

The ELECTROLYSIS of FUSED ACETATES
and PROPIONATES.

THESIS
for
Degree of Ph.D.

presented by

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University of Edinburgh,

September, 1931.



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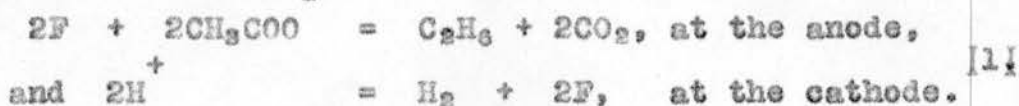
INTRODUCTION.

The electrolysis of fused salts is a field which has been little explored. The electrolysis of acetates in aqueous solution, on the other hand, has been studied by many workers, and ever since the discovery by Kolbe, ^[1] in 1849, that ethane was synthesised at the anode the mechanism of the synthesis has been disputed.

The significance of the present research lies as much in its bearing on this problem as in its intrinsic interest. An account will therefore be given of the reaction in solution and the experiments designed to distinguish between the alternative mechanisms, before passing to electrolysis in the fused state.

The Reaction in Solution.

The formation of ethane by electrolysis of an acetate solution is the simplest case of a Kolbe reaction. The net process is:-

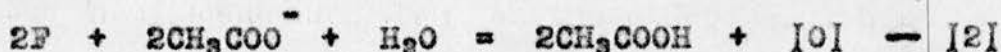


If no other reaction occurs then the ratio $[C_2H_6]:[H_2]$ should be unity, and $[CO_2]$ should equal $2[C_2H_6]$.

This was never the case in practice. The discrepancy]

discrepancy was explained by the occurrence of two side-reactions.

[1] Evolution of oxygen at the anode, most probably by interaction of acetate ions with water:-



[2] The complete oxidation either of acetate ions or of acetic acid by oxygen evolved as in equation [2], according to



assuming that it is the discharged ions that are oxidised.

There are thus three anode reactions, each corresponding to a definite amount of cathode Hydrogen. The total cathode hydrogen is the sum of the hydrogen equivalent to the three processes, i.e.

$$[H_2] = [C_2H_6] + 2[O_2] + 2[CO_2] - 2[C_2H_6]$$

or

$$[C_2H_6] = \frac{2[CO_2] + 2[O_2] - [H_2]}{3} \quad \text{--- [4]}$$

The same equation results from the assumption that it is acetic acid that is oxidised.

On account of the difficulty of determining the carbon dioxide this relation has never been quantitatively tested. Qualitatively, however, it has been shewn that a variable amount of oxygen is evolved and that $[CO_2]$ is greater than $2[C_2H_6]$.

The equation [1] represents the net result of

of the anode process. According to one school it also represents the mechanism; i.e. ethane is a primary product formed by the interaction of two discharged ions. This "Discharged Ion Theory", as it is called, was first advanced by Crum Brown and Walker^[2] and has since been supported by Murray,^[3] Hamonet,^[4] Preuner and Ludlam,^[5] and Fairweather and Walker.^[6]

The rival theory, the "Oxidation Theory", holds that the synthesis proceeds in two stages:-



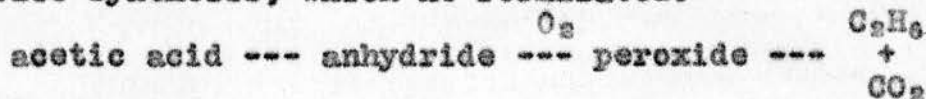
i.e. that ethane is derived from a secondary reaction. The primary reaction, which is identical with equation [2], is often called the "Faraday reaction".

This theory was the original one advanced by Kolbe.^[7] It has been supported by Bunge,^[8] Schall,^[9] Gibson,^[10] Robertson,^[11] Foerster and Piguet,^[12] and especially by Fichter and his co-workers.

The names "Discharged Ion" and "Oxidation" are to a certain extent misleading since on either theory discharge of ions is a necessity. Also the discharge of an ion is itself oxidation in the widest sense of the term. But it is not therefore justifiable to say, as Fichter does, that there is no difference between the theories. The difference may not be as deep as was at one time thought, but it still exists. The crucial point is whether the reaction of equation [5] actually occurs.

According to Fichter the secondary reaction is itself complex and proceeds by way of peroxide and peracid formation. This peroxide theory is based on the generalisation that the products of an electrochemical reaction can always be obtained from a purely chemical reaction, and that the mechanism is therefore the same in the two reactions. Peracids, for example, can be obtained either electrolytically or by oxidation with hydrogen peroxide. According to Fichter this shews that the electrolytic formation is an oxidation by Faraday oxygen.

[13] Schutzenberger had shewn that ethane could be obtained from acetic anhydride and later [18] Schall had shewn that acetyl peroxide was intermediate in this reaction. Fichter therefore concluded that this must also be the mechanism of the Kolbe synthesis, which he formulated:-



Subsequently he withdrew the claim that acetic anhydride was an intermediate.

Isolation of acetyl peroxide from the electrolyte has been attempted, but never successfully; this is ascribed to its high instability.

To test the theory Fichter exploded the peroxide. The products were hydrocarbon and carbon dioxide, but the hydrocarbon contained more methane than ethane. An explosion, however, can hardly reproduce[

reproduce electrolytic conditions and Fichter explains away the methane as due to "pyrogenic splitting".

The peroxide was decomposed other than explosively by Walker,^[14] in aqueous and alcoholic solution as well as in the pure form. The product was variable; but with one exception much more methane than ethane was formed. The exception was when decomposition was effected by ultra-violet light; here only 14—20% of the hydrocarbon was methane.

The absence of methane from the anode gas was the strongest objection to the peroxide theory. Recently Shukla and Walker^[15] have obtained methane at the anode when the current density is very small. It may even become the chief hydrocarbon product under these conditions. It is probable that a small amount of methane - up to 2% of the hydrocarbon - is always present under normal conditions of current density. This removes the chief objection to the peroxide theory; on the other hand, the conditions under which it is obtained are precisely those in which, according to Fichter, it should be absent. Pyrogenic splitting can hardly occur at current densities of 3 milliamps per square cm.

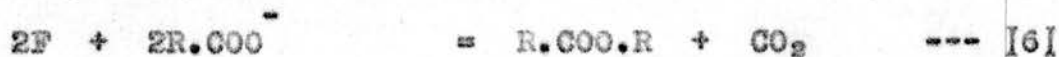
The formula of acetyl peroxide,

$$\begin{array}{c} \text{CH}_3\text{COO} \\ | \\ \text{CH}_3\text{COO} \end{array}$$
 shows that it can equally well be regarded as formed by the union of two discharged ions. Indeed it is very likely that some, at least, of the discharged ions]

ions do momentarily join up in this way. But this is not to say that their joining is a necessary condition for the reaction to continue. The peroxide theory is, therefore, not necessarily an oxidation theory.

[16]
Fichter, supporting the theory of peroxide formation by direct oxidation, bases his argument on the high oxidising power of a platinum anode -- "A platinum anode has the highest oxidising power.... why should this vanish in the presence of sodium acetate?" Yet in the same paper he records successful synthesis at graphite anodes, which have no such oxidising power. There are other inconsistencies. The temperature effect is claimed to support the peroxide theory:- "the formation of an intermediate requires suitable cooling". Yet secondary decomposition of the peroxide to ethane is attributed to high local temperature at the anode. It is difficult to see how low temperature for the formation, and high temperature for the decomposition of a peroxide can co-exist at the same electrode surface.

The formation of saturated hydrocarbons is not the only reaction which may occur at the anode. Esters and alcohols may also be formed, the latter in weakly alkaline solution.



While]

While with higher acids unsaturated hydrocarbons are obtained. Propionates, for example, give ethylene:-



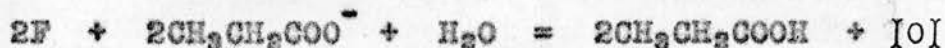
Traces of ethylene have been claimed by Petersen [17]

to be formed from acetates by the reaction



for which the corresponding reaction with propionates would be propylene formation.

All these reactions have been written for convenience in the briefer "Discharged Ion" form, but in each case an alternative equation, which expresses the reaction as oxidation of an acid, may be written. Equation [8], e.g., becomes



Although it is natural to assume that these reactions are either all oxidations or all discharged ion reactions, this is not necessarily true. Each reaction ought to be considered on its merits.

Much more work has been done on ethane formation than on the other reactions. The following facts have been established:-

1. The best synthesis is got with polished platinum or iridium anodes. Graphite anodes give a moderate synthesis but no synthesis is got with platinised platinum or with gold anodes.

2. The ethane yield decreases as the dilution increases.

3. The ethane yield decreased as current density decreases.

4. The ethane yield decreases as the temperature rises, and falls off to zero at 100° C.

5. A critical potential exists below which ethane is not synthesised.

These facts can be explained, though not always with the same facility, by either theory. The specificity of the anode, for example, is connected with its oxygen overvoltage by the Oxidation Theory, according to which oxygen must be evolved at a high potential for oxidation to ethane. The Discharged Ion Theory explains it as a velocity of reaction effect—platinised platinum is supposed to catalyse the Faraday reaction to such an extent that the ions never reach sufficient concentration to react.

Experiments to distinguish between the theories have been on two lines. In one type of experiment conditions are arranged to favour oxidation and discourage union of discharged ions. The other type favours discharged ions reacting and discourages oxidation.

Experiments encouraging oxidation.

The formation of ethane by oxidation of acetates does not necessarily mean that the Oxidation Theory is correct. It is oxidation in the special sense according to



which]

which is the point at issue. The action of fluorine on acetates, which has been investigated by Fichter and Humpert,^[29] cannot be regarded as a test of this equation since it can just as easily be written as an ionic reaction -



comparable with the displacement of chlorine by fluorine as an oxidation of acetic acid. In fact the ionic form is the more natural, since no acetic acid was originally present. A better test would have been the action of fluorine on acetic acid, where ionisation is small.

Similar remarks apply to Gordon's^[30] production of ethane by action of persulphate on acetate solutions. It can be formulated:-



The only real test is the action of anodic oxygen on acetic acid.

According to the Oxidation Theory unionised acetic acid is acting as an oxygen depolariser. The source of the oxygen should be a matter of indifference. When a solution containing both acetic acid and sulphuric acid is electrolysed there are very few acetate ions present, for ionisation of the weak acetic acid, already small, is further depressed by the strong acid. On the other hand, ample oxygen is available for oxidation of the unionised acetic acid.

Murray]

[13] Murray electrolysed a solution 2N. with respect to both acids. No hydrocarbon was developed at the anode and only a small amount of carbon dioxide.

[18] Schreiner, also working with 2N. sulphuric, has investigated the anodic oxidation of acetic acid thoroughly. He records a small amount of carbon monoxide and carbon dioxide, some formation of glycollic and glyoxalic acids but no hydrocarbon. Moreover, he electrolysed all the possible intermediates in the progressive oxidation of acetic acid to carbon dioxide. In no case was hydrocarbon found.

[16] Fairweather and Walker shewed that only a very small amount of sulphuric acid was necessary to cut off the Kolbe reaction. The ethane yield was normal in presence of .0018N. H_2SO_4 and zero in the presence of .0025N. H_2SO_4 . This critical concentration was identified by them with a critical concentration of acetate ions.

These results can only be explained by the Oxidation Theory on the assumption that the acetic acid to be oxidised to ethane must be "nascent" at the electrode surface. Foerster and Piguet's [11] theory of formation of films of acetic acid of finite thickness seems to be discredited by Murray's and by Schreiner's results. This is not "nascent" acetic acid.

Experiments I

Experiments to exclude oxidation.

The anode oxygen is intimately connected with the presence of water, for it can only arise by the Faraday reaction. This suggests electrolysis in non-aqueous solvents or in the fused state.

Electrolysis in acetic acid solution.

Hopfgartner¹¹⁹¹ electrolysed acetates in anhydrous acetic acid. The products were very similar to those obtained from aqueous solution. The ethane yields were rather better. He determined the carbon dioxide as well as the hydrocarbon. The percentage composition of the gas in a typical electrolysis is given in Table 1.

Table 1. Pot. acetate in acetic acid.

Electrolysis of 2.8% sol. at 15° C.:c.d.= .0014 amp cm².

O ₂	C ₂ H ₄	CO ₂	C ₂ H ₆	Cath. H ₂	$\frac{C_2H_6}{H_2}$	Excess CO ₂	Excess H ₂
0.1	0.5	67.5	31.9	37.7	0.85	2.7	4.8

The results of the last two columns are obtained by subtracting from the "CO₂" and "Cathode H₂" amounts equivalent]

equivalent to formation of ethane according to equation [1], and of ethylene according to equation [9]. The values in the last columns do not differ greatly - generally the agreement was rather better than in the example recorded. They would be exactly equal if ester formation according to equation [6] were responsible for their existence. Hopfgartner showed that ester was formed.

Here then we have all the products of the Kolbe reaction without any Faraday reaction to yield oxygen.

Electrolysis in methyl alcohol solution.

Electrolysis with methyl alcohol as solvent was carried out by Salauze.^[20] He did not determine the carbon dioxide and only determined the ethane indirectly by subtracting the voltameter hydrogen from the total gas after removal of carbon dioxide. The difference between hydrogen and ethane Salauze ascribed to ester formation. Yields as high as 98% of ethane were obtained. The method of analysis is, however, open to the criticism of not being positive enough.

Neither Hopfgartner nor Salauze record any methane, but it is possible that small amounts may have been present and escaped their notice. Hopfgartner flashed his ethane and hydrogen together: Salauze did not flash his at all.

Electrolysis[

Electrolysis of fused acetates.

Were it not for the high temperature and the possibilities of side-reactions thus opened up, the fused state would be the ideal one in which to investigate the synthesis. There is no solvent to complicate matters, only ions and possibly undissociated molecules. An ethane synthesis under these conditions would be clear proof that discharged ions were capable of reacting together.

[21]
Lassar-Cohn, in 1889, electrolysed fused potassium acetate, collecting anode and cathode gases separately. He found 7 cc. of anode gas were equivalent to 38 cc. of cathode gas. The cathode gas consisted roughly of equal parts of methane and hydrogen. Only carbon dioxide was evolved at the anode.

[22]
Berle, in 1904, also working with potassium acetate at 320° C., got similar results. He did not separate his anode and cathode gases. The source of the cathodic methane is discussed by Berle who shewed that the interaction of liberated potassium metal with the melt was responsible for it.

[23]
To avoid this difficulty Petersen, ten years later, used the eutectic mixture of lead and zinc acetates. This gave a stable melt, although the single salts decomposed spontaneously at their melting points. He also electrolysed a mixture of lead and sodium acetates and a mixture of potassium acetate with]

with an equivalent amount of anhydrous acetic acid. There was no appreciable cathode evolution except in the last case, when hydrogen was liberated. The anode gas was complex. The results of some typical analyses are recorded in Tables 2, 3 and 4 in which is given the percentage composition of the gas after removal of carbon dioxide.

Table 2. $\text{PbAc}_2 + \text{ZnAc}_2$ at 170°C .

Anode Gas	C_2H_4	H_2	O_2	CO	CH_4	C_2H_6
Expt. 1.	2.1	28.9	1.0	29.0	25.6	13.4
2.	7.1	47.0	2.6	24.2	19.1	0.0
3.	11.2	16.8	2.3	26.6	42.7	0.4

Table 3. $\text{NaAc} + \text{PbAc}_2$ at 140°C .

Anode Gas	C_2H_4	H_2	O_2	CO	CH_4	C_2H_6
Expt. 1 1st hour	2.6	12.1	1.5	6.0	55.5	22.3
2nd hour	4.2	13.0	2.0	4.7	43.0	33.1
Expt. 2	1.3	15.0	2.1	9.0	11.9	60.7

Table]

Table 4.

