>2.885</td>
<td>-</td>
<td>0.55</td>
</tr>
<tr>
<td>2.915</td>
<td>-</td>
<td>0.58</td>
</tr>
<tr>
<td>2.95</td>
<td>-</td>
<td>0.61</td>
</tr>
</tbody>
</table>
Fig. 1.

Ordinates - vol. of ethylene in c.c. per hour.

Abscissae - anode potential in volts.
Fig. 2.

Ordinates - ratio of ethylene to hydrogen.
Abscissae - anode potential in volts.
Figs. 1 and 2 show these results in graphical form. The ethylene begins to increase rapidly at about 2.6 volts. At 2.95 volts it constitutes 36.9 per cent. of the mixture, and even at very high potentials does not exceed 37.5 per cent. The sharp bend at 2.75 volts in Fig. 1 is due to a sudden increase of current at that point.

(b) N solution at 50°. The cell was immersed in a thermostat at this temperature. Anode of platinum wire of surface area 0.0165 sq. dec.

<table>
<thead>
<tr>
<th>V</th>
<th>E</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.56</td>
<td>0.007</td>
<td>0.04</td>
</tr>
<tr>
<td>2.63</td>
<td>0.04</td>
<td>0.09</td>
</tr>
<tr>
<td>2.68</td>
<td>0.14</td>
<td>0.16</td>
</tr>
<tr>
<td>2.75</td>
<td>0.51</td>
<td>0.25</td>
</tr>
<tr>
<td>2.79</td>
<td>0.87</td>
<td>0.28</td>
</tr>
<tr>
<td>2.855</td>
<td>1.96</td>
<td>0.34</td>
</tr>
<tr>
<td>2.95</td>
<td>4.10</td>
<td>0.38</td>
</tr>
<tr>
<td>3.07</td>
<td>6.90</td>
<td>0.40</td>
</tr>
<tr>
<td>3.15</td>
<td>8.55</td>
<td>0.41</td>
</tr>
</tbody>
</table>

See Figs. 3 and 4. Although there is more ethylene at low potentials at this temperature, the increase with rise of anode potential is more gradual, and the maximum attained is not so high as at 10°. At 3.15 volts the mixture contained 28 per cent., and at high potentials did not exceed 30 per cent.

(c) 4 N solution at 10°. Anode of platinum foil of surface area 0.072 sq. dec.
Fig. 3.

Ordinates - vol. of ethylene in c.c. per hour at 50°.
Abscissae - anode potential in volts.

Fig. 4.

Ordinates - ratio of ethylene to hydrogen at 50°.
Abscissae - anode potential in volts.
The following table shows the relation between anode potential and the ethylene - hydrogen ratio for this concentration:

<table>
<thead>
<tr>
<th>V.</th>
<th>R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.35</td>
<td>.01</td>
</tr>
<tr>
<td>2.46</td>
<td>.03</td>
</tr>
<tr>
<td>2.54</td>
<td>.10</td>
</tr>
<tr>
<td>2.60</td>
<td>.29</td>
</tr>
<tr>
<td>2.625</td>
<td>.43</td>
</tr>
<tr>
<td>2.71</td>
<td>.58</td>
</tr>
<tr>
<td>2.75</td>
<td>.59</td>
</tr>
</tbody>
</table>

This relation is shown in Fig. 5. The curve is of similar shape to Fig. 2 for H solution, but the whole curve is shifted -1.15 volt to the left, i.e. ethylene formation takes place at a potential -1.15 volt lower than in N solution.

Formation of butane.

(a) N solution at 10°. Anode of platinum wire of surface area .0118 sq. dec. The table shows the percentage of butane in the mixture (B).

<table>
<thead>
<tr>
<th>V.</th>
<th>B.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.76</td>
<td>0.2</td>
</tr>
<tr>
<td>2.80</td>
<td>0.2</td>
</tr>
<tr>
<td>2.89</td>
<td>0.2</td>
</tr>
<tr>
<td>2.93</td>
<td>0.2</td>
</tr>
<tr>
<td>2.99</td>
<td>0.2</td>
</tr>
<tr>
<td>3.07</td>
<td>0.6</td>
</tr>
<tr>
<td>3.17</td>
<td>3.2</td>
</tr>
<tr>
<td>3.25</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Fig. 5.

Ordinates - ratio of ethylene to hydrogen for 4N soln.
Abscissae - anode potential in volts.
Fig. 6.

Ordinates - percentage of butane.

Abscissae - anode potential in volts.
Fig. 6 shows that the butane begins to be formed in appreciable quantity at 3.05 volts, and reaches a maximum of 3.2 per cent. at 3.15 volts. No greater quantity was obtained at potentials up to 4.6 volts.

(b) 4N solution at 10°. It was not found possible to cover the desired range of potentials with one size of anode, and three were therefore used, of surface area (1) 0.072 sq. dec., (2) 0.0118 sq. dec., (3) 0.000836 sq. dec.

<table>
<thead>
<tr>
<th>Anode 1</th>
<th>Anode 2</th>
<th>Anode 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>V.</td>
<td>B.</td>
<td>V.</td>
</tr>
<tr>
<td>2.60</td>
<td>0.4</td>
<td>2.775</td>
</tr>
<tr>
<td>2.625</td>
<td>0.4</td>
<td>2.83</td>
</tr>
<tr>
<td>2.71</td>
<td>0.4</td>
<td>2.85</td>
</tr>
<tr>
<td>2.82</td>
<td>0.6</td>
<td>2.89</td>
</tr>
<tr>
<td>2.865</td>
<td>2.9</td>
<td>2.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.05</td>
</tr>
</tbody>
</table>

The three curves obtained from these figures are shown in Fig. 7. For this concentration, the amount of butane increases suddenly at 2.83 volts. With anode 2, it reaches a maximum of 3.8 per cent., but with anode 3 the maximum is 5 per cent. A potential of 4.51 volts also gave 5 per cent.

**Oxygen evolved.**

(a) N solution at 10°. Platinum anode of surface area 0.072 sq. dec. The following table shows the amount of oxygen evolved in c.c. per hour (O₂), and also the ratio of oxygen to hydrogen (R):—
Fig. 7.

Ordinates - percentage of butane for 4N soln.

Abscissae - anode potential in volts.
See Figs. 8 and 9. The amount of oxygen increases until a potential of 2.5 is reached, and begins to fall sharply at 2.6 volts. There is always a small quantity at high potentials (about 0.5 per cent.). The oxygen per hour curve shows no drop at the potential at which ethylene is formed.

(b) N solution at 50°. The corresponding figures for 50° are as follows:

<table>
<thead>
<tr>
<th>V</th>
<th>O₂</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.56</td>
<td>.052</td>
<td>.28</td>
</tr>
<tr>
<td>2.63</td>
<td>.10</td>
<td>.24</td>
</tr>
<tr>
<td>2.68</td>
<td>.14</td>
<td>.17</td>
</tr>
<tr>
<td>2.75</td>
<td>.21</td>
<td>.10</td>
</tr>
<tr>
<td>2.79</td>
<td>.24</td>
<td>.077</td>
</tr>
<tr>
<td>2.855</td>
<td>.32</td>
<td>.055</td>
</tr>
</tbody>
</table>
Fig. 8.

Ordinates - oxygen to hydrogen ratio.
Abscissae - anode potential in volts.

Fig. 9.

