T H E A N O D I C O X I D A T I O N

O F C A L C I U M L A C T A T E.

AN ESTIMATION
OF THE PRODUCTS OF ELECTROLYSIS
AND AN INVESTIGATION
INTO SOME OF THE PROBLEMS INVOLVED.

BY

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CONTENTS.

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S E C T I O N 1.

INTRODUCTION.

The subject of this thesis was chosen originally as a result of a suggestion made by a manufacturer of lactic acid. Lactic acid is made by a fermentation process from molasses and the acid is extracted from the fermentation liquors as calcium lactate. The conversion of the calcium lactate back to lactic acid is a tedious process from an industrial point of view. It was therefore suggested that the conversion may be more easily accomplished by electrolysis.

The first experimental work was conducted with this object in view, but it soon became apparent that it was unlikely that lactic acid could be produced in suitable quantities for industrial purposes by this means.

There was no reference in the literature to the electrolysis of calcium lactate, and little reference to the electrolysis of lactates in general, and what there was appeared to be conflicting, so it was decided to continue the investigation into the subject in order to determine what are the products of the anodic oxidation of calcium lactate.

HISTORICAL BACKGROUND.

The Kolbe Reaction.

Of great importance in the electrolysis of the salts of organic acids is the Kolbe reaction, discovered in 1849 (1). Kolbe observed that when the salts of fatty acids are electrolysed, hydrocarbons are evolved at the anode. For example, the electrolysis of sodium acetate was found to give ethane and carbon dioxide at the anode.

This may be represented thus:-

$$CH_3.CO.O.Na$$
$$\longrightarrow \quad CH_3.CH_3 + 2\ CO_2$$
$$CH_3.CO.O.Na$$

SODIUM ACETATE — ETHANE

Traces of methyl acetate and ethylene were also found (2). At the time, this reaction was considered to be due to the oxidation of acetic acid by oxygen formed as a result of the electrolytic decomposition of water.

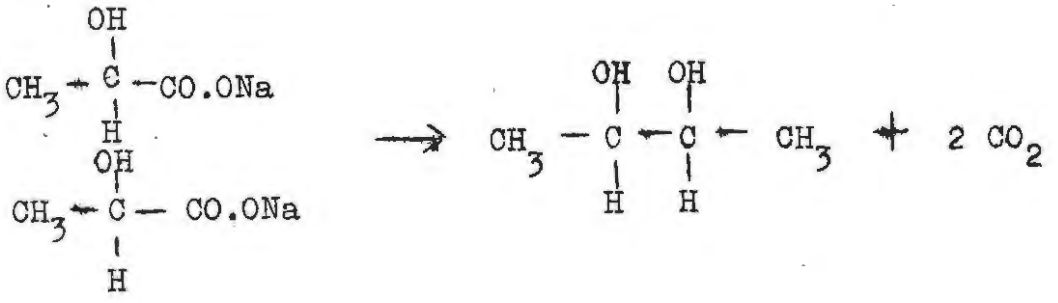
$$2\ CH_3.CO.OH + O \longrightarrow C_2H_6 + 2\ CO_2 + H_2O$$

The Kolbe reaction has since been found to be widespread. The electrolysis of salts such as sodium ethyl malonate give ethyl succinate (3), and when a mixture of the salts of two different aliphatic acids is electrolysed, the Kolbe synthesis may give rise to a mixed hydrocarbon in addition to the two hydrocarbons which would be expected if the acids were electrolysed separately (4). It was found, however, that the Kolbe reaction does not occur with the salts of dicarboxylic or aromatic acids.

James Walker (5) endeavoured to carry out the Kolbe synthesis with the salts of hydroxy acids and hoped to obtain the corresponding dihydric alcohols.

$$2\ OH.C_nH_{2n}.CO.ONa \longrightarrow (C_nH_{2n}OH)_2 + 2\ CO_2 + 2\ Na^+$$

For example, sodium lactate was expected to give butylene glycol 2,3 and CO_2 by anodic oxidation.



SODIUM LACTATE — BUTYLENE GLYCOL 2,3

However, it was found that the electrolysis of sodium lactate proceeded in quite a different manner. There was a strong smell of aldehyde. The solutions of sodium lactate, from which the aldehyde had been removed by steam distillation, were concentrated by evaporation and extracted with ether. The ethereal solutions were dried and the ether removed by distillation. According to Walker, only a few drops of liquid were left - too small a quantity for identification.

Pyruvic Acid.

Rockwell (6) electrolysed alcoholic solutions of pyruvic acid between platinum electrodes, in the presence of various quantities of:

1) NaOH
2) H_2SO_4
3) HCl
4) Na_2CO_3

Rockwell claims to have obtained lactic acid at the cathode, i.e. by cathodic reduction. Yields of up to 28% of the current theoretical lactic acid were obtained.

It was therefore felt that, if lactic acid is obtained by the cathodic reduction of pyruvic acid , it should be possible to obtain pyruvic acid by the oxidation of lactic acid. Unfortunately, pyruvic acid is itself oxidised very easily to acetic acid and carbon dioxide; thus if any pyruvic acid were obtained, the yield would be small.

Smull and Subkow (7) endeavoured to overcome this difficulty by choosing a soluble salt of lactic acid which on oxidation is converted to an insoluble pyruvate. Copper lactate was found to be most suitable. It is soluble to the extent of 6 parts per 100 in water, while copper pyruvate is practically insoluble. The aqueous copper lactate solution was electrolysed in the presence of strong copper nitrate (to increase the copper concentration) between large platinum electrodes at a current density of 40 mA. per square centimetre. The principal oxidation products were found to be acetaldehyde, acetic acid, formic acid and carbon dioxide. An insoluble green precipitate settled to the bottom of the vessel and was identified to be copper pyruvate by forming the phenyl hydrazine derivative.

This work has been severely criticised by Bradt and Fallscheer (8) who repeated these experiments and found that the green precipitate is only produced at a temperature above 60°C and does not require the passage of an electric current for its formation. Further, the precipitate was identified to be impure copper oxalate and not copper pyruvate. It was shown that the role of the current in the experiment of Subkow was merely to generate sufficient heat to bring about the chemical oxidation of copper lactate by copper nitrate.

The products of the electrochemical oxidation below 60°C were carbon dioxide, acetic acid and acetaldehyde. According to Bradt and Fallscheer, there was no

evidence of pyruvic acid in either the solution or the insoluble precipitates formed. Nor was there any evidence of formic acid as claimed by Smull and Subkow.

Electrolysis at Small Current Density.

Carpeniseanu (9) considered that if the electrolytical oxidation of lactates was carefully controlled, pyruvic acid should be obtained at the anode. Both Smull and Subkow and Bradt and Fallscheer had used large electrolysing currents, and thus it was not surprising that no pyruvates were obtained in view of the ease with which pyruvates themselves are oxidised

Carpeniseanu electrolysed a 0.01 molar solution of sodium lactate between platinum electrodes and employed a difference of potential of between 1.5 to 3.5 volts and an anode current of the order of 1 milliampere. After the electrolysis (the duration of which is not stated), a small quantity of pyruvic acid was detected by the standard colorimetric reaction with sodium nitroprusside (10). This test has been made considerably more sensitive by Carpeniseanu (11).