 $\overline{\text{KHAco}}_2$ at 155° C.

Anode Gas	C_2H_4	H_2	O_2	CO	CH_4	C_2H_6
Expt. 1.	5.5	1.3	0.5	20.0	46.7	26.0
2.	31.5	3.6	4.2	9.4	21.8	29.5
3.	15.0	2.8	1.6	12.1	35.7	32.8

The feature of these results is their variability, not only in different experiments, but even in the course of the same experiment.

The chief difficulty is the danger of thermal decomposition. The variability of results indicates that this is occurring. In control experiments Petersen shewed that at the temperature employed there is no appreciable gas evolution by thermal decomposition; but during electrolysis high local temperatures at the anode surface may be reached.

In this connection it does not seem to have been realised that keeping the current small and so minimising current heating effects is just as important as keeping the temperature of the melt low. Berle even refers to the low conductivity of mixtures of acetates as a drawback, stating that this prevented him from using a sodium-potassium acetate mixture.

The anode gas is seen to differ considerably from

from that normally obtained in a Kolbe synthesis, especially in its large carbon monoxide, hydrogen and methane percentages. In view of the many signs of secondary decomposition it was considered worth while investigating the electrolysis further, taking special care to minimise these effects.

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THE ELECTROLYSIS OF FUSED ACETATES.

EXPERIMENTAL

Materials.

A ternary mixture of the acetates of lithium sodium and potassium was employed.

Lithium Acetate:- Precipitated lithium carbonate was washed repeatedly with water and finally with alcohol till soluble impurities were removed.

A solution of glacial acetic acid in water slightly in excess of the equivalent amount was added, and the carbon dioxide expelled by boiling.

Sodium Acetate:- Clean metallic sodium was dissolved in a minimum of methyl alcohol. A slight excess of acetic acid solution was added and the solution boiled.

Potassium Acetate:- Kahlbaum potassium carbonate was found to be sufficiently pure; the acetate was prepared from the carbonate in the same way as lithium acetate.

A series of small scale tests shewed that the most suitable molar proportions of the three constituents were

$$\text{Li} : \text{Na} : \text{K} = 7 : 10 : 10.$$

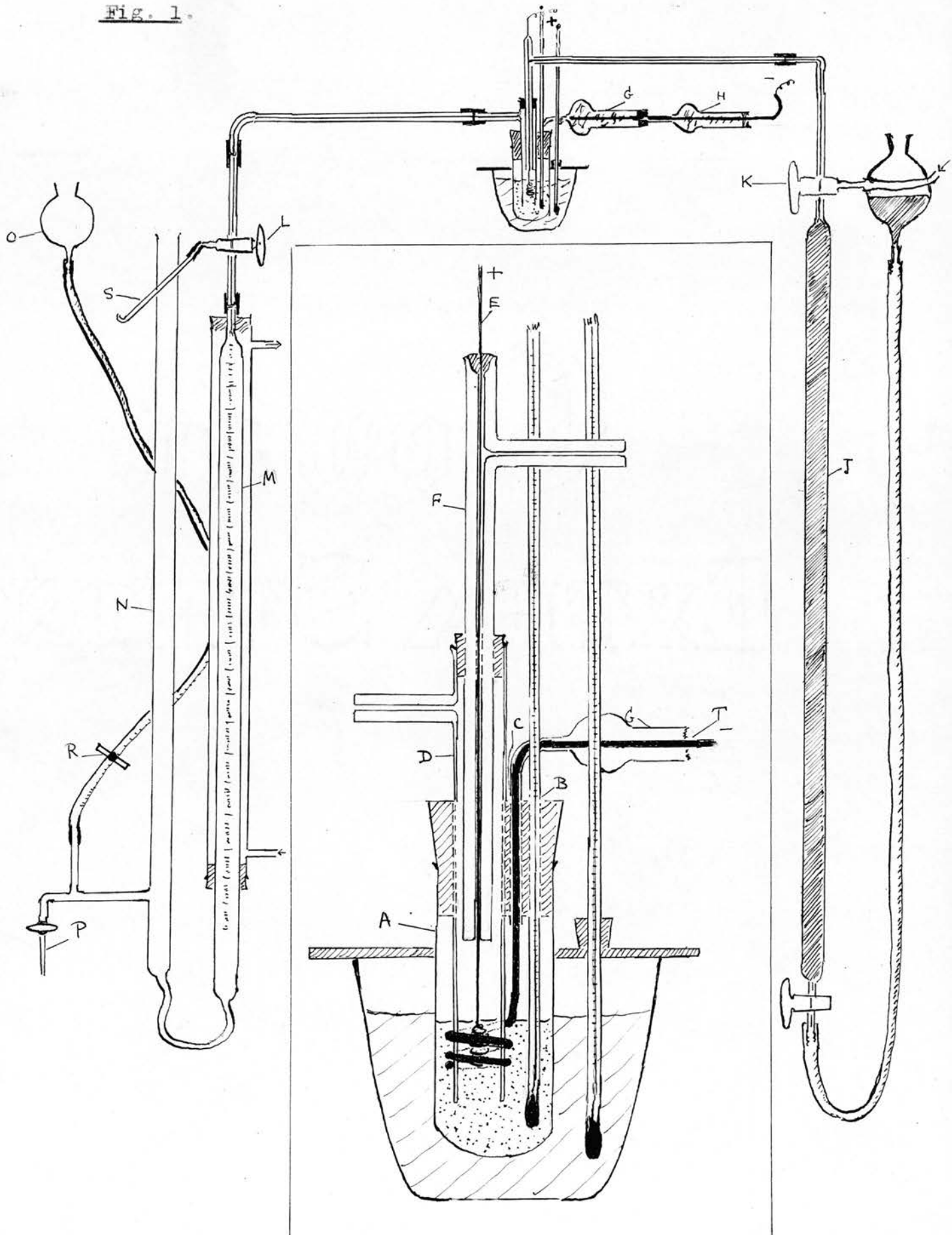
Such a mixture had a melting point of about 160° C.

A still lower melting point could be secured by using more]

more lithium acetate but the melt became exceedingly viscous. The precise ratios are of little importance. At different times three batches of stock solution were prepared, and although the molar ratios were somewhat different, no difference in the composition of the anode gas could be detected.

To prepare the melt a portion of the stock solution was simply evaporated down in a Pyrex test-tube. As heating bath a mixture of crude lithium, sodium, potassium acetates was used. Any excess acid and residual methyl alcohol was expelled along with the water, and the solution passed quite smoothly into the fused state. The approach of the fused state was indicated by sharp crackling as water refluxed down the side of the test-tube. Bubbling ceased at about 230°C . Heating was continued for some time longer till the temperature had risen to 280°C . The temperature was then allowed to drop to 230°C . and the melt put under the suction of a filter pump to remove any traces of water. A drying tube was interposed between the filter pump and the melt. With the application of suction the melt began to bubble again. The suction was gradually increased as the bubbling fell off. After about half an hour of this treatment, the melt became quite quiet and was normally clear and transparent. The separation of brown flakes noted by Berle^[22] did occur in isolated instances. When only a few of these were present]

Fig. 1.



present in a clear melt the electrolysis was continued and the results were indistinguishable from those with the normal melt.

If the melt was appreciably coloured it was discarded.

Apparatus for electrolysis.

The design of apparatus was kept as simple as possible to lessen the danger of the melt solidifying. At first, mercury at the bottom of a test-tube was tried as cathode, the anode being a flat spiral of platinum a centimetre above. But a certain amount of evolution of gas occurred at the mercury. It became clear that the electrodes must be separated. The apparatus finally adopted and used throughout is shewn in Fig. 1 and inset. [See page 19a]

The cell "A" was a shortened 1" test-tube fitting on to a rubber stopper bored with four holes. One of these "B" carried a thermometer, another "C" carried a tube through which the cathode wire was threaded and the third carried a tube "D" which served to separate anode from cathode. The fourth hole was normally plugged but might be used, for example, if it was desired to take a sample of the melt.

The anode "E", a length of polished platinum wire of guage 0.5 mm., was housed in a capillary tube "F" fitted into the tube "D".

The cathode "T", a piece of pure lead wire of gauge]

gauge 2.3 mm. was coiled round the outside of "D" and ascended through two drying tubes "G" and "H". The drying tubes were perhaps a needless precaution.

The capillary "F" had a side-tube which was connected to a carbon dioxide gas-holder "J". The carbon dioxide was led into the gas-holder from a cylinder through the 3-way tap "K".

The outer tube "D" also had a side-tube through which the anode gas emerged and passed down through the 3-way tap "L" into the collecting burette "M". "M" was a modified gas burette whose levelling-tube "N" bore a side-tube branching either to a reservoir "O" or to a drain-cock "P".

The method of collection of the gas was similar to that used in a Victor-Meyer molecular weight apparatus. As the gas was evolved the confining liquid was run off through "P" at such a rate that the levels in "M" and "N" remained the same. Water saturated with carbon dioxide was used as confining liquid.

The gas could be expelled through the extension of the 3-way tap "L" by opening the screw clip "R". A tube "S" could be fitted on to "L" for this purpose.

When electrolysis was proceeding a hydrogen voltameter was in series with the cell. A 50cc. burette inverted over a platinum cathode in dilute sulphuric[

sulphuric acid served for this purpose. Both the voltameter and the anode gas burette were calibrated. Voltameter readings were corrected for the pressure of the column of solution.

Conduct of Electrolysis. "J" was filled with mercury up to the tap and "M" was filled with CO₂-water. The melt, after the preliminary treatment already described, was transferred to the tube "A" which was then attached to the rubber stopper. A straight tube was attached to the extension of "L" and arranged just to dip beneath water. A gentle current of carbon dioxide was then passed from the cylinder till all the air above the anode was displaced. Meanwhile the voltameter solution was saturated with hydrogen by passing a small current, the cell, of course, being disconnected.

A supply of carbon dioxide was then stored in the gas-holder "J", after which the carbon dioxide was shut off and "K" and "L" put into communication with the cell. A few cc. of carbon dioxide were passed from "J" into "M". The levels in "M" and "N" were then equalised so that the levels of the melt inside and outside the anode tube must also be the same. The straight tube attached to "L" was replaced by a tube with upturned end and the few cc. of gas in "M" expelled. The temperature was adjusted to 200° C.

Electrolysis[

Electrolysis may now be begun. A 40 volt bank of accumulators was the source of emf. The actual voltage across the cell could be measured by a tapping voltmeter. After the current was switched on, readings were taken at definite intervals of the anode gas, voltameter hydrogen and voltage across cell. The ratio anode gas : hydrogen was calculated. Any change in composition of the anode gas would almost certainly result in a change in this ratio. As this ratio will constantly be referred to, the name "yield" will be applied to it. [For perfect synthesis yield = 3].

It was found necessary to interrupt the current at intervals if the yield was to be maintained. If no interruption were made the yield, at first about 2.5, began to decrease after a few minutes. The decrease continued until actually more hydrogen than anode gas was being evolved. Concurrently with this change the actual current passed, as measured by rate of hydrogen evolution, rose; the temperature also rose. Clearly there is little significance in an analysis of this gas. On the other hand, by interrupting the current after a minute's electrolysis and pausing for a minute, then another minute's electrolysis followed by a minute's pause, and so on, the yield could be maintained at or about its original value.

This[

This method of electrolysis was therefore always adopted. The exact duration of the intervals did not matter. After the electrolysis had been going for some time the current always fell off somewhat. In one experiment, e.g., it was at first 0.2 amps. and sank to 0.08 amps. With smaller currents longer intervals of electrolysis could be used without the yield decaying.

To collect the gas for analysis the levels in "N" and "M" were equalised and the temperature adjusted to the same value as that at the beginning of the experiment [200° C.]. The readings of the anode gas burette and the hydrogen burette were taken. The anode gas on the far side of the 3-way tap "L" was then displaced into "M" by passage of some 15cc. of carbon dioxide from "J". The taps "L" and "K" were closed. The cell is now in the same condition as at the beginning. All the electrolytic gas is in the burette "M" and its volume is given by the reading referred to.

The barometric pressure, the temperature of the water jacket of the anode gas burette, and the temperature of the hydrogen burette were read. The gas was then collected. If the gas was to be analysed immediately it was collected over water: otherwise mercury was used.

The actual readings for a typical run are given in the following table.

Table 5.Details of Electrolysis.

Run No. 8.

Melt at 200° C.

Bar. Pressure 742 mm.

Hydrogen " 19° C.

Voltage across cell 31-34 volts.

Anode gas " 19° C.

Particulars	Hydrogen	Anode gas	Interval in secs.	Current in amps.	Yield
Corrected burette readings	50.08	-0.2			
Actual burette readings	49.80		180	0.20	2.4
	45.5	10.0	360	0.14	2.4
	39.7	23.6	600	0.11	2.4
	32.4	40.7	720	0.08	2.4
	25.6	57.2			2.5
Final burette readings	21.10	68.3			
Corrected " "	21.83	68.14			
Volumes at 19° C., 726mm.	28.25	68.34			
Converted to pressures in Bourne-Hutt at 11° C., mark "0"	mm. 565	mm. 1367	Mean Yield		2.42

The melt was quite clear and colourless before electrolysis and until 50 cc. were collected, when it became opaque and darker.

In early experiments the electrolysis was stopped when

when this darkening began. It was later found that there was no need for this. No change in the composition of the anode gas coincident with the darkening could be detected.

The darkening is evidently not a fundamental decomposition of acetate. This was confirmed by pouring the almost black melt into water. Much less residue than one would suppose was left. Carbon was practically absent. The residue consisted of particles of lead and lead carbonate. After filtering off the residue, the filtrate could be worked up again to a melt. On two occasions such a recovered melt was electrolysed. The anode gas differed only slightly from that from the normal melt.

Acidity of melt.

During the course of several runs samples of the melt were taken at intervals, added to water and the acidity tested. It was found that the melt, at first neutral, became progressively more alkaline as the run proceeded. At the end of the run the melt was poured into water. The p_H of the resulting solution was about 10. This effect must be due to alkali metals not all being absorbed in the lead cathode. A certain amount of cathode evolution of gas was, in fact, always observed.

The question arises whether this was due to the kind of action of potassium on the melt observed by I

by Berle. Samples of the cathode gas were collected and found to be pure hydrogen. The absence of methane shews that no drastic decomposition of the melt is occurring. Hydrogen evolution may be due to a trace of water.

Thermal decomposition of the melt.

Control experiments.

The anode gas is presumably electrolytic in origin but it is possible that some thermal decomposition may be superimposed.

A control experiment was therefore done in which the conditions of electrolysis were reproduced as closely as possible except that no current was passed. The melt, prepared as for electrolysis, was confined in a test-tube whose stopper carried a thermometer, an inlet tube, an exit tube and a platinum spiral which dipped into the melt. Air was displaced by a gentle current of carbon dioxide. The temperature was maintained at $200 - 210^{\circ}\text{C}$. for three hours during which time a slow stream of carbon dioxide continued to pass and drove any evolved gas into a nitrometer charged with potash solution. Two tubes cooled, one by ice and the other by CO_2 -snow, were inserted between the exit tube and the nitrometer.

As the gas reached the nitrometer it was almost wholly quenched and only 2 cc. were collected in three hours. Analysis shewed that this consisted almost]

almost entirely of oxygen and nitrogen. Carbon monoxide and hydrogen were absent and an explosion with electrolytic gas added, yielded only 2.5 mm. of carbon dioxide. This corresponds to 0.1 cc. of methane - a mere trace.

The oxygen and nitrogen were shown to be impurity in the cylinder carbon dioxide.

A drop of water with an acid reaction had collected in the ice-cooled tube. There was no condensate in the CO_2 -snow-cooled tube. There was no smell of ester.