Ordinates - oxygen evolved in c.c. per hour
Abscissae - anode potential in volts.
These figures are plotted on curves 10 and 11. The fall in the amount of oxygen evolved is less sudden at 50° than at 10°, and the amount remaining at high potentials is distinctly greater. Fig. 11 shows a remarkably steady rise in the oxygen evolved per hour with increasing anode potential.

**Complete oxidation of electrolyte.** On the Discharged Ion Theory, the current passing in the cell may be divided into two portions, that carried by anions which after discharge react with water to give oxygen, and that carried by anions which after discharge react with each other. The total oxygen generated at the anode is then evidently expressed by \( \frac{1}{2}(H_2 - C_2H_4 - C_6H_{10}) \), and the excess of this over the oxygen actually found in the gas sample gives the oxygen which is missing, i.e. which has been used up in oxidising the electrolyte to carbon dioxide and water. The fraction of the available oxygen so used is therefore

\[
\frac{\frac{1}{2}(H_2 - C_2H_4 - C_6H_{10}) - C_2H_4}{\frac{1}{2}(H_2 - C_2H_4 - C_6H_{10})}
\]

This fraction, when plotted against the anode potential, shows the progress of this reaction.

The following figures were obtained for a N solution at 10°:
Fig. 10.

Ordinates - oxygen to hydrogen ratio for 50°.
Abscissae - anode potential in volts.

Fig. 11.

Ordinates - oxygen evolved in c.c. per hour at 50°.
Abscissae - anode potential in volts.
For a normal solution at 50° the figures were:

<table>
<thead>
<tr>
<th>V</th>
<th>Fr</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.36</td>
<td>.50</td>
</tr>
<tr>
<td>2.475</td>
<td>.415</td>
</tr>
<tr>
<td>2.535</td>
<td>.24</td>
</tr>
<tr>
<td>2.60</td>
<td>.24</td>
</tr>
<tr>
<td>2.66</td>
<td>.31</td>
</tr>
<tr>
<td>2.705</td>
<td>.45</td>
</tr>
<tr>
<td>2.75</td>
<td>.69</td>
</tr>
<tr>
<td>2.775</td>
<td>.80</td>
</tr>
<tr>
<td>2.79</td>
<td>.85</td>
</tr>
<tr>
<td>2.83</td>
<td>.89</td>
</tr>
<tr>
<td>2.885</td>
<td>.90</td>
</tr>
<tr>
<td>2.915</td>
<td>.89</td>
</tr>
<tr>
<td>2.95</td>
<td>.92</td>
</tr>
</tbody>
</table>

Figs. 12 and 13 show the curves drawn from these figures. It appears that there is a large amount of complete oxidation before the formation of ethylene
Fig. 12.

Ordinates - Fraction of available oxygen used for complete oxidation at 50°.

Abscissee - anode potential in volts.

Fig. 13.

Ordinates - Fraction of available oxygen used for complete oxidation, \( \times 10^3 \).

Abscissee - anode potential in volts.
commences, and that it increases suddenly simultaneously with ethylene formation, until 90 per cent. of the available oxygen is being used up in this way.

The relation between current and anode potential.

(a) N solution at 10°. Platinum anode of surface area 0.072 sq. dec. The current (C) is given in milli-amperes.

<table>
<thead>
<tr>
<th>V</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.36</td>
<td>0.4</td>
</tr>
<tr>
<td>2.475</td>
<td>0.6</td>
</tr>
<tr>
<td>2.535</td>
<td>1.2</td>
</tr>
<tr>
<td>2.60</td>
<td>2.5</td>
</tr>
<tr>
<td>2.66</td>
<td>4.4</td>
</tr>
<tr>
<td>2.705</td>
<td>6.7</td>
</tr>
<tr>
<td>2.75</td>
<td>19.0</td>
</tr>
<tr>
<td>2.775</td>
<td>58.0</td>
</tr>
</tbody>
</table>

See Fig. 14.

(b) N solution at 50°. Platinum anode of surface area 0.00165 sq. dec.

<table>
<thead>
<tr>
<th>V</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.56</td>
<td>0.44</td>
</tr>
<tr>
<td>2.63</td>
<td>1.0</td>
</tr>
<tr>
<td>2.68</td>
<td>2.0</td>
</tr>
<tr>
<td>2.75</td>
<td>4.7</td>
</tr>
<tr>
<td>2.79</td>
<td>7.6</td>
</tr>
<tr>
<td>2.855</td>
<td>14.0</td>
</tr>
<tr>
<td>2.95</td>
<td>26.1</td>
</tr>
<tr>
<td>3.07</td>
<td>41.2</td>
</tr>
<tr>
<td>3.15</td>
<td>50.2</td>
</tr>
</tbody>
</table>
Fig. 14.

Ordinates - current in milliamperes.

Abscissae - anode potential in volts.
Fig. 15.

Ordinates - current in milliamperes (50°).
Abscissae - anode potential in volts.
(c) 4N solution at 10 °. Platinum anode of surface area 0.072 sq. dec.

<table>
<thead>
<tr>
<th>V</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.35</td>
<td>0.1</td>
</tr>
<tr>
<td>2.46</td>
<td>0.5</td>
</tr>
<tr>
<td>2.54</td>
<td>0.9</td>
</tr>
<tr>
<td>2.60</td>
<td>2.2</td>
</tr>
<tr>
<td>2.625</td>
<td>5.9</td>
</tr>
<tr>
<td>2.71</td>
<td>40.0</td>
</tr>
<tr>
<td>2.75</td>
<td>60.0</td>
</tr>
</tbody>
</table>

These curves show the progress, with increasing anode potential, of all the depolarising reactions taken together. The absence of a sharp bend in Fig. 15 indicates that depolarisation is less rapid and complete at the higher temperature.

It was found to be immaterial whether the anode potential - current curves were ascended or descended: for a given value of the current, there was only one value of the anode potential.

The influence of anode material. A small anode of platinised platinum wire gave no ethylene at potentials below about 3 volts. Above this potential, the gas stream leaving the anode was so vigorous that some of the platinum black was removed, and small spots of bright platinum began to show. This may account for the small quantities of ethylene
Fig. 16.

Ordinates - current in milliamperes (4N soln.).
Abscissae - anode potential in volts.
found at higher potentials. The gas evolved consisted mainly of oxygen and hydrogen, with a little carbon dioxide. Following are the results of the analyses of three samples:

<table>
<thead>
<tr>
<th>V.</th>
<th>Curr.</th>
<th>%CO₂</th>
<th>%C₂H₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.95</td>
<td>35</td>
<td>3.4</td>
<td>nil</td>
</tr>
<tr>
<td>3.32</td>
<td>61</td>
<td>5.6</td>
<td>1.8</td>
</tr>
<tr>
<td>3.88</td>
<td>76</td>
<td>5.7</td>
<td>3.0</td>
</tr>
</tbody>
</table>

A small anode of gold wire gave no ethylene even at very high potentials. The anode suffered considerable disintegration, and the solution became brown with dispersed gold. Potentials from 3 up to 5.3 volts were tried, but the composition of the evolved gas remained unaltered - it was a mixture of oxygen and hydrogen with 2 per cent. of carbon dioxide.

The Electrolysis of Non-aqueous Solutions of Salts.