By plotting anode voltage/current density curves for 0.01 molar solutions of sodium pyruvate and sodium lactate, Carpeniseanu was able to show that the pyruvate and lactate ions have practically the same oxidation potentials. This explains the rapidity with which the pyruvate ion is oxidised on formation.

The following alternate reactions for the electrolytic oxidation were suggested by Carpeniseanu:

a) $CH_3CHOH.COO^- + \frac{1}{2} O_2 \longrightarrow CH_3.CO.COO^- + H_2O$

LACTATE ION. PYRUVATE ION.

b) $2\ CH_3.CHOH.COO^- \rightarrow 2\ e + CH_3.CHO + CO + H_2O + CH_3.CO.COOH$

Equation (b) was suggested because a small quantity of carbon monoxide was found in the anode gases. This mechanism could only occur if the lactate ion is actually discharged at the anode. Whether this is possible is open to conjecture. It is generally believed today that the hydroxyl ion is the only ion to be deposited on the anode from the majority of aqueous solutions.

The Effect of Concentration.

Von Miller and Hofer (12) electrolysed aqueous solutions of potassium lactate in various concentrations between platinum electrodes. The anode and cathode compartments were separated by a porous plate. The percentage composition of the anode gases for each electrolyte concentration has been recorded.

Potassium Salt/Water	% CO_2	% O_2	% CO
1:5	98	0.6	-
1:10	67 - 55.8	28 - 37	2.6 - 4
1:20	38 - 20	51.8 - 70	3.2 - 4.3

The electrolysis of the concentrated solution gave acetaldehyde and carbon dioxide at the anode, but no oxygen was evolved. However, as the dilution of the electrolyte was increased, there was a corresponding increase in the yield of oxygen. Furthermore, according to these workers, carbon monoxide makes its appearance among the anode gases at greater dilution. This point is of interest and has been fully discussed in Sub-Section 7A.

No acetic acid was detectable, but a small quantity of formic acid was found in the anode compartment. If the latter was kept somewhat alkaline, aldol and crotonaldehyde were found instead of acetaldehyde.

Alkaline Solution.

Tommila (13) carried out the electrolysis of lactic acid in strongly alkaline solution between smooth platinum electrodes. The normality of the sodium hydroxide was 5 N. After electrolysing for $3\frac{1}{2}$ hours with a current density of 1 ampere per sq. cm. and an applied voltage of 2.3 to 3.0 volts, a large variety of anode products was obtained, viz:-

O_2, CO, H_2, CH_4, C_2H_6, CH_3COOH, HCOOH, CH_3CHO and CO_2.

Furthermore, the anolyte gave a distinct reaction for formaldehyde. Thetemperature was maintained between 0^oC and 5^oC throughout.

A survey of the literature thus reveals that a variety of products may result from the anodic oxidation of lactates. These naturally depend largely upon the conditions of electrolysis. However, in some cases there appears to be some disagreement between the workers.

A summary of the end products obtained by the various workers has been included for reference purposes.

SUMMARY OF END PRODUCTS.

WORKER.	CONDITIONS.	END PRODUCTS.
Walker.	Sodium lactate.	CH_3CHO and a few drops of liquid not identified.
Smull and Subkow.	Copper lactate in presence of copper nitrate.	CH_3CHO, CH_3COOH HCOOH, CO_2, pyruvic acid.

WORKER.	CONDITIONS.	END PRODUCTS.
Bradt and Fallscheer.	Copper lactate in presence of copper nitrate:	
	a) below 60°C	CO_2, CH_3COOH, CH_3CHO. No formic or pyruvic acids.
	b) above 60°C	The above products plus $(COOH)_2$.
Carpeniseanu.	Sodium lactate	Pyruvic acid, CO_2, CH_3CHO, CH_3COOH, also a small quantity of CO.
Von Miller and Hofer.	Potassium lactate	CO_2, O_2, CO, CH_3CHO, HCOOH. (No CH_3COOH.)
	Potassium lactate in alkaline solution.	CO_2, O_2, CO, aldol, crotonaldehyde.
Tommila.	Lactic acid in 5 N sodium hydroxide.	O_2, CO, H_2, CH_4, C_2H_6, CH_3COOH, HCOOH, CH_3CHO, CO_2, (plus trace of HCHO).

S E C T I O N 2.

THE CONSTRUCTION OF THE CELL AND THE SEARCH FOR BUTYLENE GLYCOL 2,3.

It was decided to carry out a series of electrolyses similar to those performed by Walker (5) in order to determine whether butylene glycol 2,3 is produced by the electrolysis of calcium lactate. At the same time it was hoped to determine whether lactic acid is also a product of electrolysis.

It will be recalled that after the electrolysis of sodium lactate, Walker concentrated the electrolyte and endeavoured to remove the glycol (if any) by extraction with ether. The ether was evaporated off and Walker was left with a few drops of liquid - "a quantity too small for investigation."

However, butylene glycol 2,3 is only slightly soluble in ether (14). The smallness of the yield obtained by Walker may have been a direct result of the limited solubility of the glycol in ether, and therefore it was decided to seek a more suitable means of separation.

The Electrolyte.

The calcium lactate, which was used throughout these investigations, was supplied by a manufacturing firm in Port Elizabeth. It was carefully examined for anion impurities, such a chloride and sulphate, and was found sufficiently pure as not to warrant recrystallisation. Calcium lactate is only moderately soluble in the cold (approximately 1 part calcium lactate to 9 parts water (15)), but the solubility increases greatly in hot solution. No fixed solubility for a particular temperature can be given because there is a variation in solubility resulting from

the different processes of manufacture (16).

Thirty-four grams of calcium lactate, $Ca(C_3H_5O_3)_2$ 5 H_2O, was dissolved in one litre of water. This weight was arbitrarily chosen because it was the maximum amount that could be dissolved in the cold with a reasonable amount of agitation. Stronger solutions were avoided to ensure that no precipitation occurred during the electrolysis. The solution was then filtered by suction to remove a small amount of insoluble matter. The solution was thus approximately 0.11 molar with respect to calcium lactate. Solutions of this concentration were used throughout the investigation except where otherwise stated.

THE APPARATUS.

The Construction of the Cell.

Some difficulty was experienced in finding a suitable electrolysis vessel. A lipless Pyrex beaker would have been eminently suitable, but none was available. Several unsuccessful attemps were made to remove the lip from ordinary beakers. It was finally decided to remove the bottom of a reagent bottle with the aid of a diamond cutter and a hot wire. This operation prooved successful. The cut edge of the bottle was smoothed with a wire gauze.

The cell had a diameter of 8 cms. and a depth of 14 cms., excluding the slope towards the neck. The latter was permanently closed with a stopper, while a large stopper "S" was cut to the thickness of 2.5 cms. and was used to close the mouth of the cell. (See Figure 1.)

The porous pot "P" was prepared by sealing the base of a No. 4 Pyrex sintered glass crucible to a Pyrex glass tube, 12 cms. in length and 3 cms. in diameter. The disc should be sufficiently porous so as not to restrict the anode current unduly, yet it should prevent diffusion

between the anolyte and catholyte as far as possible. An alundum extraction thimble, impregnated with silicon dioxide, as used by Bradt and Fallscheer (8), was found to be too porous for this purpose.

As shown in Figure 1, the porous pot was held in position by Stopper "S".