Hence the melt does not decompose on its own account at the working temperature. The possibility of decomposition by local overheating is not excluded though the technique of electrolysis is designed to minimise this. In order to see what amount of overheating would be necessary to decompose the melt the above experiment was repeated heating the melt in a bath of fusible metal and increasing the temperature until decomposition set in. This did not happen till 370°C . [circ.] was reached. During six hours heating 50 cc. of CO_2 -free gas was collected, and analysed in two portions. The hydrocarbon residue was fractionated with liquid air. Only a trace of condensable hydrocarbon was obtained. The volatile hydrocarbon flashed as pure methane [$d/c = 2.00$].

Below[

Below is given the percentage composition of the two successive samples after subtracting oxygen and nitrogen.

Table 6. Thermal Decomposition.

Unsaturated Hydrocarbon	CO	CH ₄	H ₂	Condensable Hydrocarbon
36.4	4.5	45.5	13.1	0.5
47.0	1.5	41.2	9.6	0.8

The evolved gas is thus not uniform in composition. About 0.2 cc. of a pungent liquid collected in the cooling tubes. No analysis was attempted.

ANALYSIS of ANODE GAS.

The anode gas was analysed over mercury in a Bone-Newitt apparatus. This works on the constant volume principle. The absorptions are all done in the same pipette using fresh reagent for each. The volume is then adjusted to a constant volume mark and the pressure read with the aid of a travelling telescope. The measuring tubes are water-jacketed and the rise and fall of the mercury is regulated by water pressure. No correction of readings for water vapour tension is necessary as the whole apparatus is kept moistened with stock 10% sulphuric acid, which solution is used to wash out the pipette after each absorption. The pressures are read to 0.1 mm. Tests shewed that the error in measuring an absorption, assuming no solubility effects, should not exceed 0.2mm.

The capacity of the measuring tube when the zero constant volume mark was used was measured and found to be 35.3 cc.

Preliminary experiments shewed that the gas contained carbon dioxide, carbon monoxide, small amounts of oxygen and a hydrocarbon residue which flashed as though it were ethane with a small proportion of methane. Traces of hydrogen and unsaturated hydrocarbon, and a small residue of nitrogen were usually present.

Carbon

Carbon dioxide.

The collected gas contained a large proportion of carbon dioxide -- some 70% from the electrolysis together with that used to sweep out the apparatus. If it were determined directly the amount of the residual gas would be small and its analysis correspondingly less accurate.

The carbon dioxide was therefore determined indirectly, by difference. The pressure which the known volume of total anode gas would exert in the Bone-Newitt apparatus was calculated by application of the gas laws. The calculated pressure may, of course, exceed measurable pressures. The collected gas was therefore put over potash without previous measurement. The difference between the calculated total and the "after KOH" value gives the carbon dioxide provided only the remaining gas is all anode gas. The presence of nitrogen shews that this condition is not fulfilled. The nitrogen must have been introduced accidentally, as air. The amount of carbon dioxide is therefore

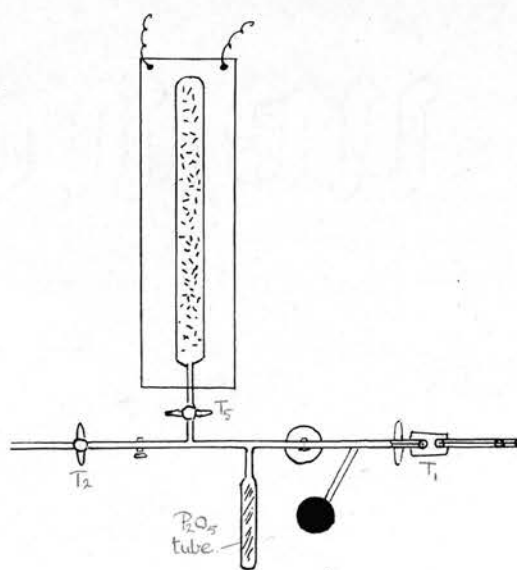
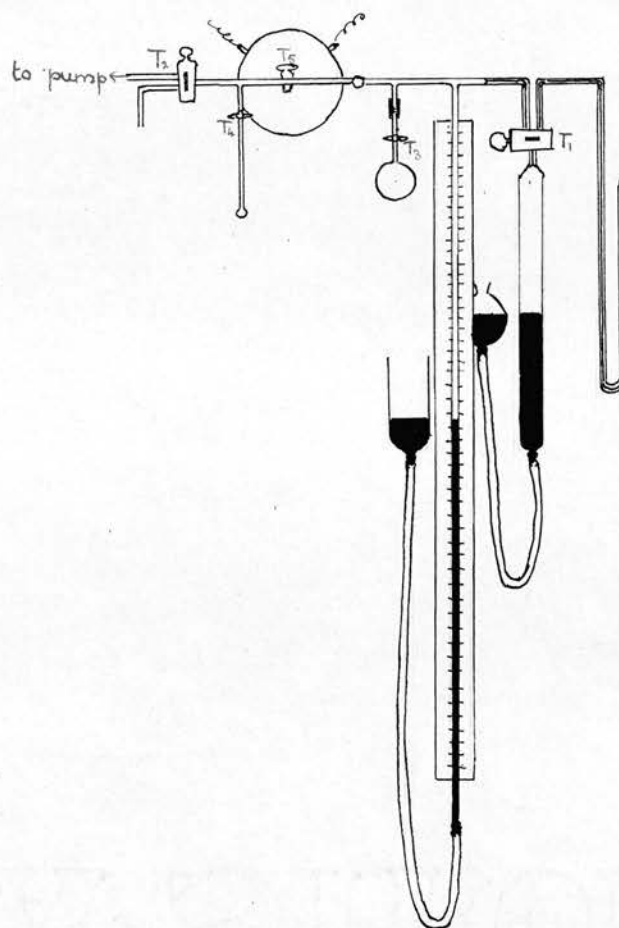
calc. total - after KOH pressure + calc.air pressure.

Oxygen.

Oxygen was determined by absorption in alkaline pyrogallol. The pyrogallol solution was stored separately and mixed with alkali in the absorption pipette. Within limits of error the oxygen]

31a.

Fig. 2.



oxygen was never greater than a quarter of the nitrogen. Oxygen is therefore not an anode product.

Carbon monoxide.

Carbon monoxide was determined by absorption in ammoniacal cuprous chloride solution. Two absorptions were normally used and occasionally three, when large amounts were present. Any ammonia was then absorbed by 10% sulphuric acid.

The cuprous solution was the only reagent in which an appreciable solubility effect occurred. In a test in which 250 mm. of CO-free ethane were repeatedly put over the reagent the mean contraction for five such "absorptions" was 2.5 mm.

The reagent was therefore saturated with ethane. Two litres of ethane were bubbled slowly through 60 cc. of the reagent which was then tested:-

Before "absorption"	490.7 mm.
After 1st "	490.4 "
After 2nd "	490.0 "

These results were satisfactory.

The reagent lost ethane slowly on standing: ethanated reagent was only employed when it was known that the residue was at least 90% ethane.

The amount of carbon monoxide in the anode gas was normally small and variable. In case the variability was not bona fide but due to faults in analysis, carbon monoxide was determined by an alternative method in four runs, namely by oxidation with copper oxide. At temperatures between 250° and 1

and 300° C. copper oxide oxidises carbon monoxide and hydrogen but not hydrocarbons.^[24] The reduction in pressure after treatment with copper oxide gives the hydrogen, the subsequent contraction with potash gives the carbon monoxide.

The experimental procedure differed only slightly from that described by Broom.^[25] A tube of about 50 cc. capacity was half-filled with ignited copper oxide and sealed in a horizontal position to the apparatus described on page 31a [Fig.2]. The tube was supported in an electric furnace.

Tests shewed that some oxidation of hydrocarbon occurred at 290° C. but none at 270° C. Oxidation was, however, slower at the lower temperature.

In Run 11 the gas was put over the oxide three times for one hour at 270° C. After the first treatment there was a hydrogen reduction of 10 mm. and a potash contraction of 29 mm. After the second treatment the values were respectively 0 mm. and 4 mm. The third treatment was to see whether this 4 mm. represented unoxidised carbon monoxide or whether methane was burning. Both contractions were zero.

A period of three hours at 270° C. suggests itself as suitable and was used when carbon monoxide was determined in this way.

Hydrogen.

Hydrogen was determined by absorption with palladium]

palladium black at 100° C. The apparatus and procedure are described in detail by Grice and Payman.^[26]

Tests in which known small amounts of hydrogen were added to nitrogen shewed that the method was satisfactory.

The amount of hydrogen was small and often doubtful. The palladium treatment was a precautionary measure rather than anything else, for hydrogen impurity would have a large effect on the results of analysis of the hydrocarbon.

Unsaturated hydrocarbon.

This was absorbed in a solution of bromine in 10% potassium bromide. Bromine vapour was then removed by potash.

This absorption was frequently omitted, especially when less than 30 cc. of anode gas were analysed, as the contraction was always very small and the bromine tended to foul the mercury. A trace of ethylene would not make much difference to the analysis of the hydrocarbon even if it survived the two absorptions with cuprous chloride.

Hydrocarbon residue.

Explosion of the hydrocarbon residue shewed that some gas having a higher value of r/c than ethane was present. This is almost certainly methane.

In[

In order definitely to prove this a separation with liquid air was done with the hydrocarbon of several typical runs. The method is discussed by Shukla and Walker.^[15] The apparatus is shown in Fig. 2, p.31a. It was found necessary to allow the cooling bulb to stand in the liquid air for a considerable time. When the cooling was first applied the mercury shot upwards in the manometer tube and appeared to become steady in a few minutes. But a slow rise then began, and continued, often for over an hour. If the volatile gas were pumped off before the rise had stopped the separation was not good.

Two hours were usually allowed for cooling. The volatile gas was then pumped off by means of a Töpler pump and flashed. In a series of experiments the following values were got for r/c :-

1.8, 1.8, 1.6, 1.9, 1.8, 2.0 [Mean 1.8]

The only combustible gas noncondensable by liquid air which has not already been removed is methane [$r/c = 2.0$]. The difference between 1.8 and 2.0 may be due to some ethane vapour or to some carbon monoxide which has escaped absorption. The total of methane is small, so that a trace of carbon monoxide [$r/c = 0.5$] would markedly affect the r/c value. In support of this the explosions with the lowest r/c were those of the volatile portions of runs in which considerable amounts of carbon monoxide had been present.

Analysis

Analysis of the hydrocarbon residue.

The position of methane in regard to the peroxide theory makes it important that the methane percentage should be known accurately. This was the most troublesome of the analytical problems. Two methods were used, explosion with excess oxygen and density determination.

1. Explosion.

This is the usual method; it has two chief difficulties. [1] On account of the large volume of oxygen necessary the amount of ethane which can safely be flashed is small; not more than 40 mm. is recommended.

[2] The graph of r/c against composition of a binary mixture is not a straight line but is convex to the composition axis. Small amounts of methane in ethane therefore make less difference to the r/c value than do small amounts of ethane in methane. If the error in "r" and "c" be ± 0.2 mm. then the maximum error for methane is ± 0.6 mm. and for ethane ± 0.4 mm. Since 40 mm. of hydrocarbon contains only some 2 mm. of methane it is clear that the accuracy of the methane percentage will be low.

The second difficulty is inherent in the method of calculation, but something may be done about the first by a modification in procedure:-

As much oxygen as the apparatus can comfortably measure is taken, measured and stored in the explosion]

explosion tube. The hydrocarbon residue is then measured and added in three successive portions to the oxygen. After each addition the gas in the explosion tube is mixed and flashed. In this way the carbon dioxide produced in each explosion acts as a diluent for the next explosion.

As much as 130 mm. of gas can safely be flashed by this "multiple flash" method and the accuracy correspondingly increased. This method was therefore used wherever possible. When these large amounts of hydrocarbon are flashed a correction of V/c for deviations from the gas-laws becomes justifiable. Such corrections are discussed in Appendix I. The results of flash analysis given are all based on corrected values of V/c .

For accuracy in explosion analysis it is necessary to standardise as far as possible the conditions of flashing. Even then freak results are occasionally obtained. A slow, silent, blue flash seems to be best.

2. Density of hydrocarbon.

On account of the rather uncertain nature of explosion analysis it was thought advisable to check the composition of the hydrocarbon by determining the density of the gas.

Two density bulbs were used in these determinations. Their capacities up to and including the

the bore of the tap were determined in the usual way. They were found to be 18.963 cc. and 57.075 cc. The large bulb was only employed on three occasions. The bulbs were handled as little as possible, and never directly by the fingers, chamois leather gloves being used.

The apparatus used for filling the bulb — and also for fractionations with liquid air and determination of carbon monoxide by oxidation — is shewn in Fig. 2, p.31a. The apparatus was exhausted up to and including the bore of the tap of the syphon pipette. Gas was then introduced into the pipette and admitted to the density bulb. The gas was left overnight to dry. Next day a bath of distilled water at room temperature was brought under the bulb. The barometric height, the temperature of the water bath and the reading in the manometer limb were recorded, and the tap of the bulb closed. The pressure on the gas was atmospheric less the difference between the manometer level and the reservoir level.

This difference is obtained indirectly:— Tap T_2 is opened to the air; the manometer level then falls until it is the same as the reservoir level. But this has also changed. If the fall in the manometer level be $a-b$ the resultant rise in the reservoir level is

$$\frac{[a-b] r^2}{R^2}$$

Where r is the radius of the manometer tube

and R " " " " " reservoir.

Both]

Both r and R were measured with accuracy. It was

found that $\frac{r^2}{R^2} = \frac{0.2252}{1.41^2} = 0.025.$

Surface tension corrections cancel out with this method of determining the pressure.

The bulb was transferred to a dessicator where it was hung until all trace of surface moisture had disappeared. It was weighed in a K hlmann micro-balance with the usual precautions for accurate weighing. A counterpoise, blown of the same glass as the bulb, was suspended on the opposite pan so that only fractional pieces were needed in weighing. These were calibrated against a standard 10 mg. weight.

The bulb was then evacuated and weighed again.

The Standard Density, D_s , at 0°C . 760 mm. is given by

$$D_s = \frac{[w_1 - w_2] \cdot 760 \cdot T}{v \cdot p \cdot 273} = \frac{K \cdot [w_1 - w_2] \cdot T}{p}$$

where w_1 = wt. of bulb + gas

w_2 = wt. of evacuated bulb

T = absolute temperature of gas.

p = pressure of gas

v = capacity of bulb

For the small bulb $K = 0.1458$

For " large " $K = 0.04846.$

Accuracy]

Accuracy of density results.

The pressure p involves three readings one of which, the barometric height, is accurate to 0.1 mm; in the other two, tenths of a millimetre are estimated. When the pressure is near to atmospheric the error should be less than 0.1%.

The temperature is read on a calibrated thermometer graduated in tenths of a degree. The error here should be less than 0.1%.

The bulb was weighed to the nearest hundredth of a milligram. The degree of constancy of the weight of the evacuated bulb in a series of determinations gives an indication of the accuracy of the weighings.

The weights which, together with the counterpoise, balanced the evacuated bulb in three series of determinations are tabulated:-

Table 7. Wt. balancing evacuated bulb.

Small bulb	Small bulb	Large bulb
0.00066 gm.	0.00030 gm.	0.01865 gm.
0.00065 "	0.00030 "	0.01870 "
0.00064 "	0.00029 "	0.01867 "
0.00065 "	0.00030 "	0.01870 "
	0.00029 "	0.01868 "
	0.00028 "	0.01874 "

Regreasing of the tap is responsible for the difference between the first and second columns. The third column shews that the advantage of a larger weight of gas is to some extent offset by the lesser accuracy of the weighings.

Normally the small bulb contained 25 mg., and the large bulb 70 mg. of gas. The weighing error should therefore not much exceed 0.1%.