Solvents which ionise salts to a degree sufficient to give an appreciable conductivity are very limited in number. Methyl alcohol is perhaps the most convenient. The electrolysis in this solvent of sodium acetate and of sodium methyl succinate has already been mentioned. To show that it was immaterial as far as synthesis was concerned which solvent was used, a solution of anhydrous sodium acetate in glacial acetic acid (with the addition of a small quantity of acetic anhydride to ensure the absence of water),
was electrolysed at 10 volts with (1) a platinum anode, and (2) a gold anode. In each case the current was allowed to pass for some time before a sample of the gas was taken, in order to saturate the liquid with gas. The platinum anode gave a gas the percentage composition of which was: CO₂, 41.8; C₂H₆, 26.2; CO, 1.51; H₂, 30.5; O₂, nil. With the gold anode the composition of the gas was: CO₂, 46.9; C₂H₆, 22.5; CO, 1.4; H₂, 29.2; O₂, nil. Synthesis is clearly taking place here without the intervention of the solvent.

A solution of anhydrous potassium propionate in propionic acid was found a very poor conductor. A solution of that salt in methyl alcohol was therefore made, great precautions being taken to prevent the presence of any water. The potassium propionate was heated to 200° in a vacuum for 5 hours, and the methyl alcohol was dried over quicklime at the boiling point, and finally over calcium metal. Calcium chloride tubes were attached to the limbs of the electrolytic cell, and by using the propionate solution itself as an intermediate buffer solution, ingress of water via the capillary leading to the calomel electrode was avoided. The solution was normal with respect to both salt and free acid, and the anode used was of platinum wire.

As previously mentioned, the electrical reaction consisting in the discharge of the ions must take place very rapidly as compared with any ensuing
chemical reactions, and the anode would be expected to be polarised in consequence of the accumulation of C,H₅COO residues. This expectation was realised:
on applying a potential to the electrodes of the cell, the initial current fell away immediately to a small fraction of its original value. The current became constant in five to ten minutes, and the anode acquired a potential of 2.06 volts with 0.05 milliampere passing. An anode potential-current curve was constructed in the usual way; this is shown in Fig. 18. It will be seen that depolarisation occurred at 2.6 to 2.7 volts, which must necessarily have been due to the interaction of the discharged ions to give ethylene and butane. Hydrogen bubbles were first observed at the fairly large cathode at 2.67 volts. The anode surface was observed in a strong light by the aid of a microscope, and at 2.745 volts a stream of less dense liquid was seen rising from the anode, but no gas evolution took place till high current values were reached. The point at which gas was evolved from the anode varied in different experiments: in the early ones (i.e., before the solution became saturated with the gases) 40 milliamperes gave very occasional bubbles, not from the anode surface itself, but from the density stream an inch above the anode. This density stream consisted of carbon dioxide, ethylene, and butane in solution (one volume of methyl alcohol dissolves about four volumes of carbon dioxide and of ethylene, and about fifteen to twenty
Fig. 17.

N potassium propionate in CH$_3$OH - gold anode.
Ordinates - current in milliamperes.
Abscissae - anode potential in volts.

Fig. 18.

N potassium propionate in CH$_3$OH - platinum anode.
Ordinates - current in milliamperes.
Abscissae - anode potential in volts.
volumes of butane). Owing to this great solubility it was not possible to obtain representative gas samples at different anode potentials.

A similar curve was constructed for an anode of gold wire (see Fig. 17).

In order to obtain a sample of the gases evolved under these conditions, a N solution of potassium propionate in equal volumes of methyl alcohol and propionic acid was electrolysed at 12 volts and 100 milliamperes for 43 hours, at the end of which time it was calculated that the propionic acid present would be reduced to approximately normal concentration. The gas being evolved had then the following composition: \( \text{C}_2\text{H}_4, 12.3; \text{C}_4\text{H}_{10}, 36.0; \text{O}_2, 0.5; \text{CO}, 0.5; \text{H}_2, 50.7 \). The experiment was repeated with a gold anode, which gave a gas of approximately the same composition.

It need hardly be pointed out that this is a very valuable method for the preparation of butane.

Similar experiments were performed with a N solution of potassium ethyl malonate, EtOOC.CH\(_2\)COOK, in methyl alcohol, hydrogen ethyl malonate being added (normal). The salt was previously dried by heating to 100° in a vacuum for 5 hours. A current - anode potential curve was obtained for a platinum anode (Fig. 19). With a gold anode constant readings could not be obtained for currents above 15 milliamperes. This was due to a brown film forming on the anode surface, which could be removed mechanically by the
Fig. 19.

N solution of potassium ethyl malonate in CH₃OH.

Ordinates - current in milliamperes.

Abscissae - anode potential in volts.
momentary application of a high potential accross the cell.

With both platinum and gold anodes, a current of 15 milliamperes for 18 hours gave a quantity of diethyl succinate.

The Electrolytic Oxidation of Acetic Acid.

So far, no direct and conclusive proof of the Discharged Ion Theory has been recorded. It might be held that, although the discharged ions interact in non-aqueous solutions, synthesis in aqueous solutions may be due either partly or entirely to oxidation of the free acid.

It was thought that if, in a solution of acetic acid, the acetate ions could be prevented from discharging, while at the same time the oxidation conditions were maintained unaltered, it would be possible to ascertain to which of the two reactions the formation of ethane was attributable. This has been accomplished by adding a small quantity of sulphuric acid to a concentrated solution of acetic acid in water. The highly ionised sulphuric acid reduces the ionisation of the acetic acid, already small owing to the high concentration of the solution, to a negligible amount; the current is then carried almost exclusively by the sulphate and hydrosulphate ions. These, after discharge, react with water to give active oxygen, the action of which on acetic acid can then be studied without interference due to
the discharge of acetate ions.

This experiment was entirely successful, and showed beyond doubt that ethane is produced by the interaction of discharged acetate ions, and that electrolytic oxygen, when it oxidises acetic acid, does so completely and not partially.

In the following table, acetic and sulphuric acids are shown as parts by volume in 100 parts of solution; P.D. is the potential difference applied to the electrodes.

<table>
<thead>
<tr>
<th>CH₃COOH</th>
<th>H₂SO₄</th>
<th>P.D.</th>
<th>%C₂H₆</th>
<th>%CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>nil</td>
<td>42</td>
<td>16.8</td>
<td>47.8</td>
</tr>
<tr>
<td>90</td>
<td>5</td>
<td>4</td>
<td>0.4</td>
<td>35.4</td>
</tr>
<tr>
<td>90</td>
<td>1</td>
<td>4</td>
<td>0.6</td>
<td>22.9</td>
</tr>
<tr>
<td>90</td>
<td>0.1</td>
<td>12</td>
<td>0.9</td>
<td>26.2</td>
</tr>
<tr>
<td>90</td>
<td>0.01</td>
<td>42</td>
<td>0.7*</td>
<td>25.8</td>
</tr>
<tr>
<td>90</td>
<td>0.001</td>
<td>41</td>
<td>17.6</td>
<td>44.5</td>
</tr>
</tbody>
</table>

*Duplicate analysis.

It will be seen that a 90 per cent. solution of acetic acid was used in all the experiments, and that varying quantities of sulphuric acid were added. An e.m.f. sufficient to allow a current of 10-50 milliamperes to pass was applied to the platinum electrodes, and the electrolysis allowed to proceed for 20 to 30 hours before the gas was collected in order to establish equilibrium between the solution and the evolved gases. With no sulphuric acid present, the gas contained 16.8 per cent of ethane.
and 47.8 per cent. of carbon dioxide. The presence of even one hundredth per cent. of sulphuric acid reduced the amount of ethane to 0.7 per cent. Little oxygen was evolved in any of the experiments: it was used up in completely oxidising the acetic acid, as is shown by the presence of 20-35 per cent. of carbon dioxide even in absence of ethane.