Two pairs of electrodes were cut from platinum foil. The first had dimensions of 1 cm. by 1 cm. and the second, 1 cm. by 3 cm. All measurements were made as accurately as possible with the aid of calipers. A short length of platinum wire was sealed to each electrode and the wire in turn was sealed into soda glass tubing of 3 mm. bore. Electrical contact was made with mercury and copper wire in the usual manner.

An 8A rubber stopper was used to position the cathode in the porous pot, while a 4A stopper was fitted to the anode to facilitate its removal during the electrolysis, should the need arise (Figure 1).

Gas escape vents were provided for both the anode and cathode compartments.

The electrodes were thoroughly cleaned by boiling in concentrated nitric acid.

The Chemistry Department's D.C. power supply was used as the source of E.M.F. The applied voltage was varied from 0 to 20 volts by inserting rheostats of 70 ohms and 8.5 ohms across the source of supply. The small rheostat was included for fine adjustment. A voltmeter "V" was placed between the rheostat slide and the negative of the battery, as shown in Figure 1, to read the voltage applied to the electrodes. As this is not required to be read with any great degree of accuracy, an ordinary Sieman's voltmeter with scales, 0 - 3 volts, 0 - 15 volts and 0 - 150 volts was used. The milliameter, a Cambridge Universal testing set, was inserted to measure the anode

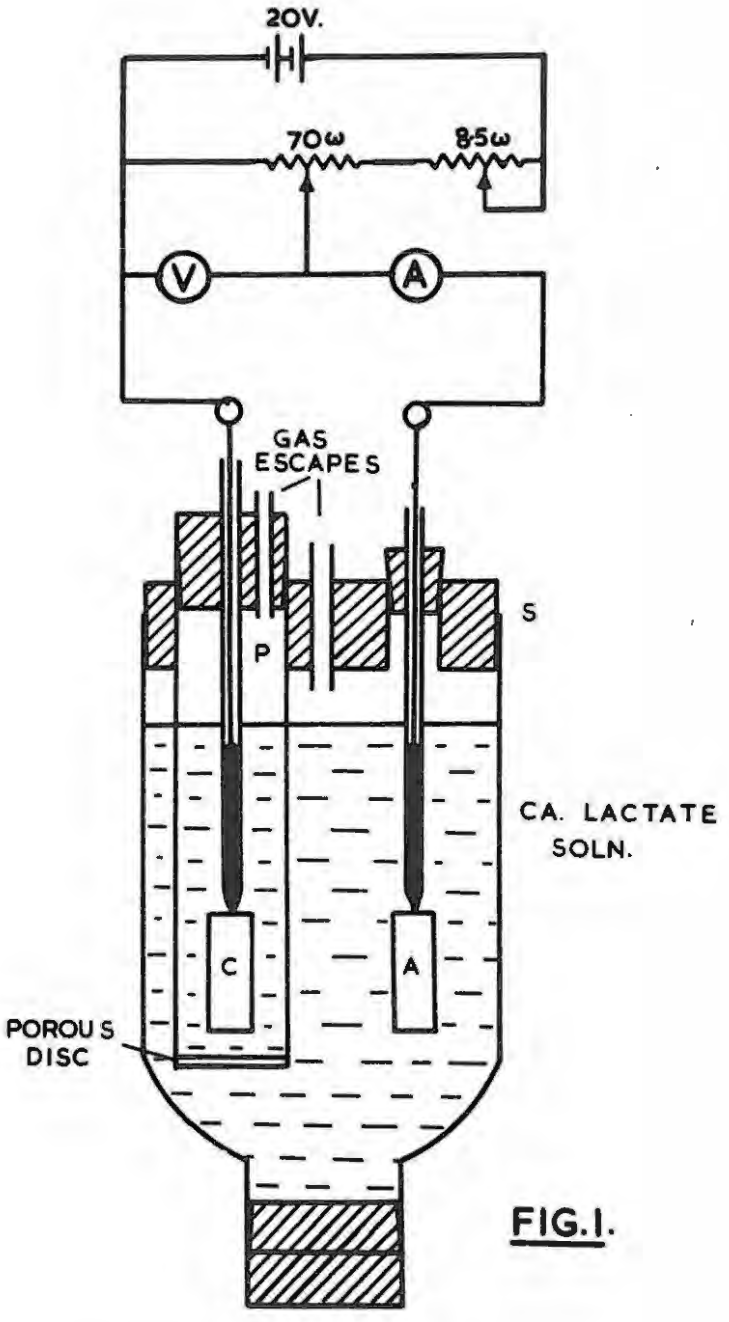


FIG.1.

ELECTROLYSIS VESSEL

current. This is an accurate instrument capable of reading a wide range of currents from 1.5 amperes to 0.5 microamperes. The accurate measurement of current was not required in this particular experiment, but was necessary for subsequent work which was performed.

The Electrolysis.

Approximately 350 ml. of the 0.1 molar calcium lactate solution was placed in the electrolysing vessel. Sufficient electrolyte was placed in the porous pot to make the liquid level coincident with that of the main solution. This ensured that there was no gravity diffusion through the porous disc.

The electrolysis was carried out with the 6 sq. cm. electrodes, the cathode being within the porous pot. An E.M.F. of 12 volts was applied initially and the current was maintained at 60 milliamperes.

At both the anode and cathode there was a vigorous evolution of gas which was allowed to escape. After a short while, the odour of aldehyde became distinctly perceptable. The electrolysis was continued for about two hours when it became evident that the cathode was slowly becoming coated with a white deposit. As the deposit thickened, the anode current gradually fell to a few milliamperes. The deposit had a crystalline appearance and could be easily scraped from the electrode. The current returned to its original value after this treatment. However, within a short period, the cathode became fully caked once more. On investigation, the cathode solution was found to be strongly alkaline. Continuous electrolysis could only be restored by replacing the cathode solution with fresh calcium lactate solution.

The alkalinity was obviously due to the formation of calcium hydroxide during the electrolysis. If carbon dioxide was evolved at the cathode, there was a possibility

that the crystalline solid was calcium carbonate.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

The deposit was proved to be a carbonate by the standard qualitative test with lime water. Oxalate was shown to be absent.

If the cathode solution was allowed to become very alkaline, a thick white turbidity slowly formed under the porous disc in the anode compartment, and eventually formed a layer on the floor of the electrolysis vessel. This behaviour was believed to be due to the diffusion of calcium hydroxide through the porous disc and its combination with dissolved CO_2 in the anolyte to form a cloud of calcium carbonate.

On testing with litmus paper, it was found that the anode solution had become distinctly acid. After six hours electrolysis at an anode current of 60 mA., the anode solution had become approximately 0.03 N with respect to acid. The electrolysis was continued for ten hours, when the anode solution, which had become approximately 0.05 N with respect to acid, was removed from the electrolysis vessel for examination. The cathode solution was replaced every two hours throughout the electrolysis.

Vacuum Distillation.

Various means of extracting ethylene glycol 2,3 in a pure form were examined.

Bulylene glycol is not volatile with steam and has a boiling point of 182.5°C at 742 mms. pressure (17). It has a melting point of 24°- 27°C and is miscible with water and ethyl alcohol but is only slightly soluble in ether (14).

Vacuum distillation appeared to be the most suitable means of first concentrating the products of

electrolysis and then isolating the glycol if any were produced.