Assuming a 0.1% error in pressure, temperature and weight, gives a maximum error of 0.3% in density and a probable error of half that amount.

For the density of air [$D_a = 1.293$] the following figures were obtained:-

Table 8. Density of air.

Small bulb	Large bulb
1.291	1.295
1.290	1.294
1.293	1.296
Mean 1.291	Mean 1.295

The deviation from the mean is within the limits of error according to the above estimation.

Calculation of composition from density.

In order to calculate the composition of the gas it is necessary to

to know the percentage of nitrogen present. This is given with fair accuracy by the results of explosion analysis. Fortunately since the density of nitrogen is close to that of the hydrocarbon it is not necessary to know it more than to the nearest per centum. The details of this calculation, and the method in which deviations from the gas laws may be corrected for, are given in Appendix II.

In the following table are given the detailed observations for two typical density determinations.

Table 9.

Density of Hydrocarbon Residue.

Particulars	Run 8 [Normal]	Run 30 [Carbon Anode]
1st Reading of manometer "a"	415.9 mm.	656.2 mm.
2nd " " " " "b"	416.8 mm.	504.9 "
[a - b]	-0.9 "	151.3 "
Correction for change in reservoir level	0.0 "	+3.8 "
Correction for temperature	0.0 "	-0.4 "
Corrected a - b	-0.9 "	154.7 "
Corrected barometric pressure "P"	747.3 "	756.2 "
Pressure of gas P - [a - b]	748.2 "	601.5 "
Absolute temperature of gas	292.3° A	289.2° A
Wt. of bulb + gas	0.02395 gm.	0.01906 gm.
Wt. of evacuated bulb	0.00064 "	0.00098 "
Wt. of gas	0.02331 "	0.01808 "
Standard Density D _s	1.328	1.267
Provisional Composition:		
Nitrogen	2.4%	4.0%
Methane	3.9%	13.0%
Ethane	93.7%	83.0%
Partial pressure of ethane	700 mm.	500 mm.
Density of ethane at this pressure	1.355	1.351
Partial pressure of methane	10 mm.	80 mm.
Density of methane at this pressure	0.715	0.715
Corrected Composition:		
Nitrogen	2.4%	4.0%
Methane	3.8%	12.5%
Ethane	93.8%	83.5%

It has been estimated that the fourth figure in the density should be accurate to ± 2 . A difference of this amount alters the methane percentage by 0.3. As the hydrocarbon is roughly 30% of the total anode gas the methane percentage proper should be accurate to ± 1 . A mixture of methane and ethane containing 5% methane gives an R/c of 1.269 while one containing 5.3% methane gives an R/c of 1.271. The accuracy obtainable by density determination is therefore better than that obtainable by flashing even if the latter method always gave the theoretical results. To obtain this accuracy at least 100^{cc} of anode gas, equivalent to about 30 cc. hydrocarbon must be collected. When a smaller volume is used and a density taken under reduced pressure the accuracy will be rather less.

The results obtained by the two methods are compared in Table 10 which includes all the results to which both methods were applied.

Table 10. Analysis by Density and Explosion Compared.

Ref.No.	Pressure in density bulb in cm.	Standard Density D _s	% CH ₄ in hydrocarbon			Mean r/c
			from Density	from Flash	Diff.	
2-5 ⁺	74	1.322	5.0	6.1	1.1	1.273
6	74	1.323	4.8	6.4	1.6	1.274
7	76	1.323	4.8	6.5	1.7	1.274
8-9	75	1.328	3.8	5.3	1.5	1.270
10	46	1.307	6.3	6.8	0.5	1.276
11 ⁺	72	1.323	4.8	4.2	-0.6	1.265
12	76	1.327	3.9	4.5	0.6	1.267
13	76	1.331	3.5	4.1	0.6	1.265
14-15	76	1.314	5.9	5.9	0.0	1.272
18	46	1.274	10.5	14.7	4.2	1.308
19	33	1.231	18.0	21.4	3.4	1.342
21	76	1.319	5.4	5.5	0.1	1.270
22	76	1.316	5.6	5.6	0.0	1.270
25B	48	1.225	20.2	22.5	2.3	1.347
27	75	1.229	19.4	20.0	0.6	1.334
30	60	1.267	13.0	14.1	1.1	1.306
31	74	1.250	16.1	17.2	1.1	1.320

⁺
Large density bulb used.

The variation is rather irregular but there is no doubt that the methane according to density is lower than the methane according to flashing. The average difference is 1%.

It appeared most likely that the explosion results were at fault. This was confirmed by preparing pure ethane. Ethane from electrolysis of acid potassium acetate solution was fractionated by liquid air. A density of the purified ethane using the large bulb gave $D_4 = 1.356$ [Correct result 1.3565]^[27].

Several samples were then flashed [multiple flash method]. Using three flashes the values for $\frac{F}{c}$ were 1.258, 1.260, 1.251. Using two flashes the values were rather higher: 1.264, 1.255, 1.258, 1.263.

In analysing the condensable gas obtained by fractionating hydrocarbon residues as described on p.34, it was also observed that the gas did not flash exactly as pure ethane. Values for $\frac{F}{c}$ obtained were 1.255, 1.249, 1.252, 1.257.

Thus, on an average, with the technique adopted, ethane flashes as if it contained 1-2% of methane. This is similar to the discrepancy between density and flash analysis. The density value is therefore the trustworthy one.

Before passing to presentment and discussion of the results of analysis, the detailed observations for

for a typical gas analysis are given in the following table. The collection and determination of density of one of the samples have already been given in detail.

Table 11.

Complete Gas Analysis.

Observations	Run 8	Run 9		
Calculated Total	1367.	1238.		
After KOH	436.8	397.4		
" pyro	433.5	392.9		
" bromine	431.4	391.5		
" cuprous chloride	423.3	383.6		
" palladium	420.5	382.4		
Samples combined and density determination done. $D_4 = 1.328$				
Taken O ₂ added Total After flashing After KOH Corrected r. Corrected c. $\frac{r}{c}$	Samples flashed			
	125.4	119.0		
	571.5	565.2		
	696.9	684.2		
	394.2	396.4		
	156.9	170.5		
	302.7 - 0.3	287.8 - 0.3		
	237.3 + 0.5	225.9 + 0.5		
	1.271	1.270		
% Composition from density % Composition from flash	Nitrogen	Methane	Ethane	
	[2.4] 2.4	3.8 5.2	93.8 92.4	
Nitrogen Equivalent oxygen " air	Run 8		Run 9	
	Amounts	Percent.	Amounts	Percent.
	10.0 2.5 12.5		9.0 2.2 11.2	
Total anode gas	1367+2 ⁺	100.0	1238+2 ⁺	100.0
Ethylene	2.1	0.2	1.4	0.1
Hydrogen	2.8	0.2	1.2	0.1
[Oxygen]	[0.8]	[0.0]	[2.]	[0.2]
Carbon monoxide	8.1	0.6	8.0	0.6
Methane	{15.5 22.0	{1.1 1.6	{14.0 20.0	{1.1 1.6
Carbon dioxide	942	68.9	852	69.0
Ethane	{395+2 ⁺ 389	{29.0 28.5	{359+2 ⁺ 353	{29.1 28.6
Voltameter hydrogen	565	42.0	501	40.5

+

Correction for imperfection of butane [see Appendix I].

RESULTSExplanatory.

In the absence of statements to the contrary the results are for a ternary mixture of lithium, sodium and potassium acetates at 200° C., electrolysed at an anode of smooth platinum wire of surface area 1 sq. cm.

The tables of results are grouped in pairs. The results of analysis [percentage composition] are recorded in the "A" tables.

Where the letter "d" is put alongside the reference number the hydrocarbon residue has been analysed by density as well as by flashing. The values given are those deduced from density. Otherwise the results are deduced from flashing alone. In such cases the methane is probably 0.3% too high and the ethane the same amount too low.

The "B" tables give some significant quantities deduced from these results. Under "Available CO₂" and "Available H₂" are recorded the amounts of these gases left over from the total amounts after subtracting amounts equivalent to the evolved ethane.

Under "Excess CO₂" and "Excess H₂" are recorded the amounts of CO₂ and H₂ left over from the "available" amounts after subtracting amounts equivalent[

equivalent to the methane and carbon monoxide according to a mechanism for which evidence will be developed in the course of presentation of results. The method of calculation is indicated in the table.

If the suggested mechanisms are correct, and if no anode product has been missed, the "Excess" amounts should be zero. Alternatively, "Excess CO_2 " should equal $\frac{1}{2}$ "Excess H_2 ", which would indicate that all the "Excess H_2 " was equivalent to carbon dioxide evolved in total oxidation⁺. In very few cases are either of these alternatives fulfilled. The "Excess CO_2 " is generally greater than $\frac{1}{2}$ "Excess H_2 ". The amount by which the "Excess CO_2 " exceeds $\frac{1}{2}$ "Excess H_2 " is recorded as "Unaccounted CO_2 ".

Analysis of successive samples.

It has been stated that the composition of the anode gas depended to a large extent on the method of conducting the electrolysis, and that to secure a product of constant composition it was necessary periodically to interrupt the current. The constancy of the yield was taken as criterion for constancy of composition. Justification for this was given by several experiments in which successive samples]

+

Evidence will be given that oxidation, although apparently improbable, cannot be excluded.

samples were analysed. A typical result is given.

Table 12.A.

Successive Samples.

Ref. No.	Actual Vol. in c.c.	Yield	C ₂ H ₄	H ₂	CO x	CH ₄ m	CO ₂ c	C ₂ H ₆ e
1 A.	16.	2.40	0.3	0.2	0.8	1.6	69.6	27.7
1 B.	16.	2.47	0.2	0.1	0.7	1.2	68.9	28.8
1 C.	16.	2.25	0.3	0.2	2.0	2.9	68.1	26.4

Table 12.B.

Successive Samples.

Ref. No.	Volta. H ₂ V	Available CO ₂ C-2e	Available H ₂ v-e	Excess CO ₂ [c-2e]-m	Excess H ₂ [v-e]-[x+m/2]	Unaccounted CO ₂
1 A.	41.6	14.2	13.9	12.6	12.3	6.5
1 B.	40.5	11.3	11.7	10.1	10.4	4.9
1 C.	44.3	15.3	17.9	12.4	14.4	5.2


The variation in carbon monoxide, methane and ethane coincident with the decrease in yield is typical and will be further illustrated in other tables. The figures given are probably not all significant, on account of the smallness of the samples.

In Table 13, which follows, larger amounts of gas were collected. With practice it was found possible to collect considerable amounts—up to 150cc.—without]

without the yield varying by more than 0.1. This gives sufficient gas for a density determination. In some cases samples giving the same preliminary analysis were combined in order to have sufficient volume for a density determination. Such results are indicated in the table. They are recorded separately, although the methane is necessarily the same.

The purpose of combining hydrocarbon from Runs 2-5 was to allow the large density bulb to be used. Runs 10-13 were done with a modified apparatus described on page 56 and the carbon monoxide and hydrogen were determined by oxidation with copper oxide.

It has been stated that the conductivity of the melt was always higher during the evolution of the first 10-20 cc. It was possible that this gas differed from the normal product, although comparison of Run 1A with the Runs of Table 13 does not bear this out. In view of the uncertainty attaching to the methane and carbon monoxide percentages in analysis of small amounts, the first 10 cc. from a large number of electrolyses were collected separately and combined. The result of analysis is given in Table 14. The possibility of error in the "calculated total pressure" is magnified by this procedure. The "CO₂" is therefore not likely to be accurate. After the actual results[



results, amended values assuming that " CO_2 " = 69% are inserted. In view of the large effect this has on Run 14 its results are not as reliable as those of Run 15, in which the effect is small.

Table 13.A.

Normal Runs.

Ref. No.	Actual Vol. in c.c.	Yield	C ₂ H ₄	H ₂	CO x	CH ₄ m	CO ₂ c	C ₂ H ₆ e
2	108	2.30		0.1	0.9	1.5	68.3	29.2
3 d	71	2.48		0.2	0.7	1.5	68.8	28.8
4	49	2.42		0.1	1.3	1.5	68.9	28.2
5	45	2.35		0.3	0.9	1.5	68.8	28.5
6 d	120	2.42		0.1	0.8	1.5	68.9	28.7
7 d	138	2.43	0.1	0.1	0.7	1.4	68.5	29.2
8 d	68	2.38	0.2	0.2	0.6	1.1	68.9	29.0
9	52	2.48	0.1	0.1	0.6	1.1	69.0	29.1
10 d	60	2.34	0.2	0.1	1.08	1.7	68.8	28.1
11 d	213	2.23	0.2	0.3	0.92	1.5	68.8	28.3
12 d	160	2.32	0.2	0.2	0.39	1.2	68.8	29.2
13 d	147	2.41	0.2	0.2	0.47	1.2	68.8	29.1
Mean		2.40	0.2	0.2	0.8	1.3	68.8	28.9

Table 13.B.

Normal Runs.

Ref. No.	Volts. H ₂ v	Available CO ₂ c - 2e	Available H ₂ v - e	Excess CO ₂ [c - 2e] - m	Excess H ₂ [v - e] - [x + $\frac{m}{2}$]	Unacc. CO ₂
2	43.4	9.9	14.2	8.4	12.5	2.1
3	40.3	11.2	11.5	9.7	10.0	4.7
4	41.4	12.5	13.2	11.0	11.2	5.4
5	42.6	11.8	14.1	10.3	12.4	4.1
6	41.3	11.5	12.6	10.0	11.1	4.5
7	41.1	10.1	11.9	8.6	10.5	3.3
8	42.0	11.0	13.0	9.5	11.8	3.6
9	40.4	10.8	11.3	9.3	10.1	4.2
10	42.8	12.6	14.7	10.9	12.8	4.5
11	44.9	12.2	16.6	10.7	14.9	3.2
12	43.1	10.4	13.9	9.2	12.9	2.7
13	41.1	10.6	12.0	9.4	11.0	3.9
Mean	41.6	11.0	12.7	9.7	11.3	4.1

Table 14.A.

Combined First Portions.

Ref. No.	Actual Vol. in cc.	Yield	C ₂ H ₄	H ₂	CO x	CH ₄ m	CO ₂ c	C ₂ H ₆ e
14	55	2.5	-	0.2	0.4	1.5	73.0	25.0
15	62	2.4	-	0.2	0.8	1.7	70.0	27.5
Amended								
14		2.2	-	0.2	0.5	1.7	69.0	28.7
15		2.3	-	0.2	0.8	1.8	69.0	28.2

Table 14.B.

Combined First Portions.

Ref. No.	Volts. H ₂ v	Available CO ₂ c-2e	Available H ₂ v-e	Excess CO ₂	Excess H ₂	Unacc. CO ₂
14	40.0	23.0	15.0	21.5	13.8	14.6
15	42.0	15.0	14.5	13.3	12.9	6.8
Amended						
14	46.0	11.6	17.3	9.8	16.0	1.8
15	43.3	12.6	15.1	10.8	13.4	4.1

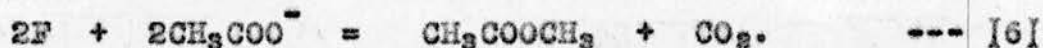
Comparison of Tables 14.A and 13.A shews that there is little difference between the initial gas and the normal anode product: the methane is somewhat higher.

Discussion of Normal Anode Product.

The constitution of the anode gas is very similar to that got in aqueous solution. In solution deviations from 100% synthesis can be explained on

on the assumption that Faraday electrolysis and complete oxidation occur as side-reactions. Such explanations look to be unavailable here, though it should be said that results at lower yields, and with other anode materials, seem only to be explicable when some oxidation is postulated.