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Conclusions and Summary.

The Discharged Ion Theory accounts for the formation of an unsaturated hydrocarbon during the electrolysis of a salt of a fatty acid by assuming that two discharged ions interact to give a molecule of the free acid and one of the unsaturated compound. Thus for propionic acid:

\[ 2\text{CH}_3\text{.CH}_1\text{.COO} = \text{CH}_3\text{.CH}_1\text{.COOH} + \text{CH}_2=\text{CH}_2 + \text{CO}_2. \]

On the Oxidation Theory, however, it is produced by the following reaction:

\[ \text{CH}_3\text{.CH}_1\text{.COOH} + \text{O} = \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} + \text{CO}_2, \]

while the butane is similarly formed by the oxidation of two molecules of propionic acid by one atom of active oxygen. There are then three possible oxidation reactions, giving (1) carbon dioxide and water, (2) ethylene, and (3) butane. The relative amounts of oxygen required for these reactions are as 14:2:1. It would therefore be expected, if the Oxidation Theory were true, that butane would be formed at low anode potentials where the oxygen is in low concentration at the anode, and that as the potential was raised, ethylene, and finally carbon dioxide and water would be the chief products.

Le Blanc states "If the organic substance be used as a reducing agent at the anode, it is evident that, according to the magnitude of the applied potential,

* "Textbook of Electrochemistry", 1907, p.314."
the first, second, third, and perhaps still higher stages of oxidation of the compound may be formed."

It is found, however, that these compounds appear in the reverse order: a large amount of complete oxidation takes place before any ethylene is formed, and the ethylene reaches its maximum before any butane is formed. As has been pointed out, complete oxidation also precedes synthesis in the electrolysis of potassium ethyl malonate. The Oxidation Theory would seem to be untenable for this reason alone.

Figs. 2 and 8 show that the oxygen – hydrogen ratio begins to fall simultaneously with the rise in the ethylene – hydrogen ratio, and continues to fall until the maximum amount of ethylene has been formed. This fall seems to be due to a corresponding rise in the amount of complete oxidation. That ethylene formation and complete oxidation should be so intimately related (compare Figs. 2 and 13) is at first sight somewhat strange. Suppose, however, that the sudden increase of complete oxidation were to take place at a higher potential. This would mean that at 2.6 to 2.7 volts the concentration of \( \text{C}_2\text{H}_5\text{COO} \) residues is sufficiently great to allow them to react with each other, but not sufficiently great to allow them to react vigorously with oxygen, which seems improbable. On the other hand, this large amount of complete oxidation cannot take place at a potential lower than that at which ethylene is formed, otherwise
the C₂H₅COO residues would never attain a sufficiently high concentration to give synthesis at all, owing to their removal as carbon dioxide and water. It is assumed in this connection that the atomic oxygen reacts more readily with the discharged ions than it does with propionic acid, on account of the extremely reactive state of the former. The two reactions under discussion must therefore proceed at approximately the same anode potential.

If the curves showing the relation between current and anode potential for 10° and for 50° (Figs. 14 and 15) be examined, it will be seen that, while they begin to ascend at about the same point, the gradient of the 50° curve is less steep than that of the 10° curve. That is to say, although depolarisation commences at the same potential, it is not so complete at 50° as it is at 10°. Now at 50°, the chemical reactions involved would be supposed to take place with increased velocity. It may therefore be asked why depolarisation is not more rapid and complete at the higher temperature. Complete oxidation is, on the whole, more vigorous at 50° than at 10° (Figs. 12 and 13), and also more free oxygen is evolved at 50° above 2.75 volts (Figs. 8 and 10). Clearly, then, more oxygen is being formed at the anode at the higher temperature. Taken in conjunction with the diminished yield of ethylene at 50°, these results may be explained by supposing that the increase of temperature increases the rate of reaction of the
discharged ions with water more than it increases their rate of interaction.

In general, a reduction in the concentration of the electrolyte produces a smaller yield of the synthetic product. It is probable that, owing to the greater concentration of water in dilute solution, the reaction of discharged ions on water is favoured at the expense of the synthetic reaction.

A phenomenon which is somewhat difficult of explanation is the profound influence of the anode material on synthesis in aqueous solution. Not only is there no synthesis at a gold anode, but there is practically no oxidation of the electrolyte. While it may be held that platinum catalyses oxidation, it cannot be said that it catalyses synthesis, since gold gives synthesis in absence of water. It seems preferable to approach this problem from the standpoint that synthesis must always occur provided that there is a sufficient concentration of discharged ions at the anode. We are then led to the conclusion that the velocity of the reaction of discharged ions with water at a gold anode is much greater than at a platinum anode, so that the concentration of discharged ions does not reach a value sufficiently high to give synthesis. But since platinum is exceptional in giving synthesis, the reason for this must be found in terms of some property peculiar to that metal.

It has not been found possible to connect current density with synthesis in any definite way: the anode
potential seems to give a better measure of the concentration of the reactive substances at the anode.

Since depolarisation in aqueous solution is chiefly due to two reactions, namely synthesis and complete oxidation, and since, as has been shown, these two reactions must proceed at the same anode potential, it would be expected that the depolarisation potential would be approximately the same in either aqueous or non-aqueous solution. That this is the case may be seen from Figs. 14 and 18.

Summary.

1. It has been proved that electrosynthesis takes place through the direct union of the discharged anions, (a) by showing that the arguments used by Gibson and Robertson in support of the Oxidation Theory are largely fallacious, (b) by confirming the results of other workers who found that synthesis can and does take place in non-aqueous solutions, to which the Oxidation Theory is not applicable, and (c) by proving that the electrolytic oxidation of acetic acid goes completely and not partially under ordinary electrosynthetic conditions, and that the presence of the discharged acetate ions themselves is indispensable for the formation of ethane.

2. In the electrolysis of potassium propionate, it is found that:

   (a) Butane is formed at 3.05 volts in N solution, and reaches a maximum of 3.2 per cent. of the
evolved gases at 3.15 volts. In 4N solution it is formed at 2.83 volts, and reaches a maximum of about 5 per cent.

(b) The quantity of ethylene begins to increase rapidly at 2.6 volts, and reaches a maximum of 37 per cent at 3.07 volts. In 4N solution, this increase begins at 2.45 volts, and the maximum of 36 per cent is reached at 2.85 volts.

(c) At 50° no butane is formed even at high anode potentials, and the yield of ethylene is reduced to 30 per cent.

(d) There is no drop in the amount of oxygen evolved per unit time when ethylene begins to be formed, such as is recorded by Gibson and Robertson for other electrolytes.

(e) Complete oxidation takes place to a great extent at low anode potentials, which indicates the powerful character of electrolytic oxygen as an oxidising agent, and renders it extremely improbable that partial oxidation takes place at higher potentials.

(f) Platinised platinum and gold anodes give little or no synthesis in aqueous solution.

3. 36 per cent of butane is present in the gases from electrolysis of an anhydrous methyl alcoholic solution of potassium propionate. It is suggested that this is a convenient method for the preparation of butane.