The distillation was carried out in the usual manner using a Claisen flask of 250 ml. capacity. The aqueous distillate was condensed in a Liebig condenser and was collected in a 250 ml. distilling flask. Initially, an oil pump was used to reduce the pressure and the necessary drying and purification towers were incorporated. A simple manometer was employed to measure the pressure.

Approximately 150 ml. of the anode solution was placed in the Claisen flask. It is undesirable to use a larger volume of liquid as there is then a tendency for the liquid to "boil" over into the distilling flask. The latter was packed in ice to prevent an undue amount of water vapour from being absorbed in the drying towers.

The liquid in the Claisen flask was warmed over a water bath. It was found most convenient to maintain thetemperature between 45° and 50°C, and to regulate the pressure so that distillate came over at approximately 30° to 35°C. In this way, most of the condensation took place in the Liebig condenser.

The distillation was continued until the temperature of the distillate started to fall. This indicated that all the water had been removed. Approximately 5 ml. of viscous colourless oil remained undistilled in the Claisen flask. The oil solidified into a white mass on cooling. As expected, this rather waxy white solid contained a good deal of calcium lactate. The next step was thus to remove the oil from the calcium lactate by a further vacuum distillation. Owing to the small quantity of liquid to be distilled, a much smaller apparatus was required. The distillation was accomplished using two thick walled suction tubes. This is an ordinary Pyrex test tube fitted with a short side arm. Into the first suction tube was

placed the oil to be distilled. A thermometer, reading to 200°C, was incorporated to read the temperature of the distillate. The side arm of the first tube was fitted to the mouth of the second, while the side arm of the second tube was joined to the suction pump. The undistilled oil was warmed in a bath of glycerine, while the receptacle for the distillate was water cooled. As the glycerine bath was slowly heated, a further quantity of water was distilled off. When all the water appeared to have been removed, the receptacle was replaced and the bath temperature was further increased. At a corrected reduced pressure of 10 mms. mercury and a bath temperature of about 140°C, a colourless oil commenced to distil over. The temperature of the boiling vapour was 110°C. Approximately 1 ml. of viscous oil was collected. The bath temperature was increased to 190°C but the temperature of the distillate remained between 108°C and 112°C. A dark brown viscous liquid remained undistilled. The receptacle was replaced once more and the temperature of the bath was slowly increased to 240°C. A small quantity of amber-coloured oil was distilled but the temperature of the vapour remained constant at 109°C for a pressure of 5 mms. mercury. The distillation was then discontinued, whereupon the brown viscous residue solidified on cooling.

The Examination of the Oily Distillate.

The oil was very acidic. Two drops of the liquid required 12 ml. of 0.1 N sodium hydroxide to neutralise it. The distillate had a sweetish smell resembling lactic acid. Thus it became evident that if butylene glycol 2,3 was present at all, it could only be in small quantity.

Qualitative tests were applied to the oil, which pointed to its being lactic acid. However, the identification of the acid was reserved for a later experiment.

There was still the possibility to be considered that the oily distillate consisted of a mixture of the acid and the glycol. (Butylene glycol 2,3 boils at 182.5°C at atmospheric pressure, but no reference in the literature was found to the boiling point under reduced pressure. Unfortunately, none of this compound was available for a determination to be made.)

It was then decided to eliminate the acid by neutralisation with 6 N sodium hydroxide prior to the vacuum distillation. The acid would thus remain undistilled as its sodium salt while the glycol (if any) would be distilled over as before.

Another 150 ml. portion of anode solution was neutralised using litmus as an indicator. Water was removed under reduced pressure as before, leaving a viscous material behind. This was further vacuum distilled over the glycerine bath. As in the previous distillation a little water came over at 35°C (25 - 30 mm. mercury), but, although the glycerine bath was heated to 240°C, there was no distillation of oil. A white solid residue remained.

Thus it appeared that no butylene glycol 2,3 is produced by the electrolysis of calcium lactate under the conditions described.

Electrolysis of More Concentrated Solution.

Murray (18) has shown that the Kolbe reaction takes place only when concentrated solutions of potassium acetate are electrolysed. Using smooth platinum electrodes, Murray obtained the following results for a current density of 0.25 amperes per sq. cm.

Potassium Acetate Concentration (By Weight).	Ethane Efficiency.
60%	80%
12%	74%
3.6%	16%
0.5%	0%

In the electrolysis of calcium lactate previously described, the concentration of the electrolyte was of the order of 3.5%, excluding the water of crystallisation. It was felt, therefore, that if the concentration of calcium lactate was increased, butylene glycol 2,3 may become a product of electrolysis after all.

The solubility of calcium lactate is restricted in water at room temperature, but the solubility increases greatly with rise in temperature. It was thus decided to carry out an electrolysis at a temperature of 60°C using a more concentrated solution.

Forty grams of calcium lactate was dissolved in 350 ml. of water by warming. This gives a 10% solution approximately. The solution was placed in the electrolysis vessel, which was surrounded by a water bath to maintain the temperature at 60°C. The 6 sq. cm. electrodes were employed.

Initially, the cathode was placed in the porous pot. Six volts was applied and resulted in an anode current of 150 to 200 milliamperes. The cathode very soon became coated with a sticky white mass which consisted of calcium lactate and calcium carbonate. The electrolysis could only be maintained by changing the cathode solution repeatedly. The porous disc became clogged rapidly and required frequent cleaning. In view of these difficulties, this mode of electrolysis was discontinued.

The anode was placed in the porous pot for the subsequent electrolysis. In this case a voltage of 12 volts was applied which resulted in a current of about 280 milliamperes. Once more the temperature was maintained at 60°C. There was a vigorous evolution of gas at both electrodes, but more particularly at the cathode. After a while, a white crystalline deposit settled on the cathode but this was easily removed. The anolyte (about 50 ml. in volume) was replaced every two hours and retained for examination.

After the electrolysis, the accumulated anode solution had a normality of approximately 0.9 N with respect to acid.

150 ml. of this solution was neutralised with 6 N NaOH and vacuum distilled in the same manner as previously described. When all the water had been removed, the residue was further vacuum distilled over a glycerine bath. Although the bath was heated to 240°C, there was no evidence of any distillate.

By way of a control, it was intended to vacuum distil butylene glycol 2,3 in the presence of sodium hydroxide in order to determine whether the latter had any deleterious effect on the glycol and thereby prevent its distillation. Unfortunately, no butylene glycol 2,3 was obtainable.

To ensure that the acidic oil was produced by the electrolysis and not during the vacuum distillation, a quantity of calcium lactate solution was distilled under the same conditions as before. There was no trace of any oil.

It was thus concluded that the Kolbe reaction does not hold for the electrolysis of calcium lactate solution whatever the concentration.

SUMMARY OF SECTION 2.

1) An electrolysis vessel with porous pot and two sets of platinum electrodes were constructed.

2) Electrolyses were carried out with aqueous solutions of calcium lactate containing:

   a) 34 grams per litre
   b) approximately 117 grams per litre

   in order to determine whether butylene glycol 2,3 is formed at the anode.

3) After each electrolysis, the anolyte was vacuum distilled. A viscous oily liquid was obtained which was strongly acidic. It was shown to contain no butylene glycol 2,3.

S E C T I O N 3.

THE IDENTIFICATION OF THE ALDEHYDE.