Probably the methane and carbon monoxide should be associated with carbon dioxide and cathode hydrogen, but they are too small in amount appreciably to lessen the amounts of "Available" carbon dioxide and hydrogen. It will be observed that the "Available CO_2 " and "Available H_2 " are generally not very different from each other. Ignoring the methane and carbon monoxide this may be explained by ester formation according to



The smell of methyl acetate had, indeed, been detected in the electrolytic gas, but it seemed unlikely that much ester could be synthesised under the experimental conditions. Any ester vapour was apparently removed by collection over water, for an attempt to freeze it out in the apparatus of Fig.2, failed to give any contraction: it is certainly removed in the normal course of the analysis, by the repeated use of caustic potash.

To determine whether or not appreciable ester was formed, a series of electrolyses under normal conditions[

conditions was done in which two cooling tubes were interposed between the anode tube and the collecting burette. The first tube was a plain U-tube and was cooled in ice; this was to trap any water or acetic acid. The second was a U-tube with a thin-walled bulb sealed on to the bend of the U. This was intended to trap ester, and was cooled in a CO_2 snow-ether mixture.

The anode gas was collected and analysed. With the cooling arrangements employed the carbon dioxide is likely to be low. The values found were 2 - 3% lower than the normal one of 68.8%. As this value is sufficiently well vouched for in Table 13, it is permissible to calculate the percentages of the other gases on the assumption that carbon dioxide is 68.8%. The results thus amended are recorded as runs 10-13 in Table 13.

By "nursing" the yield the electrolysis was prolonged as long as possible. A small amount of liquid condensed in each tube [about 0.02 cc.]. Both condensates smelt strongly of ester. The CO_2 snow-cooled tubes were sealed off.

In one run a modified cooling tube with a J-capillary instead of a bulb sealed on was used. The condensate was induced into the small end of the J-tube, which was then cut and used to find the b.p. of the liquid. The condensate, however, did not have a sharp b.p. Bubbling was most brisk between 54° C. and

and 60° C. At 62 C. the liquid had disappeared.

The b.p. of methyl acetate is 57° C., so that the result does not disagree with the assumption that most of the liquid is methyl acetate. Methyl alcohol and acetone are also possibilities.

Acetone was shewn to be absent by negative results with Frommer's salicylaldehyde test:- [28]

2 cc. of a solution of the condensate were taken and 0.2 gm. KOH added and dissolved - then a drop of salicylaldehyde. On heating to 50 C. there was no red colouration.

A scale of controls shewed that an orange red colouration persisted down to 0.001 - 0.0005 % of acetone.

To test for methyl acetate saponification with dilute alkali was tried. Titration after an hour shewed that some of the alkali had been used up. Methyl acetate is therefore present. An attempt was made to determine this quantitatively:-

Ester determination.

Preliminary experiments with 10-20 milligrams of methyl acetate shewed that saponification by $\frac{N}{50}$ carbonate-free alkali was a feasible method of analysis. In two experiments 94% and 96% of the weight taken was accounted for by alkali used in saponification.

Two]

Two of the sealed CO₂ snow-cooled tubes were therefore analysed:-

10 cc. of cold CO₂-free water was put in a Jena flask and the bulb introduced and smashed beneath the surface. Two-fifths of the liquid was removed to test for acetone as described above. The free acid in the remaining three-fifths was neutralised by a drop or two of alkali. Excess alkali was added and the flask stoppered. Concurrently a control was done in which an empty bulb was smashed beneath water and the same volume of excess alkali added. The flasks were left overnight and then heated for an hour to 50° C. to saponify the last traces of ester.

The tubes were weighed before fracture and the broken glass later recovered and weighed. Tests shewed that this recovery was practicable, but in the first experiment some of the glass was lost. The results are therefore not recorded.

Table 15. Saponification of "Ester" with 0.01751N. NaOH.

Particulars	A [Run 12]		B [Run 13]	
	Experiment	Control	Experiment	Control
Wt. of bulb in gm.			0.2498	0.1505
Wt. of recovered glass [gm.]			0.2337	0.1489
Wt. of condensate "			0.0161	[0.0016]
$\frac{3}{5}$ analysed:-				
Vol. of alkali to neutralise free acid	0.15 cc.	0.00 cc.	0.05 cc.	0.00 cc.
Wt. of free acid	0.16 mg.	-	0.05 mg.	-
Additional alkali added	13.91 cc.	13.91 cc.	17.90 cc.	17.90 cc.
Acid required	5.85 "	12.35 "	10.22 "	16.94 "
Acid equivalent to ester	6.50 "	-	6.72 "	-
Wt. of ester	9.5 mg.	-	9.2 mg.	-
Total Wt. of ester	15.9 mg.	-	15.4 mg.	-
" " " free acid	0.3 "	-	0.1 "	-

The contents of the tube cooled in ice were analysed similarly; only a trace of ester - less than 0.3 mg. - was present and very little free acid. The condensate is probably water.

The condensate in the CO₂ snow-cooled tube appears to consist in the main of methyl acetate. The amount trapped corresponds in each case to 3% ester in the anode gas. It is improbable that all the ester vapour has been trapped. It would require some 10% of ester completely to account for all the "Available" carbon dioxide and hydrogen. How much of this amount may fairly be attributed to ester formation is still open to question. What can be said is that ester is formed and in more than a mere trace.

The [

The methane and carbon monoxide are still unexplained. Both these gases are decomposition products of acetyl peroxide though no equation for their formation is obvious. They are therefore to be expected on the peroxide theory.

Methane is not an uncommon product in reactions involving acetic acid and acetates. It has been shown [p.28] to be formed by thermal decomposition of the fused acetate mixture at temperatures exceeding 360° C.: carbon monoxide is also formed under these conditions. The possibility of a thermal origin for these gases cannot be overlooked. On the other hand, methane can be formed by electrolytic processes, witness Shukla and Walker's ^[15] experiments. These authors do not advance any suggestion for the mechanism of methane formation. According to ^[30] Gordon the formation of methane by the action of persulphates on acetates is a catalytic process, not an oxidation:-



The existence of methane in the first 10 cc. of anode gas - as established in Table 14 - is evidence against its decompositional origin.

The smallness of the amounts both of methane and of carbon monoxide makes it difficult to test any suggested mechanism for their formation, from the normal results recorded in Table 13. In runs of lower yields[

yields, or under modified conditions, they are formed in larger amount. Assuming that the mechanism of their formation does not change, it may be possible to deduce the mechanism from a consideration of such runs. In Table 16 some runs in which the yield was lower are recorded. The mean of the normal results is inserted for comparison. Runs 16-18 were obtained using the ordinary collecting method, the yield having declined on its own account to the value recorded.

In Runs 19 and 20 no attempt to control the yield by interrupting the current was made. This caused the temperature to rise to about 220°C . These runs are under conditions comparable with those used by previous workers.

Table 16.A.

Runs at Various Yields.

Ref. No.	Actual Vol. in cc.	Yield	C ₂ H ₄	H ₂	CO x	CH ₄ m	CO ₂ c	C ₂ H ₆ e
Mean of Tab.13	-	2.40	0.2	0.2	0.8	1.3	68.8	28.9
16	41	2.06	-	0.3	1.9	2.0	69.7	26.1
17	30	1.90	-	0.1	2.8	2.8	70.5	23.7
18 d	71	1.64	-	0.3	3.1	2.9	69.7	24.6
19 d	87	1.06	0.2	0.6	4.8	2.9	78.5	13.0
20	65	0.92	0.1	1.3	6.9	2.2	83.	6.2

Table 16.B.

Runs at Various Yields.

Ref. No.	Volts. H ₂ v	Available CO ₂ c-2e	Available H ₂ v-e	Excess CO ₂ [c-2e]-m	Excess H ₂ [v-e]-[x+m/2]	Unacc. CO ₂
Mean of Tab.13	41.6	11.0	12.7	9.7	11.3	4.1
16	48.6	17.5	22.5	15.5	19.6	5.7
17	52.6	23.1	28.9	20.3	24.7	8.0
18	61.1	20.5	36.5	17.6	32.0	1.6
19	94	53	81	50	74	12
20	109	71	103	68	95	21

The results of Table 16 support the view that methane and carbon monoxide are formed electrolytically, i.e. by actions in which the discharged ions take part. If thermal decomposition occurred it would be additional to the electrolytic gas and independent of cathode hydrogen. It would therefore be signalled by an increase rather than a decrease in the yield.

An alternative explanation, to which reference has already been made [p.49] is that oxidation is occurring. For total oxidation the anode gas — carbon dioxide — is half the voltameter hydrogen. This would go some way to account for the large amounts of "Available" hydrogen and carbon dioxide: carbon monoxide might arise through partial oxidation. There is, however, no obvious source for the oxygen.

There are several reasons which point to a trace of water as the source of oxygen. The melt does not readily part with water, as shewn by the necessity for applying suction to it. It is therefore impossible to be certain that no water is present. The condensing of water in an ice-cooled tube during the run has been referred to in the course of establishing the presence of ester. The reaction of water with a discharged ion would liberate oxygen. No oxygen is evolved, but this is not to be expected; for

for under the experimental conditions oxygen would be used in oxidation of discharged ions. Such oxidation would liberate fresh water. In this way a trace of water might be sufficient for considerable oxidation. In fact, if any oxygen is evolved, whether by reaction of ions with water or not, oxidation will tend to be autocatalytic. The temperature of the melt, on the other hand, tends to prevent water from being present in more than a trace.

This gives a good explanation of the necessity for periodically interrupting the electrolysis if the yield is to be maintained. The result of electrolysis with a platinised anode [q.v.] is also most readily explained by assuming a trace of water to be present.

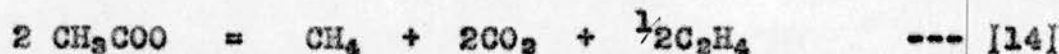
Some possible modes of formation of methane and carbon monoxide are discussed below. It is not claimed that the equations given are other than tentative. The amount of methane is represented by "a" and the amount of carbon monoxide by "x". The amounts to be subtracted from the "Available H_2 " and "Available CO_2 " are given for each suggested mechanism.

1. Methane.

A. Interaction between ions.

The methane cannot come from a single ion. It is possible to write several equations[

equations in which methane arises by interaction of two discharged ions, though none appear probable, e.g.



None of these equations agrees with the recorded results. Formaldehyde would have been detected by smell, carbon monoxide is not formed in sufficient amount to justify [13], and [14] is vetoed by the smallness of the ethylene content.

B. Oxidation.

An equation to yield methane by oxidation can be written:-



equivalent hydrogen = 4m; equivalent carbon dioxide = 3m.

The equation seems improbable.

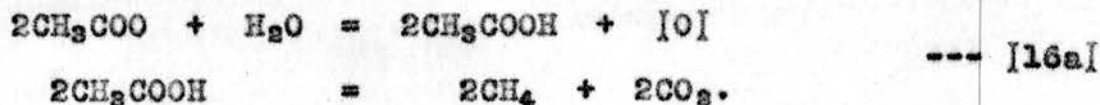
C. Reaction with water.

The simplest equation is



equivalent hydrogen = $\frac{m}{2}$; equivalent carbon dioxide = m.

Another reaction which gives the same result from a different mechanism is



This is similar to the reaction proposed by Gordon for formation of methane in the interaction of persulphates with acetates.

The [

The oxygen must be assumed to be used in oxidation.

2. Carbon Monoxide.

A. Interaction between ions.

It is not feasible to obtain carbon monoxide from a single ion. From two ions a variety of reactions may be written. Many of these are clearly fantastic, e.g.

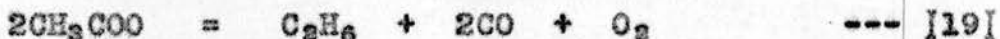


Others give incidental products not, in fact, obtained, e.g.



Methyl ether would have been detected in the fractionation of the hydrocarbon residue. Run 18 contained 3% of carbon monoxide and the hydrocarbon residue was fractionated. The condensable portion gave an $\frac{F}{c}$ of 1.265, higher than ethane, whereas methyl ether would depress it below the ethane value.

The simplest equation is



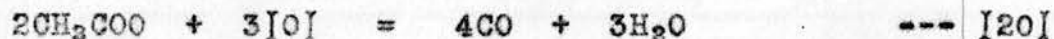
Equivalent hydrogen already accounted for; equivalent carbon dioxide = -x, i.e. the carbon monoxide requires to be added to, not subtracted from the "Available CO_2 ". The oxygen would be used in oxidation, not evolved.

This equation is tantamount to the decomposition[

decomposition of carbon dioxide into carbon monoxide and oxygen and is unlikely in view of the large amount of energy necessary for this reaction.

B. Oxidation.

If oxidation is partial instead of complete carbon monoxide is formed. The equation for formation of carbon monoxide in this way is⁺



Equivalent hydrogen = x: Equivalent carbon dioxide = 0.

C. Interaction with water.

No equation is obvious.

There are thus only two mechanisms for methane and two for carbon monoxide which suggest themselves as reasonable. And even these four are not all equally probable.

In[

+

A more likely equation for the actual reaction is

$$2\text{CH}_3\text{COO} + 5[\text{O}] = 2\text{CO}_2 + 2\text{CO} + 3\text{H}_2\text{O}, \quad \text{--- [20a]}$$
 in which partial oxidation and complete oxidation accompany each other. But since complete oxidation is taken account of separately it is more convenient to use equation 20. Both 20 and 20a give the same value for "Unaccounted CO_2 ".

In an attempt to discriminate between these mechanisms electrolyses under modified conditions were carried out:-

[1] Electrolysis in the presence of anhydrous acetic acid.

This was designed to test whether methane arose from the decomposition of acetic acid. Increase of methane under these conditions would be strong evidence in favour of this mechanism as the source of the methane. Absence of increase would not be such strong evidence against it, because it is possible that the acid requires to be nascent at the anode surface for it to decompose.

The melt was prepared as usual up to the point of transferring it to the cell. A small amount of glacial acetic was then added and stirred into the melt - 0.3 cc. in Run 21 and 1.2 cc. in Run 22. The exact amounts do not matter since much of the acid is vapourised.

Table I

Table 17.A. Electrolysis with Glacial Acetic added.

Ref. No.	Actual Vol. in cc.	Yield	C_2H_4	H_2	CO x	CH_4 m	CO_2 c	C_2H_6 e
21 d	108	2.39	0.2	0.3	0.8	1.6	69.1	28.0
22 d	107	2.44	0.2	0.0	1.0	1.7	68.7	28.5
Mean		2.42	0.2	0.2	0.9	1.65	68.9	28.2

Table 17.B. Electrolysis with Glacial Acetic added.

Ref. No.	Volta. H_2 v	Available CO_2 [c-2e]	Available H_2	Excess CO_2 [c-2e] - m	Excess H_2 [v-e] - [x+m/2]	Unacc. CO_2
21	41.8	13.1	13.8	11.5	12.2	5.4
22	41.0	11.7	12.5	10.0	10.6	4.7
Mean	41.4	12.4	13.2	10.7	11.5	5.0

The ethane synthesis under these conditions is comparable with the best runs of Table 13. The methane is only slightly higher. This is evidence against formation of methane by catalytic splitting of acetic acid. Two interesting experimental points were the absence of the usual darkening of the melt[even after 100 cc. had been collected it was still clear] and the way in which the yield retained its value without the necessity for interrupting the current so frequently.

[2] Electrolysis with water added.

This was designed to test equation 16 [methane formation by interaction of ions with water]. The melt was prepared as usual up to the stage of transference to the cell tube. In Run 23 some ten drops of water were then added. The melt spluttered a good deal and much of the water was vaporised but with stirring some of it mixed with the melt which became quiet again. A larger amount of water was added in Run 24.

Table 18.A. Electrolysis with water added.