4. It is demonstrated that the discharged ions
themselves exert a back electromotive force at the anode, as would be expected from theoretical considerations.
Part 2: - The Electrosynthesis of Four New Dibasic Acids of the Oxalic Acid Series, with a Discussion on the Melting Points of this Series.
The only practicable method available for the preparation of the higher members of the series of normal saturated dibasic acids is the well known electrosynthetic method of Crum Brown and Walker, in which concentrated aqueous solutions of the alkali ethyl salts of acids lower in the series are electrolysed between platinum electrodes. Thus, from the potassium ethyl salt of sebacic acid, they synthesised the di-ethyl ester of hexadecanedi-carboxylic acid:

$$2\text{EtOOC} \cdot (\text{CH}_2)_8 \cdot \text{COOK} = 2\text{K} + 2\text{CO}_2 + \text{EtOOC} \cdot (\text{CH}_2)_6 \cdot \text{COOEt}$$

This was formerly the highest member of the series prepared synthetically. In attempts to synthesise by this means acids of still higher molecular weight, two difficulties are encountered:

1. The temperature of the liquid undergoing electrolysis must be kept above the melting point of the synthetic di-ester, in order that the latter may not solidify on the anode and prevent the passage of the current;
2. The alkali ethyl salts of the higher dibasic acids are of a soapy nature, and cannot readily be dealt with in concentrated solution. Two of the conditions favourable to electrosynthesis, low temperature and high concentration, are thus unattainable. The first, indeed, sets a limit to the process, as it is clearly not possible to synthesise esters having melting points much above 80°.
Since the di-esters which are the starting-points of these syntheses are themselves prepared by electrolysis of sodium ethyl salts of acids lower in the series, it is of importance that the process of their half-saponification should be made as nearly quantitative as possible in order to avoid loss of material. This can always be accomplished by conducting the operation in very dilute alcoholic solution (2 per cent.), when the ester salt remains in solution, whereas the di-sodium salt, which is formed to the extent of about 20 per cent., is precipitated, and may be used again after reconversion into the di-ester.

The higher dibasic acids resemble in many of their properties the corresponding monobasic fatty acids. Those containing a chain of twenty methylene groups and upwards are very sparingly soluble in the cold in the common organic solvents, and their di-ethyl esters are also sparingly soluble in cold alcohol and ether. Decane- and dodecanedicarboxylic acids may readily be obtained in a very pure state by recrystallising alternately from water and chloroform; but the solubility in water of acids higher in the series is negligibly small. For this reason they can be precipitated almost quantitatively from solutions of their alkali salts by saturating with carbon dioxide. The soapy character of their salts is observed to commence with tetradecanedicarboxylic
Petersen synthesised paraffin hydrocarbons of high molecular weight by electrolysis of salts of the fatty acids: e.g. potassium stearate gave tetra-triacontane:

$$2\text{CH}_3\cdot(\text{CH}_2)_{16}\cdot\text{COOK} = 2\text{K} + 2\text{CO}_2 + \text{C}_3\text{H}_{76}$$

He met the difficulty of electrolysing a soapy solution by using as solvent aqueous alcohol (containing about 40 per cent. of alcohol), and avoiding alkalinity by adding from time to time an alcoholic solution of the free acid. A repetition of this work gave a good yield of hydrocarbon; but when a solution of sodium ethyl hexadecanedicarboxylate, EtOOC.(CH$_2$)$_{16}$COONa, was electrolysed under identical conditions, no synthesis took place. It was eventually found that synthesis could be effected by reducing the quantity of alcohol to the minimum necessary to avoid frothing of the solution.

In this way four new acids were prepared, namely, eicosanedicarboxylic acid, HOOC.(CH$_2$)$_{18}$COOH; tetra-cosanedicarboxylic acid, HOOC.(CH$_2$)$_{24}$COOH; octaco-sanedicarboxylic acid, HOOC.(CH$_2$)$_{28}$COOH; and dotriacontanedicarboxylic acid, HOOC.(CH$_2$)$_{31}$COOH. The first of these was obtained in good yield, but the rest in comparatively small yield, evidently owing to the soapy character of the sodium ethyl salts being electrolysed in these cases.

*Zeit. für Elektrochem., 12, 144.
acid, which has a total of sixteen carbon atoms. In the monobasic fatty acid series this property commences with lauric acid (C₁₂).

A normal by-product of electrolysis of the compound EtOOC.\(\left(CH_2\right)_n\)COONa is the unsaturated ester EtOOC.\(\left(CH_2\right)_n\)CH=CH₂. The position of the unsaturated linkage, however, has not previously been established with certainty except in the simplest cases. This has now been done for the compounds in which \(n\) has values of 6, 7, and 10. The method used was to treat the dibromo-compound obtained by the addition of bromine to the unsaturated acid, with aqueous sodium hydroxide, and to oxidise the dihydroxy-acid so formed with potassium permanganate to a saturated dibasic acid. Thus hexenecarboxylic acid yielded adipic acid:-

\[
\begin{align*}
CH_2=CH.(CH_2)_4.COOH &\rightarrow CH.Br.CHBr.(CH_2)_4.COOH \\
&\rightarrow CH.OH.CH(OH).(CH_2)_4.COOH &\rightarrow HOOC.(CH_2)_4.COOH.
\end{align*}
\]

Similarly heptenecarboxylic acid and undecenoic acid yielded pimelic and sebacic acids respectively.

EXPERIMENTAL.

SYNTHESIS OF EICOSANEDICARBOXYLIC ACID.

Preparation of Decanedicarboxylic Acid, \( \text{HOOC.(CH}_2\text{)_10.COOH} \). Although this acid can be electro-synthesised from pimelic acid, it was thought advisable to synthesise it from undecenoic acid, as the former acid is troublesome to obtain in quantity. This was carried out according to the following scheme:

\[
\begin{align*}
\text{CH}_2=\text{CH.}(\text{CH}_2)_8.\text{COOH} & \xrightarrow{\text{HBr}} \text{CH}_2\text{Br.CH}_2(\text{CH}_2)_8.\text{COOH} \\
\text{KCN} & \xrightarrow{} \text{CH}_2\text{CN.(CH}_2)_8.\text{COOH} \xrightarrow{\text{HCl}} \text{HOOC.(CH}_2\text{)_10.\text{COOH}}.
\end{align*}
\]

Walker and Lumsden found that when undecenoic acid was treated in toluene solution with dry hydrogen bromide, the bromine atom attached itself almost exclusively to the terminal carbon atom of the chain, but that in ether solution the isomeric compound was formed. Several attempts to obtain the \( \omega \)-bromo-acid in toluene solution gave variable results, and very small yields. Other solvents were accordingly tried, and light petroleum ether was finally selected as being the most suitable.

A 10 per cent. solution of pure undecenoic acid in this solvent was treated at 0° with hydrogen bromide, free from bromine and dried over phosphorus pentoxide, when \( \omega \)-bromoundecenoic acid separated out and was filtered off. The yield was 10 to 12 grams.

from 10 grams of undecenoic acid. This was recrystallised from cold petroleum ether before being used for the next stage of the preparation. The bromo-acid (50 grams) was dissolved in rectified spirits (200 c.c.), and boiled for twelve hours under a reflux with a solution of 30 grams of potassium cyanide in 100 c.c. of water. The alcohol was then removed by distillation and the cyano-acid hydrolysed with concentrated hydrochloric acid at the boiling point. Decanedicarboxylic acid separated out on cooling, and was recrystallised from chloroform. The yield by this method was 65 per cent. of the theoretical, which is greater than that obtained by Walker and Lumsden (36 per cent.) who dissolved the bromo-acid in the calculated quantity of dilute alkali before boiling with cyanide. The reason for the lower yield in the latter case is to be found in the instability of the bromo-acid to alkalis.