Qualitative Tests.

A few millilitres of the anode solution in a test tube gave a strong red colour with two millilitres of Schiff's reagent. This shows the presence of an aldehyde.

(The Schiff's reagent was prepared as follows (19):-

> One gram of rosaniline salt was dissolved in 100 ml. warm water. Sulphur dioxide was passed until no further reaction occurred. The solution was filtered and the filtrate was kept as a stock solution. Ten millilitres of the stock solution was diluted to 1 litre; 50 ml. of a saturated aqueous solution of sulphur dioxide was added and the solution was allowed to stand over night.)

The smell gave no indication as to the identity of the aldehyde. In fact, it smelt rather like diluted propionaldehyde. In the first instance, the identification of the aldehyde was attempted using qualitative tests, but the concentration in the anode solution was so small that tests were not conclusive. However, some of the work done on these tests will be described for the sake of completeness.

For comparison purposes, dilute solutions of acetaldehyde, propionaldehyde and formaldehyde were prepared of approximately the same strength as the anode solution. This was done colorimetrically, using Schiff's reagent.

The first test was that of sodium nitroprusside in the presence of sodium hydroxide (20). To two millilitres of each of the aldehyde solutions was added an equal volume of 0.5% aqueous sodium nitroprusside, followed by 5 drops of aqueous sodium hydroxide.

Formaldehyde and propionaldehyde solutions gave a clear yellow solution. Acetaldehyde solution gave a pale amber solution. The anode solution gave a pale amber solution similar to that for acetaldehyde. The amber colour faded fairly rapidly and finally gave a colour intermediate between the amber and the yellew.

This inconclusive test therefore suggested acetaldehyde.

Ammoniacal silver oxide was used in the next test. This was prepared by the addition of 1 ml. sodium hydroxide to 1 ml. silver nitrate solution followed by ammonium hydroxide until the precipitate just disappeared. A few drops of ammonical silver oxide was added to:-

1) Calcium Lactate Solution. No blackening, even on standing.
2) Anode Solution. Slight blackening commences after about 10 seconds.
3) Formaldehyde Solution (approximately 1/500 dilution). The solution turns black immediately.
4) Acetaldehyde and Propionaldehyde Solutions turn black comparatively slowly.

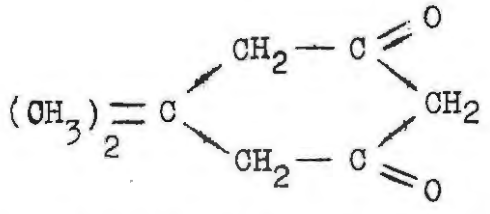
The blackening of the anode solution was slightly faster than that for acetaldehyde and propionaldehyde but was far slower than that for the formaldehyde solution.

This test thus suggests that principal aldehyde formed at the anode is not formaldehyde although a trace may be present.

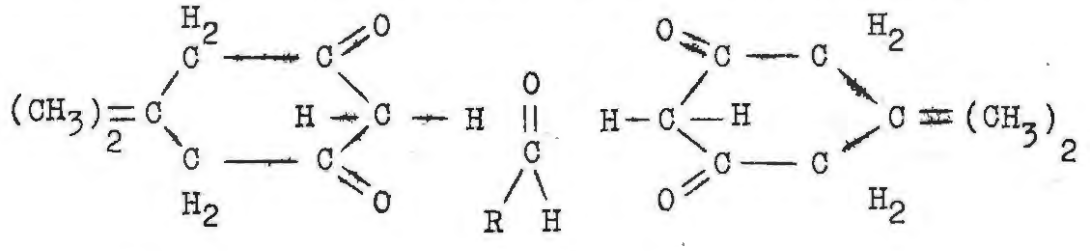
Preparation of an Addition Product.

Although the spot tests suggested that the aldehyde formed at the anode was acetaldehyde, it was decided to confirm the identity of the aldehyde by the preparation of an addition compound with a characteristic melting point. The use of dimethyl dihydro-resorcinol or "Methone" appeared to have the best possibilities as the derivatives are easy to prepare and have widely differing melting points (21), (22), (23). This is important when there is a possibility of there being a mixture of aldehydes.

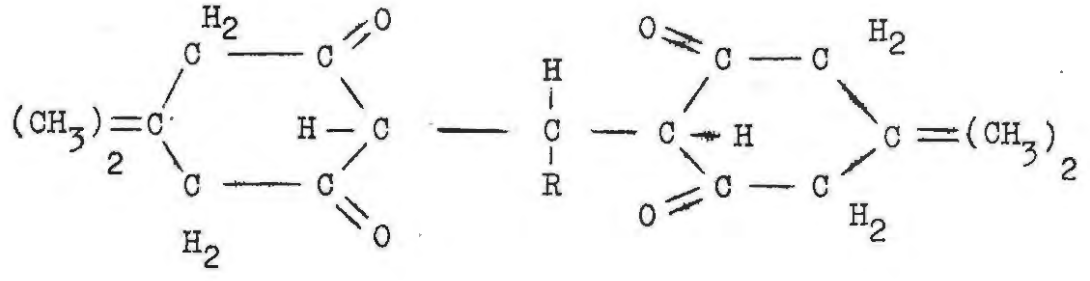
Dimethyl dihydro-resorcinol has the formula:



When a saturated solution of this compound is added to an aqueous solution of an aldehyde, two molecules of "Methone" combine with one of the aldehyde thus:



to form



The saturated solution of the precipitant was obtained by boiling half a gram of "Methone" with 100 ml. of distilled water. The solution was filtered after cooling.

Dilute solutions of formaldehyde, acetaldehyde and propionaldehyde were prepared of approximately the same aldehyde concentration as the anode solution.

Twenty millilitres of the saturated "Methone" solution was added to approximately 20 millilitres of the aldehyde solutions in turn. The solutions were allowed to stand.

Formaldehyde.

The derivative formed rapidly as a white needle-like precipitate. This was filtered and washed thoroughly with water and dried in an oven at 100°C.

The melting point of the precipitate was found to be 189°C. (Repeated twice.)

This value corresponds exactly with that of Vörlander (21).

Acetaldehyde.

The derivative formed slowly, was flocculent and settled to the bottom of the beaker. The precipitate was filtered, washed and dried at 100°C in an air oven.

The melting point of the derivative was found to be 140°C and 141°C. (Repeated twice.)

This agrees with the values obtained from the literature:

139°C (21), 140°C (24), 141°C (25).

Propionaldehyde.

This derivative formed more quickly than the acetaldehyde derivative. The precipitate tended to float on the surface of the liquid and had a gelatinous appearance.

The precipitate was treated as described above. After drying, it had the appearance of shiny leaflets and a melting point of 154°C and 153°C. (Repeated twice.)

Vörlander obtained leaflets from alcohol with a melting point of 154°C to 156°C. Another worker obtained 155°C (24).

Anode Solution.

A white precipitate formed on standing which settled to the bottom. This was filtered, washed with water and dried at 100°C in an air oven. This derivative had a melting point of 141°C.

A mixed melt between the anode solution derivative and the acetaldehyde derivative gave no depression in melting point.

The anode solution derivative was recrystallised twice from 95% alcohol and gave a melting point of 142°C. When recrystallised from acetone, the derivative had a melting point of 139°C.

Calcium Lactate.