Ref. No.	Actual Vol. in cc.	Yield	C_2H_4	H_2	CO x	CH_4 m	CO_2 c	C_2H_6 e
23 A	13	1.7	-	0.0	0.6	4.2	76.2	19.0
23 B	16	2.0	-	0.2	0.5	2.5	72.9	23.9
24 A	21	0.89	-	0.0	1.2	4.6	83.6	10.4
24 B	44	0.95	-	0.0	0.6	2.6	84.1	12.6

Table 18.B. Electrolysis with water added.

Ref. No.	Volts. H_2 v	Available CO_2 c-2e	Available H_2 v-e	Excess CO_2 [c-2e]-m	Excess H_2 [v-e]-[x+m/2]	Unaccounted CO_2
23 A	59.0	38.2	40.0	34.0	37.6	15.2
23 B	50.1	25.1	26.2	22.6	24.4	10.4
24 A	110.8	63	100	58.4	96.4	10.2
24 B	106.5	59	94	56.41	92.1	10.4

The effect of water is thus to decrease the yield. The results differ from the low yield results of Table 16 in that carbon monoxide is normal.

Methane and carbon dioxide have gone up, while ethane has dropped; all these effects are more pronounced the more water is added. It is impracticable to go very far with the addition of water to the melt, in fact only the vitreous nature of the ternary mixture makes it possible to investigate the effect at all, but the direction in which the results are tending is clear.

With water present oxidation becomes probable and the increase in carbon dioxide is best explained by total oxidation of discharged ions.

The smallness of the carbon monoxide makes it possible to test the two alternative mechanisms tentatively suggested for methane formation. For this purpose Run 23 in which the amount of complete oxidation is small, is best suited. Formation of methane according to



would reduce the "Available" amounts of carbon dioxide and hydrogen to 26 and 23 respectively. See [Run 23 A.]

Formation according to



would reduce the "Available" amounts to 34 and 38; similar figures are obtained from 23 B.

The]

The general trend of results favours [16] as against [15] in that even in the runs with highest yield, where the percentage of methane is small, the "Available CO₂" rarely exceeds the "Available H₂". This evidence is rather flimsy; a better reason for supporting [16] is the fact that methane does increase with added water.

This is the mechanism which is assumed for methane formation in obtaining the "Excess" values from the "Available" values in "B" Tables.

3. Electrolysis with varied anode material.

The following anode materials were used:- [1] Platinum black; [2] Grey platinum; [3] Gold; [4] Carbon.

[1] Platinum black: An anode of the same dimensions as the polished platinum one was used. The yield was very low and the synthesis poor, though both improved as the run continued. Consecutive samples were therefore collected.

[2] Grey platinum: prepared by ignition of the platinised anode. The yield and amount of synthesis were intermediate between the platinum black and the polished platinum figures. In contrast to the platinum black anode figures, the yield remained constant throughout the run.

[3] Gold: A gold wire anode of the same dimensions as the polished platinum one was used. The

The gold dispersed into the melt, which became black round the anode soon after current was switched on. The anode gas resembled that from the platinised anode, if anything the synthesis was worse.

[4] Carbon: A high-grade arc carbon was used. The anode area was roughly 3 sq.cm. A very fair synthesis was obtained.

The results are grouped together in the following table. The mean result of Table 13 [polished platinum anode] is inserted for comparison.

Table 19.A.

Variation of Anode Material.

Ref. No.	Actual Vol. in cc.	Yield	C ₂ H ₄	H ₂	CO x	CH ₄ m	CO ₂ c	C ₂ H ₆ e
Polished Platinum Anode								
Mean		2.40	0.2	0.2	0.8	1.3	68.8	28.9
Platinum Black Anode								
25 A	24	0.72	0.1	0.0	15.5	3.1	77.8	3.3
26 A	15	0.73	0.3	0.1	13.0	4.8	78.5	3.4
25 B d	60	1.37	0.3	0.5	6.3	4.4	71.8	16.7
26 B	31	0.76	0.2	0.2	8.7	3.3	80.4	7.3
26 C	45	1.19	0.4	0.0	4.8	4.3	75.6	14.9
Grey Platinum Anode								
27 d	115	1.85	0.3	0.4	3.5	5.3	68.4	22.3
Gold Anode								
28	18	0.60	-	-	21.4	0.3	77.0	1.0
29	85	0.69	0.1	0.0	14.1	2.0	79.1	4.7
Carbon Anode								
30 d	80	1.92	0.2	0.1	2.4	3.6	69.2	24.4
31 d	102	1.84	0.3	0.1	3.5	4.3	68.9	22.9

Table 19.B]

Table 19.B.

Variation of Anode Material.

Ref. No.	Volts. H_2 v	Available CO_2 c-2e	Available H_2 v-e	Excess CO_2 [c-2e]-m	Excess H_2 [v-e]-[$\pi + \frac{m}{2}$]	Unaccounted CO_2
Polished Platinum Anode						
Mean	41.6	11.0	12.7	9.7	11.3	4.1
Platinum Black Anode						
25 A	139.	71.2	136.	68	119.	9.
26 A	137.	72.	134.	67.	118.	8.
25 B	73.	38.4	56.3	34.0	47.8	8.2
26 B	132.	66.	125.	63.	115.	5.
26 C	84.1	46.8	69.	42.5	62.1	11.5
Grey Platinum Anode						
27	54.2	23.6	31.9	18.3	25.8	5.4
Gold Anode						
28	167.	73.	166.	73.	145.	0.
29	144.	70.	139.	68.	124.	6.
Carbon Anode						
30	52.1	20.4	27.7	16.8	23.5	5.1
31	54.4	23.1	31.5	18.8	25.9	5.8

The very poor synthesis at a platinised platinum or a gold anode is difficult to account for other than on the basis of a trace of water being present in the melt. Some evidence for this has already]

already been given. Such a trace can be supported by a polished platinum electrode without the ethane synthesis being greatly depressed [cf. Run 23 A.]. Apparently this is not the case at platinised or gold electrodes. One must suppose that they catalyse the reaction of the ions with water, and use the resultant oxygen to oxidise the ions. The large amount by which the "Available H₂" exceeds the "Available CO₂" can only be explained by oxidation. The carbon monoxide - the amount of which is a feature of these runs - is then explained as a product of partial oxidation, according to



This mechanism has already been discussed [p. 67].

The improvement in synthesis as the run continues is definite and distinguishes the results from other runs in which carbon monoxide is high. Possibly it is due to a deposit of carbon on the anode, virtually converting it into a carbon anode.

The mechanism of equation [20] has been assumed in calculating the "Excess" values from the "Available" values in the "B" Tables. These "Excess" values are large but they are accounted for fairly well by complete oxidation. The "Unaccounted CO₂" is in general larger if the alternative mechanism for carbon monoxide formation, viz:-



be adopted. So far as it goes this supports the mechanism]

mechanism of [20].

Although there is no evidence for a fixed ratio between methane and carbon monoxide a general connection certainly exists between them; they increase or decrease together. On the mechanism suggested this is to be expected for water is a by-product of carbon monoxide formation, while oxygen is a by-product of methane formation.

General Discussion.

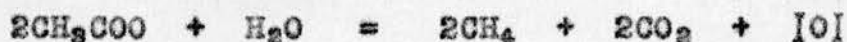
Mechanisms of formation have now been adduced for all the anode gases with the exception of hydrogen and ethylene, which are present in too small amounts for notice to be taken of them. By assuming ester formation and complete oxidation of discharged ions to the requisite extent it is always possible to strike a formal balance between cathode hydrogen and anode gases. Ester formation equal to twice "Unaccounted CO_2 " and carbon dioxide liberated by complete oxidation equal to ("Excess CO_2 " - 'ester') need to be postulated.

For example, in the mean result of Table 13 [normal anode product] ester formation must be 8.2 units and carbon dioxide from complete oxidation 1.5. The ester formation would be reduced slightly - to 7.8 - if account were taken of the trace of ethylene. At least three units of ester have been shown to be present]

present so that it is not unreasonable to suppose that these figures really represent what occurs.

The same cannot be said of many of the results at lower yields. Some of these require 20 or more units of ester formation - values which can hardly be taken seriously. The best of the low yield results from this point of view are those of Table 19 [Variation in anode material]. In many of these runs the amount of ester which has to be postulated is not very different from that for the normal anode product. One would expect it to be less rather than more, since ethane synthesis is also less, but it must be remembered that large amounts of carbon monoxide, methane and much complete oxidation occurs in most of these runs. This makes the "Unaccounted CO_2 " an approximate figure only.

Qualitatively, at any rate, the results agree with the formation of methane by the action of water on the ions:-



— in which reaction formation of acetic acid may be an intermediate stage — and with the formation of carbon monoxide by a partial oxidation of discharged ions.

The criticism may be offered that it is not fair to admit oxidation as a mechanism of formation of the by-products and deny oxidation as a mechanism of formation of ethane, the main product. But the cases]

cases are not really similar, the evidence pointing to the mechanisms suggested for methane and carbon monoxide is slender compared with the evidence for formation of ethane by union of discharged ions. No positive evidence for an oxidation mechanism for ethane formation exists, on the contrary the results of Table 18 [water added to melt] are definitely opposed to such a mechanism. The addition of water, although it increases the methane percentage, depresses the ethane percentage. And this is in general true. The bigger the amount of methane and carbon monoxide -- for which an oxidation mechanism is suggested -- the smaller the ethane value.

Comparison with Petersen's Results.

In the following table entries from Tables 1, 2 and 3 are compared with the normal anode product and with the product of continuous electrolysis [Runs 19 and 20]. The figures, which do not include carbon dioxide, are to the nearest per centum.

Table]

Table 20.

Comparison with Petersen's Results.

Particulars	C_2H_4	H_2	O_2	CO	CH_4	C_2H_6
	Petersen's Results					
$Pb\overline{Ac}_2 + Zn\overline{Ac}_2$	2 11	29 17	1 2	29 27	26 43	13 0
$Na\overline{Ac} + Pb\overline{Ac}_2$	3 1	13 15	2 2	5 9	49 12	28 61
$KH\overline{Ac}_2$	6 15	1 3	0 2	20 12	47 36	26 33
<hr/>						
$Li\overline{Ac} + Na\overline{Ac} + K\overline{Ac}$	Author's Results					
Normal Anode produce	1	1	0	3	4	92
Continuous electrolysis	1 1	3 8	0 0	23 41	13 13	60 37

The normal anode product is more reproduceable than any results obtained by Petersen. It is also more closely akin to the product of the reaction in solution. Petersen does not record voltameter hydrogen, but it is clear that his results are to be classed among low yield ones. He electrolysed continuously for two hours, and his results exhibit in exaggerated form all the effects which have been shewn to accompany decreased yield.

ELECTROLYSIS of FUSED PROPIONATES.

The difficulties encountered in acetate electrolysis appear in an enhanced degree with propionates; chief is the tendency of the melt to decompose. Berle^[22] observed that potassium propionate was too unstable to electrolyse. Petersen^[23] was able to electrolyse lead propionate at 130° C. The composition of the anode gas after removal of carbon dioxide is given in the following table. The composition of the CO₂-free gas from electrolysis of a 40% aqueous solution [Petersen^[17]], and of a 12.5% propionic acid solution at 80° C. [Hopfgartner^[19]] are recorded for comparison purposes.

Table 21. Propionate Electrolysis - Anode Gas.

Particulars	Fused Prop.		aqueous sol.	prop. acid sol.
	1.	2.		
Ethylene	40.0	52.4	88	34
Oxygen	0.3	0.5	1	1
Carbon monoxide	3.0	7.7	-	-
Hydrogen	0.3	2.3	-	-
Residue	56.4	37.1	11	65
% of residue	2.02	1.77		
Butane	-	-	11	65

There is little resemblance between the figures for fused propionates and solutions of propionates. Better results might be obtained from electrolysis of mixtures of propionates, using the method of collection developed for electrolysis of the acetate mixture. This was investigated.

Experimental.

The melting points of a series of mixtures of lithium sodium and potassium were found. The mixture with the lowest melting point turned out to be a binary lithium-sodium one of equal molar proportions. A mixture of this composition was therefore prepared. The propionic acid for this purpose was triply distilled and its purity confirmed by titration.

The melt was prepared on similar lines to the acetate melt. The propionate did not, however, pass smoothly from solution to the fused state, instead the solid separated out. Care was necessary at this stage if decomposition was to be avoided. With practice it was found possible to prepare a melt which could be heated to 280°C . for a short time to drive off the last traces of water, and yet remain clear and colourless. Before electrolysis the melt was put under suction. Much less bubbling than with acetate occurred - sometimes none at all.

Electrolysis was carried out at 230°C ., which]

which was the lowest convenient temperature. The falling-off in conductivity which has been referred to in acetate electrolysis was more pronounced here. It was necessary to raise the applied voltage slightly [45 volts as against 40 for acetate] to allow the gas to be collected in a reasonable time. Even then the slowness of evolution made it difficult to collect sufficient gas for analysis of the saturated hydrocarbon by density without the yield declining.

There seemed to be less control over the yield than with acetate. There, a lowering of yield, if detected soon, could be stopped by pausing for a while. But with the propionate the yield was apt to fall slowly throughout an electrolysis in spite of interruption of the current. On the other hand, when it did fall it never got so low as with acetate.

Thermal decomposition of propionate melt.

A control experiment with the propionate melt was done on the same lines as that described for acetate [p.26]. The working temperature of 230° C. was maintained for three hours while a current of Carbon dioxide was passed. Some 2 cc. of gas collected and was analysed. A small amount of hydrogen [0.05 cc.] was found and no other constituent except nitrogen and oxygen.

The [

The experiment was repeated using a sufficiently high temperature for decomposition to occur; this happened at about 360° C. The CO₂-free gas was analysed. Its percentage composition after subtracting oxygen and nitrogen is given in Table 22. Two separate experiments are recorded.

Table 22. Thermal Decomposition.

	Unsaturated Hydrocarbon	H ₂	CO	CH ₄	C ₂ H ₆
A.	56.5	8.9	25.6	4.4	4.7
B.	57.3	7.5	25.0	4.8	5.3

In "A" the hydrocarbon residue was fractionated, but the separation was not good. The volatile hydrocarbon gave $\frac{V}{C} = 1.7$ and the condensable hydrocarbon $\frac{V}{C} = 1.1$.

In "B" the gas was flashed without fractionation, and the results calculated assuming ethane and methane.

The absence of butane is noteworthy.

Analysis

Analysis of Gas.

Preliminary experiments shewed that the anode gas contained about 65% of carbon dioxide, a small percentage of carbon monoxide, a variable amount of unsaturated hydrocarbon and a residue of saturated hydrocarbon which gave an $\frac{V}{C}$ of about 0.95. There was also a trace of hydrogen and small amounts of oxygen, but the latter was never greater than one quarter of the nitrogen in the residue.

Composition of Hydrocarbon residue.

The $\frac{V}{C}$ value for butane is 0.875 so that some other constituent besides butane must be present. This may be either ethane or methane, or perhaps both; propane is unlikely. To clear up this point sufficient hydrocarbon residue was collected to enable a separation with liquid air to be done. The method has been described on page 34. The volatile portion contained no methane. The mixture is therefore most likely ethane and butane, though propane is not excluded. An attempt was made to test for propane by a further fractionation of the condensable portion:-

The gas was condensed again by liquid air. The liquid air bath was then replaced by a CO_2 snow-ether bath. The pressure in the manometer rose somewhat. Since butane has an appreciable vapour pressure]

pressure at -78°C . the pump was never directly connected to the cooling bulb. The method of collection used was as follows:- The tap T_1 leading to the cooling bulb was closed and the gas on the far side pumped off and collected as fraction "a". The tap T_2 leading to the pump was then closed; T_4 was opened for a few seconds then closed; T_3 was opened and the gas swept into the pump chamber. This was repeated ten times and was designed to remove any volatile constituent dissolved in the butane, leaving as nearly as possible pure butane. It was collected as fraction "b". Finally the cooling bath was removed and the supposed butane collected as fraction "c". The result of flashing these fractions is recorded in Table 23.