The pure acid was found to melt at 129° (corr.).

Ethyl Decanedicarboxylate. \( \text{EtOOC} \cdot \left( \text{CH}_2 \right)_{10} \cdot \text{COOEt} \).

The acid was esterified by the Fischer-Speier method, giving an ester of m.-pt. 15° and b.-pt. 204-205 at 15 mm. Found \( C = 67.01, H = 10.60; \) \( C_{16}H_{30}O_4 \) requires \( C = 67.06, H = 10.56 \) per cent.

Electrolysis. This operation was conducted in a beaker, the electrodes consisting of a flat spiral of thick platinum wire (anode) and a sheet of platinum foil (cathode), with a flat spiral cooling coil of glass sandwiched between them. This apparatus
was found to be more convenient than any other, in that it cooled the electrolyte in the region where heat is generated, i.e. between the electrodes. Application of cooling to the outside of a beaker or platinum crucible was found to be impracticable for soapy solutions, as these solidified on the cold surface and prevented further cooling. Moreover, the degree of cooling could be very conveniently regulated by varying the flow of water in the coil, thus enabling the optimum temperature to be maintained throughout the electrolysis.

The sodium ethyl salt, obtained by half-saponification of the di-ester in the usual way, was electrolysed in aqueous alcoholic solution (55 c.c. contained 16 grams of the salt and 5 c.c. of alcohol) at a temperature of 50-55°, a current of 3-4 amperes being passed for two hours. An oily layer settled on the surface of the liquid, and was taken up in ether, washed, and dried.

From a total of 49 grams of ethyl decanedicarboxylate, 27 grams of a solid product was obtained, which was recrystallised from petroleum ether. After a further recrystallisation from the same solvent, 15 grams of pure \text{ethyl eicosanedicarboxylate}, \text{EtOOC} \cdot (\text{CH}_2)_8 \cdot \text{COOEt}, of m.-pt. 56°, remained, representing 41 per cent of the possible yield. Found C = 73.21, H = 11.72; \text{C}_{26} \text{H}_{50} \text{O}_4 requires C = 73.18, H = 11.81 per cent.
Saponification of this ester with alcoholic potash gave the potassium salt of eicosanedicarboxylic acid. Found K = 17.6; C_{11}H_{20}O_{4}K requires K = 17.5 per cent. Eicosanedicarboxylic acid, HOOC.(CH_{2})_{20}.COOH, was precipitated from an aqueous solution of the potassium salt on acidification. It was purified by several recrystallisations from chloroform, and then melted at 123.75° (corr.).

SYNTHESIS OF TETRACOSANEDICARBOXYLIC ACID.

Ethyl dodecanedicarboxylate, EtOOC.(CH_{2})_{12}.COOEt, was first prepared by electrolysis of sodium ethyl suberate (yield 63 grams from 160 grams of suberic acid). A portion of this was saponified, and the acid purified by crystallising alternately from water and chloroform until there was no further rise in m.-pt. This was 126.5° (corr.).

Electrolysis. To 40 c.c. of an aqueous solution containing 10 grams of sodium ethyl dodecanedicarboxylate, alcohol (5 c.c.) was added, and the electrolysis carried out at a temperature of 55-60°. 50 grams of ethyl dodecanedicarboxylate yielded in this way 15 grams of a solid product, from which 2 grams of ethyl tetracosanedicarboxylate, EtOOC.(CH_{2})_{24}.COOEt, were isolated by crystallisation from petroleum ether. Its m.-pt. was 66°. Found C = 74.50, H = 12.23; C_{20}H_{38}O_{4} requires C = 74.63, H = 12.13 per cent.

Saponification followed by acidification of the
aqueous solution of the salt gave tetracosanedi-
carboxylic acid, \( \text{HOOC.(CH}_2\text{)}_{24}\text{.COOH} \). After purifica-
tion by recrystallising from chloroform, this melted
at 123.5 (corr.). Found \( C = 73.10, H = 11.86; \)
\( C_{28}H_{50}O_4 \) requires \( C = 73.19, H = 11.82 \) per cent.

**SYNTHESIS OF OCTACOSANEDICARBOXYLIC ACID.**

Ethyl tetradecanedicarboxylate, \( \text{EtOOC.(CH}_2\text{)}_{14}\text{.COOEt} \),
the starting point for this synthesis, was prepared
by electrolysis of sodium ethyl azelate. A pure
specimen of tetradecanedicarboxylic acid was found
to melt at 125° (corr.).

A solution of sodium ethyl tetradecanedicarboxyl-
ate containing 10 grams in 45 c.c. was electrolysed
with the addition of 5 c.c. of alcohol at a
temperature of 60-65°, a current of 2-3 amperes being
passed for three hours. 50 grams of ethyl tetra-
decanedicarboxylate yielded 20 grams of electrolytic
product, which was taken up in ether and dried.

Ethyl Octacosanedicarboxylate, \( \text{EtOOC.(CH}_2\text{)}_{28}\text{.COOEt} \),
crystallised out after some of the ether had been
removed. This was recrystallised from petroleum
ether, and then weighed 2 grams and melted at 74°.
Found \( C = 75.68, H = 12.40; \) \( C_{28}H_{60}O_4 \) requires
\( C = 75.77, H = 12.34 \) per cent.

Saponification with alcoholic potash gave the
potassium salt, from whose aqueous solution
octacosanedicarboxylic acid, \( \text{HOOC.(CH}_2\text{)}_{28}\text{.COOH} \),
was precipitated on acidification. After purification
this melted at 123.25°. Found C = 74.60, H = 12.25; 
C_{20}H_{38}O_4 requires C = 75.77, H = 12.34 per cent.

SYNTHESIS OF DOTRIACONTANEDICARBOXYLIC ACID.

Diethyl hexadecanedicarboxylate was obtained by electrolysis of sodium ethyl sebacate, and was half-saponified with sodium hydroxide in cold dilute alcoholic solution, an operation requiring great care if the formation of a preponderance of disodium salt is to be avoided. A complication is introduced by the low solubility of this ester in cold alcohol (2.4 grams at 15°, and less than 1 gram at 5° per 100 c.c.). A solution of 30 grams in 3 litres of rectified spirits was cooled to 5°, and sufficient alcoholic sodium hydroxide added to half-saponify only 20 grams. The temperature was kept at 5° for three days, and then at 10-15° for a week, after which time neutrality was reached. The disodium salt (5 grams) was filtered off, and the sodium ethyl salt isolated in the usual way.

Hydrogen Ethyl Hexadecanedicarboxylate, EtOOCC(CH_{16})_6-COOH. The acid was precipitated from a solution of the sodium salt on addition of hydrochloric acid. It was purified by several recrystallisations from aqueous methyl alcohol, and was found to melt at 71°. The silver salt was prepared and analysed. Found Ag = 23.82; C_{20}H_{37}O_4Ag requires Ag = 24.00 per cent.
Electrolysis. A solution of 10 grams of the sodium salt in 45 c.c. of water with the addition of 5 c.c. of alcohol, was electrolysed at 70-75° for 3 hours with a current of 2-3 amperes. Water and alcohol were added from time to time to replace loss by evaporation.

The oil which had collected on the surface of the liquid set to a white solid (2.5 grams) on cooling. This was separated from the soap which, however, retained a further quantity (2.5 grams) of product in solution. It was extracted by evaporating to complete dryness, powdering, and treating with ether in a Soxhlet apparatus.