Calcium lactate solution gave no precipitate with "Methone".

The cathode solution also gave no precipitate.

It was therefore decided without doubt that the aldehyde resulting from the anodic oxidation of calcium lactate is acetaldehyde.

The fact that the melting point of the anode solution "methone" derivative corresponded closely with that of the pure acetaldehyde derivative suggests that no other aldehydes are produced.

It will be recalled that Von Miller and Hofer (12) obtained crotonaldehyde when potassium lactate was electrolysed in alkaline solution. (The melting point of crotonaldehyde methone is 183°C (21)).

Tommila obtained a small quantity of formaldehyde when he electrolysed lactic acid in 5 N sodium hydroxide.

SUMMARY OF SECTION 3.

1) Qualitative tests were performed on the anolyte in order to determine the aldehyde formed during the electrolysis of calcium lactate. Although these tests pointed to the aldehyde being acetaldehyde, the tests were considered to be inconclusive, owing to the large dilution of the aldehyde in the anolyte.

2) The identity of the aldehyde was proved to be acetaldehyde by preparing an addition product with dimethyl dihydroresorcinol, which had the characteristic melting point of the acetaldehyde derivative.

S E C T I O N 4.

THE IDENTIFICATION OF THE ACIDS.

350 millilitres of the calcium lactate solution was electrolysed in the same manner as described in Section 2. The cathode was placed in the porous pot and, after ten hours electrolysis at an anode current of 60 mA., the anode solution was found to be 0.05 N with respect to acid. (The cathode solution was replaced every two hours.) Attempts were made to identify the acid or acids by qualitative means, but the dilution of the acids was too great to allow of reliable identification.

Means were thus sought to increase the acidity of the anolyte, without prolonging the length of the electrolysis unduly. This was satisfactorily accomplished by placing the anode in the porous pot. In this way the deposition of calcium carbonate on the cathode was delayed indefinitely, due to the larger volume of the cathode solution. The anode solution, about 50 ml. in volume, was replaced every two hours and stored in a stoppered bottle. Since a large quantity of anode solution was required, the electrolysis was continued until a litre had been collected.

Simple Qualitative Tests.

The solution was found to be 0.25 N with respect to acid. A 20 ml. portion of the anode solution was exactly neutralised by boiling with a slight excess of ammonium hydroxide. The excess ammonium hydroxide was boiled off with the aid of litmus paper. A clear light yellow solution was obtained when 1 ml. of the anode solution was treated with an equal volume of 0.15 N ferric chloride solution. This is indicative of the presence of hydroxy acids or oxalic acid. Aliphatic monobasic acids

such as formic, acetic and propionic acids give a clear red-brown coloration with ferric chloride, so it appeared from this qualitative test that none of these acids is produced by the electrolysis. (This was subsequently proved to be incorrect.)

Oxalic acid was shown to be absent. There was no trace of a precipitate which might possibly have been calcium oxalate.

Tests for tartaric, malonic and glycollic acids were negative.

Even if no lactic acid was present, the above-mentioned test for lactic acid would be positive, due to the presence of lactate ions in solution.

Vacuum Distillation.

These qualitative tests being inconclusive, it was decided to vacuum distil the anode solution. In this manner the volatile acids, which would be found in the distillate, would be separated from the non-volatile acids, which would be found in the residue.

The vacuum distillation was carried in the same manner as described in Section 2. Portions of 150 ml. were distilled at a time. Approximately 25 grams of the white waxy residue was obtained from the litre of anode solution. (For purposes of reference, this substance has been called the "waxy solid" in the text.) The aqueous distillate was retained for further investigation. (Called Portion "A".)

The white "waxy solid" melted easily, when warmed to about 50°C, to form a viscous colourless liquid. Calcium lactate forms an acid lactate with lactic acid which crystallises in fibrous masses. Thus, it was possible that the "waxy solid" was an acid-lactate.

Approximately 15 grams of the white "waxy solid" was vacuum distilled over a glycerine bath using a suction

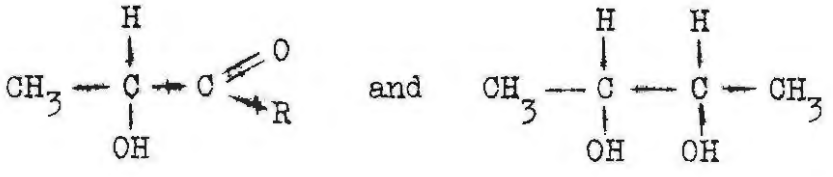
tube apparatus, as described in Section 2. The same conditions of temperature and pressure were observed as previously described. About 8 ml. of viscous oil was distilled over at a vapour temperature of 110°C and a pressure of 6 mm. of mercury. This distillate was labled Portion "B", while the involatile residue, which was dark brown in colour and hardened on cooling, was labled Portion "C".

Examination of Portion "B". (The Oily Distillate.)

In the course of the examination for butylene glycol 2,3, as described in Section 2, the oily distillate was found to be very acid, i.e. 8 N. Denige's test (27) for lactic acid and lactates was applied and gave strongly positive results. This test is sensitive and is based on the formation of acetaldehyde when lactic acid or lactates are treated with concentrated sulphuric acid and warmed to 100°C. To the cold mixture, a few drops of a 2% alcoholic solution of guaiacol is added. The acetaldehyde so formed results in a rose-red coloration. The heat of reaction of the sulphuric acid on the aqueous solution is usually sufficient to obviate the need of further heat.

Any compound which produces acetaldehyde as a result of the action of sulphuric acid will, of course, give a positive test.

Compounds such as the undermentioned fall into this category (28).



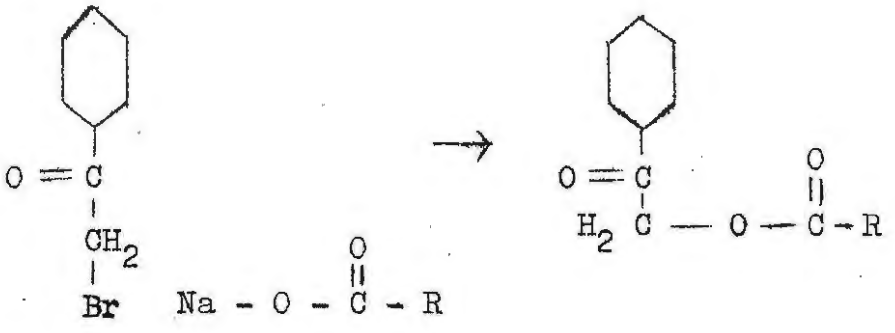
and

BUTYLENE GLYCOL 2,3.

Although it seemed most probable that the oil would prove to be lactic acid, it was decided to form an addition compound of the acid with a characteristic melting point, in view of the fact that other compounds give the guaiacol test.

Phenacyl bromide (29), p bromo phenacyl bromide (30) (31), p iodo phenacyl bromide (30) (31) and para-phenyl phenacyl bromide (32) are extensively used for the identification of a wide range of acids. Furthermore, they are especially suited for the identification of lactic acid which is difficult by most other means. Phenacyl bromide was chosen as the precipitant in this case for the simple reason that a quantity of this substance was available in the Department stores and required little purification.