Table 23. Flashing of Hydrocarbon Fractions.

	a	b	c
Volume in cc.	1.2	1.9	7.7
$\frac{F}{c}$	1.19	0.99	0.883 0.881

This shows that ethane is present and that the main constituent is butane. That the $\frac{F}{c}$ of the middle fraction is close to that of propane has probably no significance, but whether propane as well as

as ethane is present is still undecided.

A different sample was fractionated, this time into six portions. Light petrol ether, partially frozen by liquid air, was used as a cooling bath intermediate between liquid air and CO₂-snow.

The fractions were:-

- a. Uncondensed by liquid air.
- b. On far side of T₄ after petrol ether applied.
- c. Collected after 4 alternate openings of T₄ and T₂.
- d. Collected " further 12 " " "
- e. Collected after 4 alternate openings of T₄ and T₂ with CO₂-snow cooling bath.
- f. Residual gas after cooling removed.

Table 24. Flashing of Hydrocarbon Fractions.

	a	b	c	d	e	f
Vol. in cc.	0.1	0.2	0.6	1.0	1.0	6.0
$\frac{K}{C}$	1.1	1.2	1.23	1.21	0.93	0.880

If any propane were present it would be retained by the petrol ether. Most would come over in fraction e, while fraction f would contain some propane, and give a higher $\frac{K}{C}$ than fraction e of the previous experiment. The results of Table 24 discount the presence of propane in greater amounts than]

than 5%. In calculating the composition of the hydrocarbon residue it was assumed to consist of butane and ethane. Wherever possible the composition was determined by density determination as well as by flash analysis.

In the case of the corresponding acetate hydrocarbon small quantities of nitrogen do not greatly affect the density result. This is not the case with a butane ethane mixture. Nitrogen must either be known accurately or be removed. The latter method was adopted, the hydrocarbons being frozen with liquid air. This method allowed methane to be tested for. Six such separations were done and methane was absent except on one occasion, when a trace was found.

The results given by density and by flash analysis are compared in Table 25 which includes all the results in which both methods of analysis were used.

Table 25. Analysis by Density and Explosion Compared.

Ref. No.	Pressure in density bulb in cm.	Standard Density D_s	% C_2H_6 in hydrocarbon			Mean r_c
			from Density	from Flash	Diff.	
4	57	2.351	22.2	24.9	2.7	0.929
7 B	54	1.780	65.7	63.6	-1.9	1.055
9	71	1.661	75.5	76.7	1.2	1.108
10	76	2.350	23.2	27.0	3.2	0.933
11	67	2.365	21.6	25.9	4.3	0.930
14 B	44	2.143	37.4	39.8	2.4	0.970

The table shows discrepancies similar to those encountered in analysis of ethane methane mixtures, only more pronounced. The same confidence cannot be placed in the density results as it could with the acetate hydrocarbon on account of the large imperfection corrections which have to be applied [see Appendix II]. Further, many of the densities had to be done under reduced pressure.

Two determinations of $\frac{r}{c}$ were usually made; they rarely differed from the mean by more than 0.3%. It is assumed, however, that they are systematically too high. The results of Tables 23 and 24 confirm this in so far as the final fraction, which is almost certainly pure butane, flashes as if it contained 3.5% of ethane. This compares fairly well with the mean difference of 2.5 between the percentage of ethane from density and ethane from flash. As the hydrocarbon residue is some 25% of the total anode gas the ethane percentage proper, when determined by flash only is about 0.6% too high. In the tables of results the ethane and butane values recorded are not the actual determined ones but are obtained from them by adding 0.6% to the butane and subtracting the same amount from the ethane.

The other gases were estimated as described in the experimental section of acetate electrolysis. Carbon monoxide was normally determined by oxidation with copper oxide at 270° C. Any small amounts which escaped]

escaped oxidation were detected and estimated in the course of the separation with liquid air.

A sample gas analysis is given in detail in Table 26. The unsaturated hydrocarbon is assumed to be ethylene.

Table 26.

Complete Gas Analysis.

Observations	Run 11 [Prop. acid added]	
Calculated Total	2664	
After KOH	957.2	
" Br. [twice]	719.6	
" pyro	713.8	
" CuO [3 hours]	707.5	
" KOH	704.3	
Fractionated by liquid air	679. [condensable]	25.0 [volatile]
Density done. $D_4 = 2.365$		
Samples flashed		after CuCl 23.0
		O ₂ added 159.2
		Total 182.2
		after flash 166.2
		after KOH 148.9
		r. 16.0
		c. 17.3
		r _c 0.93
		hydrocarbon 5. [assume same constitution as condensable.]
		nitrogen 18.
		equiv. O ₂ 4.5
		equiv. air 23.
		"Anode O ₂ " 1.3
Density done. $D_4 = 2.365$		
Samples flashed		
Taken	89.5	64.5
O ₂ added	582.5	582.0
Total	672.0	646.5
After 3 flashes	375.8	433.6
" KOH	59.4	205.5
Corrected r.	295.9	212.7
Corrected c.	317.3	228.6
r _c	0.931	0.930
% C ₂ H ₆ from flash	25.9	
% C ₂ H ₆ " density	21.6	
		Amounts
		Percentages
Total Anode gas		2664+6 ⁺ = 2670
[Oxygen]		[1.3]
Hydrogen		6.
Carbon Monoxide		3.2+2.0 = 5.2
Ethane from density		147+1 = 148
" flash		176+1 = 177
Ethylene		236
Carbon dioxide		1730
Butane from density		532+4+6 ⁺ = 542
" flash		503+4+6 = 513
Voltameter hydrogen		1070

+

Correction for imperfection of butane [see Appendix I].

RESULTS.Explanatory.

The experiments all have their parallels in the acetate results. The tables of results are therefore grouped together. Table 27 gives the results of analysis of the first 10-15 cc., during which the evolution was brisk. Table 28 groups together runs in which larger amounts - occasionally enough for a density determination - were collected. The runs are of various yields. Table 29 records the effect of varying the conditions of electrolysis.

"Available CO_2 " and "Available H_2 " are the amounts of these gases left over after subtracting carbon dioxide and hydrogen equivalent to the recorded butane and ethylene percentages. "Excess CO_2 " and "Excess H_2 " are got by subtracting from the "Available" amounts carbon dioxide and hydrogen equivalent to the recorded ethane percentage, according to the mechanism discussed on page 98.

If the "Excess" hydrogen represents current used in complete oxidation then the equivalent carbon dioxide is $\frac{3}{7}$ "Excess H_2 ". The amount by which "Excess CO_2 " is greater than $\frac{3}{7}$ "Excess H_2 " is recorded as "Unaccounted CO_2 ".

Table 27.A Normal Conditions - First portions

Ref. No.	Actual Vol.in c.c.	Yield	H ₂	CO	C ₂ H ₆ e	C ₂ H ₄ y	CO ₂ c	C ₄ H ₁₀ b
1	16	2.35	0.1	0.3	5.2	10.6	64.7	19.0
2A	19	2.54	0.2	0.4	8.1	7.7	64.6	19.0
7A	17	2.35	0.0	0.3	9.9	8.9	65.3	17.6
5A	10	2.38	0.0	0.6	8.1	7.8	65.2	18.3
Mean		2.40	0.1	0.4	7.3	8.7	65.0	18.5

Table 27.B Normal Conditions - first portions

Ref. No.	Volta. H ₂ v	Available CO ₂ c-[2b+y]	Available H ₂ v-[b+y]	Excess CO ₂ c - [2b+y+e]	Excess H ₂	Unacc. CO ₂
1	42.5	15.9	12.9	10.7	12.9	5.2
2A	39.5	18.3	12.8	10.2	12.8	4.7
7A	42.6	20.9	16.1	13.0	16.1	6.1
5A	42.0	21.6	16.3	13.8	16.3	6.8
Mean	41.6	19.3	14.4	12.0	14.4	6.2

Table 28.A

Normal Conditions - varied yields.

Ref. No.	Actual Vol. in cc.	Yield	H ₂	CO	C ₂ H ₆ e	C ₂ H ₄ y	CO ₂ c	C ₄ H ₁₀ b
2B	23	2.06	0.8	1.4	6.4	9.4	67.1	14.9
3B	84	2.23	0.3	0.2	4.0	13.9	65.4	16.2
4 d	119	2.16	0.5	0.6	4.8	13.6	64.8	15.7
5B	45	1.94	0.5	1.6	7.2	12.1	64.9	13.7
6	49	2.01	0.4	1.2	7.8	10.8	64.3	15.5
7B d	95	1.74	1.1	3.5	15.4	8.9	63.1	7.9
8	103	1.57	1.2	3.4	15.0	9.0	63.4	7.9
9 d	131	1.58	1.3	3.6	16.8	7.4	65.1	5.4

Table 28.B

Normal Conditions - varied yields.

Ref. No.	Volta. H ₂ v	Available CO ₂ c - [2b+y]	Available H ₂ v - [b+y]	Excess CO ₂ c - [2b+y+e]	Excess H ₂	Unacc. CO ₂
2B	48.5	27.9	24.2	21.5	24.2	11.2
3B	44.8	19.1	14.7	15.1	14.7	8.8
4	46.3	19.8	17.0	15.0	17.0	7.7
5B	51.6	25.4	25.8	18.2	25.8	7.2
6	49.7	22.5	23.4	14.7	23.4	4.7
7B	57.5	38.4	40.7	23.0	40.7	5.6
8	63.7	38.6	46.8	23.6	46.8	3.6
9	63.5	46.9	50.7	30.1	50.7	8.4

+ 0.4% of methane found in Run 9.

Table 22.A Conditions of Electrolysis varied.

Ref. No.	Actual Vol. in cc.	Yield	H ₂	CO	C ₂ H ₆ e	C ₂ H ₄ y	CO ₂ c	C ₄ H ₁₀ b
Anhydrous propionic acid added								
10 d	136	2.56	0.4	0.2	6.1	8.3	64.5	20.4
11 d	113	2.49	0.2	0.2	5.5	8.8	65.0	20.3
Mean	-	2.53	0.3	0.2	5.8	8.6	64.7	20.4
Anode Material Varied								
Platinum Black								
12A	14	2.15	0.5	0.5	11.5	6.7	64.3	16.5
13A	17	2.06	0.4	0.5	9.4	6.1	66.6	16.9
Mean	-	2.10	0.4	0.5	10.4	6.4	65.5	16.7
12B	29	1.72	0.0	1.2	7.9	12.6	68.2	13.1
13B d	70	1.76	0.4	2.0	8.6	10.7	65.0	13.3
Mean	-	1.74	0.2	1.6	8.3	11.6	65.1	13.2
Gold								
14A	12	1.46	0.0	0.4	6.7	14.4	69.4	9.2
15A	14	1.45	0.0	0.4	6.2	15.5	68.8	9.0
Mean	-	1.46	0.0	0.4	6.4	15.0	69.1	9.1
14B	30	1.73	0.1	1.3	6.9	16.6	63.0	11.9
15B	41	1.71	1.2	1.6	8.4	14.4	63.3	11.1
Mean	-	1.72	0.6	1.4	7.6	15.5	63.2	11.5
Carbon								
16	105	1.92	0.0	1.2	5.9	12.2	66.7	14.0

Table 29.B Conditions of Electrolysis varied.

Ref. No.	Volta. H ₂ v	Available CO ₂ c -[2b+y]	Available H ₂ v-[b+y]	Excess CO ₂ c-[2b+y+e]	Excess H ₂	Unacc. CO ₂
Anhydrous propionic acid added						
10	39.2	15.2	10.4	9.2	10.2	4.7
11	40.1	15.5	11.0	10.0	11.0	5.3
Mean	39.6	15.4	10.6	9.6	10.6	5.0
Anode Material Varied						
Platinum Black						
12A	46.5	24.6	23.3	13.1	23.3	3.1
13A	48.7	26.7	25.7	17.3	25.7	6.3
Mean	47.6	25.7	24.5	15.3	24.5	4.8
12B	58.0	26.4	32.3	18.5	32.3	4.7
13B	57.0	27.7	33.0	19.1	33.0	5.0
Mean	57.5	27.1	32.7	18.8	32.7	4.8
Gold						
14A	68.5	36.6	44.9	29.9	44.9	10.7
15A	69.0	35.3	44.5	29.1	44.5	10.0
Mean	68.7	36.0	44.6	29.6	44.6	10.5
14B	58.0	22.6	29.5	15.7	29.5	3.0
15B	58.6	26.7	33.1	18.3	33.1	4.1
Mean	58.3	24.7	31.3	17.1	31.3	3.7
Carbon						
16	52.3	26.5	26.1	20.6	26.1	9.4

Discussion.

The results of the longer runs are not as reproduceable as those with acetate, due to the tendency of the yield to fall. As with acetate runs the composition of the first 10-15 cc. is not sensibly different from that of other high yield runs.

Ethylene is now a regular product of the synthesis but the amount present varies from run to run. Ethane has taken the place of methane but the amounts are in striking contrast. The saturated hydrocarbon never contains less than 20% of ethane whereas, with acetates, methane as low as 4% is common in high yield runs. This is the more surprising because the carbon monoxide is low, often little more than a trace. The general relationship between carbon monoxide and the lower hydrocarbon noticed for acetate can still be traced. the runs in which ethane is highest also have higher values of carbon monoxide.

The anode material has less influence on the synthesis than with acetate. A good synthesis is got with platinum black and gold as well as with carbon. With gold the ethylene percentage is abnormally high.

Runs 10 and 11, in which about 0.5 cc. of propionic acid was added to the melt, are closely parallel to the corresponding acetate runs. They are noteworthy for the high yield - higher than any other recorded result - and the ease with which the yield was [

was maintained.

The equation of formation of butane and ethylene is taken to be the ordinary one:-



Ethane can be explained by a similar mechanism to that proposed for formation of methane from acetate, viz. interaction with water. But there is less positive evidence for the presence of water. Unlike the acetate melt the propionate melt has no great affinity for water. It rejects water violently when a drop is added - so that the effect of adding water could not be investigated. The poor synthesis at a platinum black anode with acetate was interpreted as evidence for water's presence, but with propionates a very fair synthesis is got with a platinum black anode. Had it not been for the acetate results, the idea that a trace of water might be present would not have been entertained.

It is possible, however, to account for ethane without postulating the presence of water, by a mechanism which is nevertheless essentially the same as that for methane formation; namely the decomposition of "nascent" acid. In the case of acetate this can only come from the action of water on the ions. But in the case of propionate nascent propionic acid is formed in the course of ethylene formation. This[

This also accounts for the much larger ethane than methane formation. That the acid requires to be nascent is shown by Runs 10 and 11 in which propionic acid was added to the melt; the ethane percentage was not increased. The formation of acetic acid at the anode was hypothetical; the formation of propionic acid is more strongly attested. A splitting of acid at the anode surface is very probable at the temperatures employed.

Assuming this mechanism, the equivalent carbon dioxide is equal to the ethane, while the equivalent hydrogen has already been accounted for.

Hence "Excess CO_2 " = "Available CO_2 " - " C_2H_6 "
and "Excess H_2 " = "Available H_2 ".

It is a corollary that ethane should not exceed ethylene. This is not invariably the case, but the exceptions are those low yield results in which carbon monoxide is relatively high, and the "Excess" figures point to considerable oxidation occurring. Oxidation would liberate water at the anode and allow further propionic acid formation.

It is again possible to strike a formal balance between anode gas and voltameter hydrogen by assuming ester formation and complete oxidation both to occur. Ester formation equal to seven-fourths of the "Unaccounted CO_2 ", and carbon dioxide liberated in complete oxidation equal to ("Excess CO_2 " - 'ester'), must be postulated.