The dried solid ester melted at 62°, and of this 20 grams was collected. A separation into two portions was effected by taking advantage of the smaller solubility in ether of one constituent.

1. Melting point, 30-35°; weight 15 grams. This was not unsaturated, and appeared to be a mixture: its nature was not determined.

2. Melting point 80° (corr.); weight 5 grams. A molecular weight determination by Rast's camphor method gave a value of 610, showing that this was the expected synthetic ester (m.w. 595). Found C = 76.55, H = 12.58; \( C_{38}H_{74}O_{14} \) requires C = 76.70, H = 12.55 per cent. Ethyl dotriacontanedicarboxylate,

\( \text{EtOOC.} \text{CH}_{19-31} \text{COOEt} \), is sparingly soluble in cold alcohol, petroleum ether, and also in ether, from which it crystallises in microscopic rhombohedral
plates.

The ester was saponified by boiling with alcoholic potash, the potassium salt separating out after a short time. It is soluble in water, giving a soapy solution. Found K = 12.5; C_{34}H_{64}O_{4} requires 12.7 per cent.

The acid separates out when an aqueous solution of the potassium salt is saturated with carbon dioxide. It is insoluble in water, and only very sparingly so in most of the organic solvents. When recrystallised from chloroform, it appears as a white crystalline powder melting sharply at 123\(^\circ\text{corr.}\).

BY-PRODUCTS OF ELECTROLYSIS.

Undecenoic Acid, CH\(_2\)=CH.(CH\(_2\))\(_8\).COOH. From the mother liquors after crystallisation of ethyl eicosanedicarboxylate an ester was isolated which, on saponification, gave an acid of b.-pt. 160-170 at 15 mm. This was unsaturated and set to a white crystalline mass when cooled in ice. Hydrogen bromide gave a bromo-acid identical with \(\omega\)-bromundecenoic acid. A further portion was treated with bromine in chloroform solution, and the dibromo-compound (2.6 grams) boiled with aqueous caustic soda for one hour. The solution was then diluted considerably, cooled to 0\(^\circ\), and a solution of potassium permanganate (3.2 grams) added gradually. When oxidation was complete, the solution was decolorised with sulphur dioxide, evaporated to small bulk, and extracted with ether.
On removal of the ether a solid acid remained which was recrystallised from chloroform. Its m.-pt. was 132° (sebacic acid 133°). 0.1581 gram required 15.54 c.c. of N/10 alkali for neutralisation. Calculated for sebacic acid 15.65 c.c. The unsaturated acid was therefore undecenonic acid.

n-Heptenecarboxylic Acid, \( \text{CH}_2=\text{CH}.(\text{CH}_2)_5.\text{COOH} \).

An unsaturated ester of b.-pt. 200-220° was found in the mixture from electrolysis of sodium ethyl azelate. This was saponified, and the resulting acid fractionated under reduced pressure. It was found to boil at 123-125° at 15 mm. Found C = 68.04, H = 9.36; \( \text{C}_8\text{H}_{14}\text{O}_2 \) requires C = 68.04, H = 9.29 per cent.

On oxidation by the method described above, it yielded, besides a little adipic acid, an acid of m.-pt. 105°. 0.1306 gram of this required 16.34 c.c. of N/10 alkali for neutralisation. Pimelic acid melts at 105°, and the calculated volume of alkali required for the same weight is 16.31 c.c.

n-Hexenecarboxylic Acid, \( \text{CH}_2=\text{CH}.(\text{CH}_2)_4.\text{COOH} \).

From the product of electrolysis of sodium ethyl suberate, an unsaturated ester of boiling point 190° was isolated. This proved to be \( \text{ethyl n-hexenecarboxylate} \), \( \text{CH}_2=\text{CH}.(\text{CH}_2)_4.\text{COOEt} \). Found C = 69.00, H = 10.42; \( \text{C}_7\text{H}_{12}\text{O}_2 \) requires C = 69.16, H = 10.33 per cent. Saponification and acidification of the resulting salt yielded n-hexenecarboxylic acid of b.-pt. 224-226°.

A saturated dibasic acid of m.-pt. 149 was obtain-
ed by oxidation (adipic acid 150°). 0.1081 gram of this
required 14.95 c.c. of N/10 alkali for neutralisation;
calculated for adipic acid 14.79 c.c.
THE MELTING POINTS OF THE NORMAL SATURATED DIBASIC ACIDS.

The series of normal saturated dibasic acids has long attracted attention as furnishing a remarkable example of alternation in certain properties between the odd and even members. This effect is most pronounced in the melting points of the acids: when these are plotted against the number of methylene groups in the chain, two smooth curves are obtained, one for the odd and one for the even members. A similar alternation is observed also in other homologous series, e.g. the monobasic fatty acids, whose melting points rise steadily as the series ascends; the two curves lie close to each other, being separated by only a few degrees. In the series of dibasic acids, however, the odd acids lie upon an ascending curve, whereas the even ones lie upon a descending curve, i.e. the even acids have the unique property of continually decreasing melting point with increasing molecular weight.

It has not hitherto been possible to determine with certainty whether or not the two curves cut each other, as the highest member of the even series previously available was hexadecanedicarboxylic acid, and many of the melting points were not determined with sufficient accuracy.*

Following is a list of the melting points of the even dibasic acids, \((\text{CH}_2)_n(\text{COOH})_2\).

<table>
<thead>
<tr>
<th>Acid.</th>
<th>n.</th>
<th>m.-pt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Succinic</td>
<td>2</td>
<td>189°</td>
</tr>
<tr>
<td>Adipic</td>
<td>4</td>
<td>153°</td>
</tr>
<tr>
<td>Suberic</td>
<td>6</td>
<td>140°</td>
</tr>
<tr>
<td>Sebacic</td>
<td>8</td>
<td>133°</td>
</tr>
<tr>
<td>Decanedicarboxylic</td>
<td>10</td>
<td>129°(127°)</td>
</tr>
<tr>
<td>Dodecanedicarboxylic</td>
<td>12</td>
<td>126.5°(123°)</td>
</tr>
<tr>
<td>Tetradecanedicarboxylic</td>
<td>14</td>
<td>125°(124°)</td>
</tr>
<tr>
<td>Hexadecanedicarboxylic</td>
<td>16</td>
<td>124°(118°)</td>
</tr>
<tr>
<td>Eicosanedicarboxylic</td>
<td>20</td>
<td>123.75°</td>
</tr>
<tr>
<td>Tetracosanedicarboxylic</td>
<td>24</td>
<td>123.5°</td>
</tr>
<tr>
<td>Octacosanedicarboxylic</td>
<td>28</td>
<td>123.25°</td>
</tr>
<tr>
<td>Dotriacontanedicarboxylic</td>
<td>32</td>
<td>123°</td>
</tr>
</tbody>
</table>

With the exception of the first four, whose melting points may be taken as sufficiently well established, all these acids were prepared by the author in a specially pure state. The figures in brackets are the melting points formerly attributed to these acids. In all cases the acids were purified by recrystallisation from suitable solvents (chloroform or ethyl acetate) until no further rise in melting point was observed. A standardised thermometer was used, and a correction for emergent stem applied, giving an error of less than 0.25°.

In the diagram (Fig.1), the melting points have
Melting points of the dibasic acids: \(-I\) even; \(-II\) odd.