The general procedure for the use of precipitants of this nature is to prepare the sodium salt of the acid to be identified. This is fluxed for several hours with the bromide to form the corresponding phenacyl salt of the acid, thus:-



PHENACYL BROMIDE

Although, according to Reid (29), the purity of the phenacyl bromide is not important, the sample available was recrystallised from hot alcohol. White shiny plates were formed, whereas before recrystallisation, the compound had a dirty brown appearance. The melting point

was 50°C which agrees exactly with the accepted value.

In order to standardise the method and to prepare a standard sample of the addition product, the instructions of Reid (29) were followed using stock dl. lactic acid.

To prepare the sodium salt of the acid, 0.7 grams of lactic acid (1/200 gram molecular weight) was treated with slightly less than the amount of sodium carbonate required to neutralise the acid in a 75 cc. conical flask. Five ml. of water was added to effect solution. After the reaction had ceased, 1 gram of phenacyl bromide was added together with 10 ml. of 95% ethyl alcohol. The mixture was refluxed over a water bath for at least an hour. The solution was then cooled rapidly under a tap. As no precipitate formed, 10 ml. of water was added, which resulted in an immediate white milkiness. The solution was allowed to stand over night, whereupon white crystals formed, which were filtered and washed with 37% alcohol. (According to Reid, the precipitate should always be washed with alcohol of the same strength as that used for its preparation.) The precipitate was obviously impure and had a melting point of 70°C. Under the above conditions of precipitate formation, the melting point should be 91°C. Recrystallisation from 37% alcohol produced no change in the melting point. A repeat preparation produced crystals of melting point 60°C. It was soon realised that the precipitate impurity was due to the fact that an excess of phenacyl bromide was being employed, with the result that the product was a mixture of phenacyl bromide and phenacyl lactate. The discrepancy was thought to have arisen from the fact that concentrated lactic acid is very hydroscopic, and that the stock sample of acid used had absorbed a good deal of water.

For the purpose of the next preparation, the proportions of lactic acid and sodium carbonate were

doubled. It was also found that improved yields of the addition product were obtained if the time of refluxing was doubled. After cooling, 30 ml. of water was added to the mixture. No precipitate formed, but the solution turned milky. Small brown particles of obvious impurity were filtered from the solution before the precipitate had an opportunity to form. On standing, while crystals formed which were washed with 27% alcohol (35 ml. water plus 10 ml. 95% alcohol). The precipitate which was very white, melted between 92°C and 93°C. It was recrystallised from 2 ml. of 27% alcohol and this product had a sharp melt of 94°C. Further recrystallisation did not result in any improvement in purity.

The procedure finally adopted for the preparation of the standard phenacyl lactate derivative was as follows:-

> Approximately 1.5 grams of stock lactic acid was added to approximately 0.5 grams of anhydrous sodium carbonate, together with 5 ml. of water. When the reaction was complete approximately 1 gram of phenacyl bromide was added to the conical flask followed by 10 ml. of 95% alcohol. The mixture was refluxed for two hours, after which another 30 ml. of water was added. The solution was then filtered to remove any undesirable impurity. In order to speed up the precipitation, the solution was placed in a refrigerator for half an hour. There was invariably a heavy crop of crystals which was filtered and washed with 27% alcohol and recrystallised from the same solvent. This procedure consistently

gave crystals of constant melting point for the store lactic acid derivative.

Owing to the higher concentration of the anode product, only 1.2 grams of Portion "B" was used when preparing the corresponding derivative of the anode acid, using the above procedure. This derivative had a melting point of 95°C to 95.5°C after one recrystallisation from 27% alcohol.

The result that the melting point of the anode acid derivative was higher than that for the stock lactic acid was rather surprising. It appeared, therefore, that the stock acid was impure.

Vacuum Distillation of the Stock Lactic Acid.

It was therefore decided to vacuum distil a small quantity of the stock lactic acid, using the same apparatus as was used for the distillation of the anode product.

Water was distilled over initially with a bath temperature of 130°C, oil commenced distilling over at a vapour temperature of 92°C. The reduced pressure was 8 to 9 mms. of mercury. As the temperature of the bath increased from 130°C to 140°C, the temperature of the distilling vapour gradually rose to 100°C and finally to 110°C. The distillate came over very slowly at this temperature. At a bath temperature of 170°C, the distillate temperature had finally risen to 115°C. The distillation was discontinued at this stage. A colourless residue remained which formed a white emulsion when mixed with water. The residue was possibly lactide as this substance is known to be sparingly soluble in water.

The phenacyl derivative of the newly distilled portion of the stock lactic acid was prepared in the same manner as previously described. The crystals

thus obtained had a sharp melting point of 95°C after one recrystallisation from 27% alcohol.

A mixed melt was taken between the standard derivative and the anode acid derivative. This occurred sharply at 95°C, showing that the major acid produced as a result of the electrolytic oxidation of calcium lactate is indeed lactic acid.

Physical Properties of Lactic Acid, (Portion "B").

Equivalent Weight.

Owing to its hydroscopicity, it was necessary to employ a freshly distilled sample of Portion "B" when determining its equivalent weight. The freshly distilled liquid was stored in well stoppered vessels, and contact with the atmosphere was avoided as far as possible.

Approximately 0.3 grams of Portion "B" was weighed into a conical flask; about 20 ml. distilled water was added and the acid was titrated with standardised 0.1 N NaOH solution. (In duplicate.)

The values obtained for the equivalent weight were:-

99.7
99.8

The theoretical equivalent weight for lactic acid is 90, but the figure obtained experimentally is always higher, due to the presence of varying quantities of lactide (33).

From the above result, it would appear that the newly distilled Portion "B" lactic acid contained approximately 10% lactide.

Refractive Index.

The refractive index of Portion "B" was found to be 1.4350 at 23°C.

The optical activity of the acid was found to be zero.

Examination of Portion "A", (Aqueous Distillate).

This solution was found to be approximately 0.05 N with respect to acid. The Denige's test (27) for lactic acid or lactates gave negative results. Qualitative tests were used to identify the acid found in the aqueous distillate. A neutral ammonium solution of the aqueous distillate was prepared. This gave a pale wine-red coloration with 0.15 ferric chloride, which indicates the presence of one or more of formic, acetic or propionic acids in small concentration.

In order to obtain more satisfactory tests with the salt of the acid in greater concentration, approximately 150 ml. of Portion "A" was almost neutralised with approximately 0.1 N sodium hydroxide and was vacuum distilled to remove a large proportion of the water. The more concentrated neutral solution gave a much deeper amber-red colour with ferric chloride and the identification of the particular aliphatic acid was permitted.

To one millilitre of the neutral solution was added one ml. of silver nitrate. There was no reduction, but on standing, a very slight darkening of the solution occurred.

Control solutions of acetic and formic acids were prepared of approximately the same acid strength as the concentrated solution of Portion "A". The neutralised solution of formic acid gave immediate reduction with silver nitrate, whereas the netralised acetic acid solution behaved in a similar manner to that of Portion "A". Thus it was shown that formic acid was absent. The amyl alcohol test for propionic acid was also negative, so it was concluded that the acid found in the aqueous distillate (Portion "A") was acetic acid.

The Origin of the Acetic Acid.