In]

In Table 27 the amount of ester thus indicated is 11% [cf. 8% for acetate]; where the yields are lower, as in Table 28, larger values are indicated, but these are so variable that no confidence can be placed in them. The ester values deduced from Table 29 are also large and variable, with the exception of Runs 10 and 11 [propionic acid added], here the value is only 8%.

There was no doubt that some ester formation was occurring, for the smell of ethyl propionate was more noticeable than the smell of methyl acetate had been. In Runs 8 and 9 attempts were made to freeze it out and determine it by the method which had been successful with methyl acetate [cf. p.55 et seq.]. Minute condensates were obtained in both cooling tubes and saponification shewed that there was some ester in each; but the amount was small. In Run 8 only 3 mg. and in Run 9 4.5 mg. were obtained.

This is less than half the ester formation that occurred with acetate, but it is doubtful whether much significance can be attached to the difference. The higher boiling point of ethyl propionate makes it harder for this ester to escape from the melt without decomposition or condensation on the side of the anode tube. Further, the tendency of the yield to decline is unfavourable to ester determination. Runs 8 and 9, for example, have the lowest yields of any of the runs of]

of Table 28. This is in marked contrast to acetate.

The "Excess" hydrogen and "Excess" carbon dioxide are practically equal in the runs of Table 27 and in Runs 10 and 11, so that ester formation would account for them without the need for postulating appreciable total oxidation. Since there is otherwise no evidence for extensive total oxidation this is satisfactory and as good a reason as any for assuming the formation of ester.

In the runs of Tables 28 and 29 no quantitative significance can be attached to the so-called "carbon dioxide liberated in complete oxidation". It does, however, indicate total oxidation in those Runs in which, by comparison with acetate results, total oxidation is to be expected; viz. in electrolyses with platinised and gold anodes, and in the lower yield runs of Table 28.

Comparison with Petersen's results.

The anode gas from Petersen's electrolysis of fused lead propionate has already been compared with the gas from aqueous and propionic acid solutions [p. 81]. In Table 30 it is compared with the mean result of Table 27. The result]

result of thermal decomposition of the melt is also inserted.

Table 30.

Comparison of Results.

	$\text{LiPr} + \text{NaPr}$ [Author]	Pb.Pr [Petersen]	Thermal Decomp. $\text{LiPr} + \text{NaPr}$
C_2H_4	24.8	52.4	56.5
O_2	-	0.5	-
CO	1.1	7.7	8.9
H_2	0.3	2.3	25.6
CH_4	-	30.4	4.3
C_2H_6	20.9	6.7	4.7
C_4H_{10}	52.9	-	-

This table would seem to shew that under the conditions under which Petersen electrolysed considerable thermal decomposition was occurring. It is difficult to account for the methane otherwise.

Results in relation to the Peroxide Theory.

In the discussion regarding the mechanism of formation of the various anode products no mention has been made of the peroxide theory. But the conclusions formed are all equally valid from the point of view of this theory. It is only necessary to insert an additional step,



into every equation.

If a peroxide is to be formed it can only be by union of ions in this way, since the experimental conditions exclude oxidation of acetic acid.

In the case of acetate electrolysis the composition of the anode gas is qualitatively the same as that got by decomposition of the peroxide. Quantitatively it does not agree with current ideas regarding this decomposition. At a temperature of 200° C. one would expect the decomposition products to resemble those got by explosion of the peroxide, i.e. to be very rich in methane. But methane is normally low. Indeed, the conditions of decomposition of peroxide giving results most closely akin to those obtained, is the decomposition by ultra-violet light. [14] The resemblance here is sufficiently striking to put on record.

Some I

Some of the low yield results shew a closer resemblance than the normal anode product. One such run is inserted.

Table 31.

	Decomp. of Peroxide by u.v. light	Fused acetate electrolysis	
		Normal product	Run 17
C_2H_4	1.0	0.2	-
O_2	1.0	-	-
CO	1.2	0.6	2.8
CH_4	4.8	1.3	2.8
CO_2	67.6	68.8	70.5
C_2H_6	24.4	28.9	23.7
H_2	-	0.2	0.1

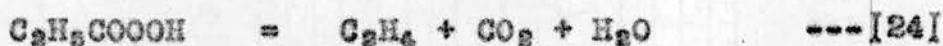
In the case of fused propionate the differences between the product of electrolysis and the product of decomposition of the corresponding peroxide are more numerous. By explosion of propionyl peroxide Fichter got a hydrocarbon which he records as 40% butane, 60% methane. This large methane content has no parallel in electrolysis, even in the low yield results, while the considerable ethane content of the anode product has no parallel in peroxide decomposition.

Further, no ethylene is formed by peroxide decomposition. For that reason Fichter postulates a]

a peracid mechanism for ethylene formation, and he has shewn that ethylene can be obtained by explosion of propionyl peracid; ethane is also formed though no equation for it is apparent. It is possible to write an equation,



for the formation of peracid, if one admits the presence of a trace of water. The peracid would then decompose and regenerate the water:-



The possibility of a trace of water has been discussed and shewn to be feasible - though less likely for propionates than for acetates.

Apart from the absence of methane - a considerable exception - the propionate results, too, can be interpreted in the light of the peroxide theory.

It is obviously idle to expect to isolate either peroxides or peracids under the experimental conditions. If these are formed at all they can only have a fleeting existence at the electrode surface. Nor by assuming their formation is the explanation of the origin of methane from acetates or ethane from propionates made any simpler. It is just as difficult to see how methane can arise from $[CH_3COO]_2$ as from $2CH_3COO$.

This]

This being so it may be questioned whether, with so many anomalies and in the absence of any definite positive evidence, it is worth while postulating a second highly unstable product at the anode surface when one such product, the discharged ions, is already present.

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SUMMARY.

1. In the electrolysis of fused acetates and propionates the main products are those of the corresponding Kolbe reaction in aqueous solution.
2. The variable results of previous workers are attributed to the occurrence of secondary decompositions. Conditions of electrolysis are described by which these effects are minimised. With acetate a uniform product can be obtained. The propionate results are less reproduceable.
3. The most probable mechanism for the syntheses is the interaction of discharged ions.
4. The transitory formation of peroxides by union of discharged ions is not excluded by the results.
5. As by-products of the electrolysis are formed - [a] methane from acetate and ethane from propionate. A tentative mechanism for this reaction, namely decomposition of nascent acetic or propionic acid, is proposed and evidence is given in support.

[b] carbon monoxide from acetate and in lesser amount from propionate. It is suggested that this arises from partial oxidation of discharged ions.

Summary [contd.]

[c] a certain amount of ester.

6. The effect of varying the Anode Material has been studied. Specificity is much more marked for acetate than for propionate. With acetate very little Kolbe synthesis is got at Platinum black or Gold anodes, although both give a moderate synthesis with propionate. A Carbon anode gives a synthesis with both acetate and propionate.

In conclusion the author has great pleasure in acknowledging his indebtedness to Sir James Walker for his encouragement and guidance throughout the research.

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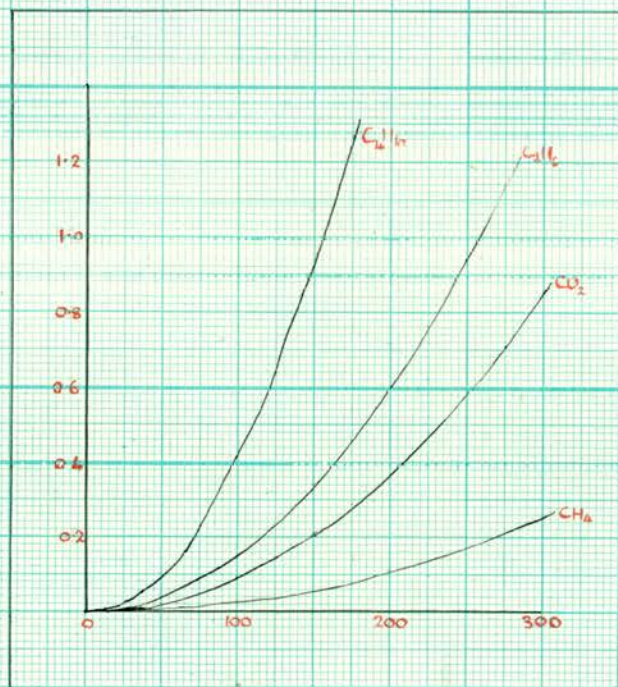
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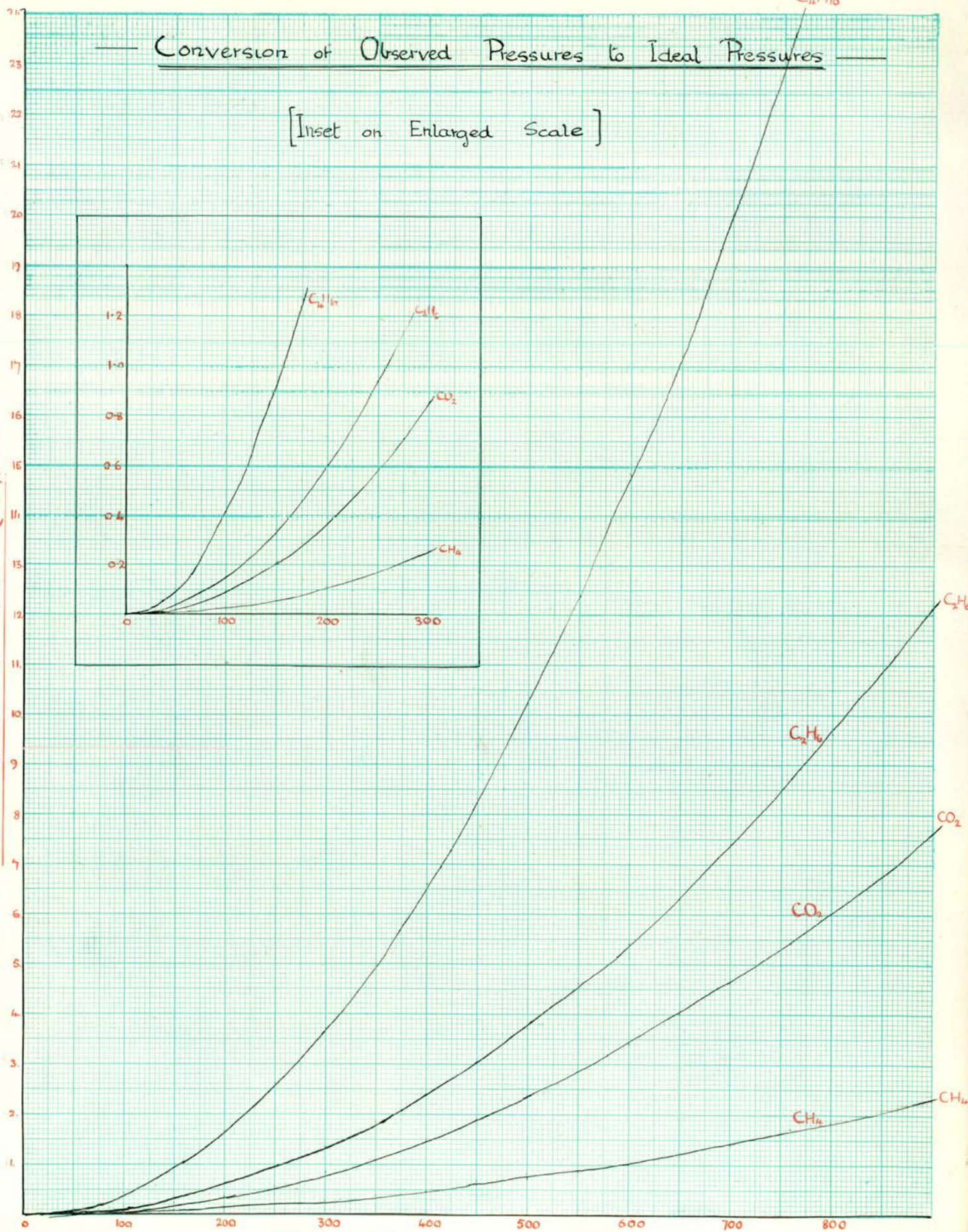
Conversion of Observed Pressures to Ideal Pressures

[Inset on Enlarged Scale]

Corrections in mm. (s).



Partial Pressures in mm. of Mercury.



APPENDIX I.Imperfection Corrections in Gas Analysis.

The effect of deviations from the gas laws on gas analysis is discussed by Broom ^[25] who gives a method of correcting for them in constant pressure analysis. The method is rather laborious, and in the case of constant volume analysis a simpler method is to plot corrections directly against partial pressure. If δ be this correction then

$$\delta = \frac{D_s - D_0}{D_0} \cdot \frac{p^2}{76} \quad \text{--- [25]}$$

where D_s = standard density at 1 atmosphere

D_0 = " " " zero pressure,
[theoretical density]

p = partial pressure of gas in cm. of mercury.

The curves for methane, ethane, butane and carbon dioxide are shown in the accompanying graph, which is plotted from the following data.

Table 32.

Gas	Standard Density D_s	Theoretical Density D_0
CH ₄	0.7168	0.7153
C ₂ H ₆	1.356	1.341
C ₄ H ₁₀	2.673	2.591
CO ₂	1.977	1.963

Equation [25] assumes that standard density varies linearly with pressure between $p = 0$ and $p = 760$.
 [31]
 Batuecas has shewn that this is a justifiable assumption for most gases.

The application of a correction to the anode carbon dioxide is unjustified in view of the method by which it is obtained.

When large amounts of saturated hydrocarbon are measured, as is the case when the gas is to be used for density determination, the correction may amount to several millimetres and is worth making. The largest corrections are those for butane.

In a flash analysis "r" and "c" may be corrected:- Suppose an ethane methane mixture has been flashed. To the "total before flash" reading δ for ethane at its known partial pressure is added: δ for methane is negligible. To the "after flash" reading δ for carbon dioxide at its known partial pressure is added.

The correction for r is thus $\delta_{C_2H_6} - \delta_{CO_2}$ [negative]
 " " c " δ_{CO_2} .

With the amounts usually employed in multiple flash analysis the "r" correction is -0.2 mm., the "c" correction +0.5 mm. This makes an appreciable difference in $\frac{r}{c}$.

APPENDIX II.Calculation of Composition from density.

The hydrocarbon residue from acetate electrolysis consists of three components, ethane, methane and nitrogen. If D_e , D_m and D_n are the standard densities of these three gases and e , m and n the fractions present, then

$$e + m + n = 1$$

$$\text{and } eD_e + mD_m + nD_n = D_s,$$

where D_s is the standard density of the mixture.

$$\text{Hence } m = \frac{D_e - [D_s - n D_e - D_n]}{D_e - D_m} \quad \text{--- [26]}$$

"n" is known from explosion analysis, hence "m" can be calculated.

For the butane-ethane mixture obtained in propionate electrolysis a similar calculation gives e , the ethane fraction.

$$e = \frac{D_b - D_s}{D_b - D_e} \quad \text{--- [27]}$$

This calculation tacitly assumes the gas laws. It is therefore strictly true only for gases whose standard density is equal to their theoretical density. As shewn in Table 32 this is not the case either with butane or ethane.

The values obtained from the first calculation]

calculation may therefore be treated as provisional, and the partial pressures of the gases in the density bulb deduced from them. The values of D_g D_m etc. at these pressures are then calculated assuming linear variation of standard density between zero pressure and atmospheric pressure [cf. Appendix I.]. These calculated density values are then used again in equation 26 or 27, as the case may be, to give the "corrected composition". [cf. p.42]

In the case of the ethane methane mixtures the correction only made an appreciable difference when the density was determined at reduced pressure. With butane ethane mixtures the correction may be considerable. In a typical density determination [Run 4] the provisional ethane percentage was 24.7 and the corrected percentage 22.2.