Vertical - melting point in degrees centigrade;
Horizontal - number of methylene groups.
been plotted against the number of methylene groups in the chain (I). The corresponding curve for the odd series is also given (II). The remarkable way in which curve flattens out after the point \( n = 16 \) has been reached is at once noticeable; there is, indeed, a difference of only one degree in the melting point due to the subsequent doubling of the hydrocarbon chain.

It has been observed that the most pronounced cases of alternation in homologous series occur (1) where there is a terminal polar group such as carboxyl, and (2) in properties involving the substances in the crystalline state, such as melting points, heats of crystallisation, solubilities, and molecular volumes.* It is therefore probable that the explanation of such alternation is to be found in the crystal structure of the substances.

In the di-esters of the dibasic acids there is no terminal polar group, and the melting points show no alternation whatever: they rise in quite a normal manner as the series is ascended, odd and even members alike lying on one and the same smooth curve (Fig. 2).

Following is a list of the melting points of the di-ethyl esters of the dibasic acids, \((\text{CH}_2)_n\cdot(\text{COOEt})_2\).

Fig. 2.

Melting points of ethyl esters of the dibasic acids.
Vertical - melting point in degrees centigrade;
horizontal - number of methylene groups.
<table>
<thead>
<tr>
<th>Ester.</th>
<th>n</th>
<th>m.-pt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azelaic</td>
<td>7</td>
<td>-16°</td>
</tr>
<tr>
<td>Sebacic</td>
<td>8</td>
<td>-1°</td>
</tr>
<tr>
<td>Decanedicarboxylic</td>
<td>10</td>
<td>15°</td>
</tr>
<tr>
<td>Undecanedicarboxylic</td>
<td>11</td>
<td>20°</td>
</tr>
<tr>
<td>Dodecanedicarboxylic</td>
<td>12</td>
<td>27°</td>
</tr>
<tr>
<td>Hexadecanedicarboxylic</td>
<td>16</td>
<td>43°</td>
</tr>
<tr>
<td>Nonadecanedicarboxylic</td>
<td>19</td>
<td>52°</td>
</tr>
<tr>
<td>Eicosanedicarboxylic</td>
<td>20</td>
<td>56°</td>
</tr>
<tr>
<td>Tetracosanedicarboxylic</td>
<td>24</td>
<td>66°</td>
</tr>
<tr>
<td>Octacosanedicarboxylic</td>
<td>28</td>
<td>74°</td>
</tr>
<tr>
<td>Dotriacontanedicarboxylic</td>
<td>32</td>
<td>80°</td>
</tr>
</tbody>
</table>

The melting point given in the literature for diethyl sebacate (-4-5°) dated from 1876*, and it was therefore thought advisable to verify it; no figure was available for diethyl azelate. Specimens of these two esters were accordingly prepared from the pure acids, and fractionated under reduced pressure. They were found to melt at -1° and -16° respectively. The esters of decane- and undecanedicarboxylic acids were similarly prepared and purified. The esters of eicosane-, tetracosane-, and octacosanedicarboxylic acids were purified by recrystallisation from petroleum ether, and that of dotriacontanedicarboxylic acid from ether.

In order to explain the fact that malonic and

glutaric acids give addition compounds with trans-chlorodiethylenediamine cobaltic chloride whereas oxalic, succinic, and adipic acids do not. Price and Brazier* have advanced the theory that the odd and even acids have different stereochemical structure, assigning the cis configuration to the odd acids and the trans to the even. Theories of this or similar nature, while perhaps offering an explanation of the existence of separate melting point curves for the odd and even acids, by no means account for the lowering of melting point with increase in molecular weight in the even series. We are led, in fact, to look for some peculiarity in the even series itself which does not exist in the odd or in any other known series.

The melting point of a crystalline solid may be regarded as being largely determined by the magnitude of the forces of cohesion within the crystal.† It has been shown that long chain compounds (hydrocarbons, fatty acids and their esters etc.) have a tendency to arrange themselves side by side as in the monomolecular films obtained by Langmuir and by Adam, especially when pressed flat, the solid substance consisting of a large number of such layers superimposed upon one another.‡ The flakiness and greasiness of such compounds has been accounted for on this

‡ Muller & Shearer, Journ. Chem. Soc., 1923, 3156.
Muller & Saville, ibid., 1925, 599.
basis as being due to these layers slipping over one another. Each layer of a compound having no terminal polar group has been found to be one molecule thick, but in the case of the fatty acids it is two molecules thick, the carboxyls being attracted to one another and lying in juxtaposition.

The half esters of the higher dibasic acids (e.g. hydrogen ethyl hexadecanedicarboxylate) closely resemble the fatty acids (e.g. stearic acid) in their flakiness and greasiness, the two substances instanced being indistinguishable in these respects. The higher dibasic acids themselves, however, do not exhibit these properties in spite of their long hydrocarbon chains, but, on the contrary, are quite hard and brittle. Moreover there is no reason to suppose that their chains are in any way different with respect to spatial arrangement from those of other chain compounds. This would seem to indicate that each is attached firmly at either end to the carboxyls of its neighbouring molecules. The major forces of cohesion which influence the melting point would thus be those between the carboxyl groups.

The phenomenon under discussion would appear to be conditioned (1) by the presence of terminal carboxyl groups and (2) by the presence of a chain containing an even number of carbon atoms between them, and may be explained by assuming that the

carboxyl groups exert some influence upon each other through the intervening chain. The nature of this influence, moreover, must be such that its transmission through an odd number of carbon atoms entirely alters its character.

As has been pointed out by Challenor and Thorpe, who were seeking an explanation of the greater chemical reactivity of the odd dibasic acids, the even acids have crossed polarities, i.e. the alternate positive and negative charges induced from the carboxyls at either end on each carbon atom of the chain, tend to neutralise each other, whereas in the odd series they tend to reinforce each other. In the odd series, therefore, the mutual attraction of the carboxyl groups may be diminished by the presence of like charges upon them, in which case their melting points would be lower than those in the even series. On this assumption the decrease in melting point as the even series is ascended may be explained by the fact that as the chain is lengthened, the transmission of the alternate polarity effect is progressively weakened, and the terminal carboxyl carbons become gradually free from the influence of the carboxyl group at the other end of the chain. If this view were correct, it would be expected that when the chain became very long, there would be little or no difference between the melting points of consecutive

odd and even acids. That this is indeed the case is very strikingly demonstrated in Fig. 1, in which the two curves appear to approach each other asymptotically.

It has not so far been proved that the alternate polarity effect persists over a number of carbon atoms in a chain united by single bonds, but it is possible that the cohesional forces in the crystals as measured by the melting points constitute a more delicate means of detection of such an effect than has hitherto been used.
Summary of Part 2.

(1) Four new dibasic acids have been electrosynthesized, namely, eicosanedicarboxylic acid, HOOC\left(CH\sub{2}\right)_{18}COOH; tetracosanedicarboxylic acid, HOOC\left(CH\sub{2}\right)_{24}COOH; octacosanedicarboxylic acid, HOOC\left(CH\sub{2}\right)_{30}COOH; and dotriacontanedicarboxylic acid, HOOC\left(CH\sub{2}\right)_{32}COOH.

(2) Some of the unsaturated by-products of electrolysis have been investigated.

(3) The melting points of decanedicarboxylic acid, dodecanedicarboxylic acid, tetradecanedicarboxylic acid, and hexadecanedicarboxylic acid have been revised.

(4) A suggested explanation of the decrease in melting point as the series of even dibasic acids is ascended has been given in terms of the crystal structure of these acids.