Once the presence of lactic acid had been established in the anode solution, it was of importance to determine whether the acetic acid found in the aqueous distillate (Portion "A") was produced by the electrolysis or as a result of the vacuum distillation. It will be recalled that the ferric chloride test gave no indication of acetic acid in the undistilled anode solution. This appeared to indicate that the acetic acid found in the aqueous distillate was produced during the process of vacuum distillation. However, the source of the acetic was proved conclusively and simply by the performance of a control vacuum distillation of a calcium lactate solution containing added lactic acid in the same concentration as that found in the anode solution after electrolysis. The same conditions of bath temperature and reduced pressure were observed, i.e. 40°C and 50 mms. mercury. No acetic acid was found in the distillate which indicates that the acetic acid is not produced as a result of the vacuum distillation of lactic acid or calcium lactate. In order to demonstrate, likewise, that the acetic acid found in Portion "A" is not produced by the oxidation of acetaldehyde during the distillation, a similar control distillation was carried out on a lactic acid/calcium lactate solution containing a measured quantity of dilute aqueous acetaldehyde solution. Aqueous acetaldehyde solutions sometimes contain a certain amount of acetic acid, but this was estimated before the distillation and was allowed for. Analysis of the distillate showed that the acetaldehyde in the solution is removed completely from apparatus and is not oxidised to acetic acid by the distillation.

It was therefore concluded from these experiments that acetic acid is a product of the anodic oxidation of calcium lactate.

The Residue, (Portion "C").

The brown residue contained a small amount of undistilled lactic acid and had an odour reminiscent of burnt sugar. It was sparingly soluble in water and alcohol.

If calcium lactate is heated, it loses a molecule of water and, at 250°C, forms a tumified mass containing calcium dilactylate (BEIL. III 279).

$$O(CH.CH_3.COO)_2Ca$$

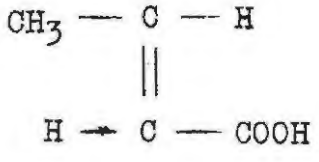
This substance is sparingly soluble in water and alcohol. It was therefore considered probable that the residue (Portion "C") contained a certain amount of calcium dilactylate.

Examination of the Waxy Anode Product for Other Acids.

The concentrated waxy anode product, which had been obtained by distilling off water and which contained calcium lactate and lactic acid, appeared to be an ideal medium on which to carry out tests for other non-volatile acids. The acids sought, in particular, were crotonic and pyruvic acids.

Crotonic Acid.

Von Miller and Hofer (12) claimed to have obtained crotonaldehyde when electrolysing potassium lactate in alkaline solution. Although it did not seem clear how this acid could possibly be formed, it was decided to seek this acid in the concentrated anode product.



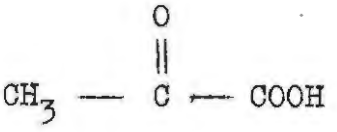
CROTONIC ACID

Crotonic acid adds on bromine across the double bond very easily. Dilute bromine water is decolourised when added to crotonic acid. This therefore affords a simple test for the acid.

0.2 grams of crotonic acid was dissolved in a litre of water. Using this crotonic acid solution for comparison purposes, semi-quantitative decolourising tests were carried out on the waxy anode product.

The tests indicated that, if crotonic acid was present at all, it was present in concentration not greater than 1 part per 4,000 in the waxy anode product, or 1 part in 600,000 in the anode solution. Thus crotonic acid was virtually absent.

Pyruvic Acid.



The standard test for pyruvic acid is that of Simon (34). The acid, when dissolved in concentrated ammonia and treated with a concentrated aqueous solution of sodium nitroprusside, slowly gives a characteristic violet blue or greenish colour. The addition of strong potassium hydroxide changes the colour to red, while acetic acid reverts the colour to blue once more.

Inconclusive results were obtained when this test was applied to the waxy anode product. This was due largely to the insensitivity of the test. However, the method of Simon has been considerably improved by Carpeniseanu, who found that much greater sensitivity was attained by using more dilute reagents (35).

According to Carpeniseanu, the method can be made quantitative with an accuracy of 5% by using standard sodium pyruvate solutions for colorimetric comparison purposes.

Solutions Required.

1) Acetic Acid Solution:- 40 parts glacial acetic acid to 60 parts water.

2) Sodium Nitroprusside Solution:- Freshly prepared 1% aqueous solution.

3) Ammonium Hydroxide:- Density 1.18 grams per cubic centimeter.

4) A standard Sodium Pyruvate Solution was prepared by weighing out approximately 0.6 grams, sodium pyruvate, and making to 1 litre. The standard solution has been referred to as Solution "P".

Pyruvic acid is not a good standard because the reagent decomposes into ∝ keto ∮ valero lactone ∮ carboxylic acid on standing. (BEIL. XVIII, 451.)

Procedure.

Two grams of the waxy anode product were dissolved in 20 ml. of water. This solution was called Solution "Q".

To 2 ml. of Solution "Q" was added:-

0.5 ml. of the acetic acid solution
1.0 ml. of the sodium nitroprusside solution
1.5 ml. of the NH_4OH solution, in the order given.

On standing, a very distinct green coloration was obtained which confirmed the presence of pyruvic acid in the anode product. It was also proved by control experiments that the distinctive green colour was not produced by any of the other compounds known to be present in the anode solution.

In order to obtain an estimate of the quantity of pyruvate present in the solid anode product, the colorimetric procedure described by Carpeniseanu was employed. Using a microburette, the following solutions were buretted into test tubes of uniform bore:

1) 2.0 ml. distilled water
2) 1.8 ml. " " + 0.2 ml. standard Solution "P"
3) 1.6 ml. " " + 0.4 ml. " " "
4) 1.4 ml. " " + 0.6 ml. " " "

etc., etc.

9) 0.4 ml. distilled water + 1.6 ml. standard Solution "P"
10) 0.2 ml. " " + 1.8 ml. " " "
11) 0.0 ml. " " + 2.0 ml. " " "
12) 2.0 ml. of Solution "Q".

To each of the test tubes was added the acetic acid, sodium nitroprusside and ammonia in the same quantity and order as described previously. The tubes were then allowed to stand for at least an hour, when the depth of green colour was examined through the length of the tube against a white background.

As a result of this analysis, pyruvic acid was calculated to be present in the waxy anode product to the extent of 0.95% by weight and to account for 1.56% of the acidity.

Expressed in a different manner; when 350 ml. of the calcium lactate solution was electrolysed for 5 hours at a total anode current of 60 mA., using 6 square

cm. electrodes, pyruvic acid was produced to the extent of approximately 1 part per 40,000 of the anode solution.

This corresponds to an efficiency of production of 0.0085 gram equivalents per Faraday.

SUMMARY OF SECTION 4.

1) Electrolyses were carried out with the anode in the porous pot in order to obtain a more concentrated anode solution. This was replaced every two hours and had a normality of 0.25 N with respect to acid.

2) The anode solution was vacuum distilled in order to separate the easily volatile acids from the less volatile acids.

3) The aqueous distillate was found to contain acetic acid, which was also shown to be a product of the electrolysis.

4) The less volatile acid, or oily distillate, Portion "B", was identified to be lactic acid by the formation of an addition compound with a characteristic melting point.

5) The application of the more sensitive test of Carpeniseanu revealed the presence of small quantities of pyruvic acid, together with the lactic acid.

6) Other acids such as formic, oxalic and glycollic were shown to be absent. Crotonic acid may be present as a trace.

S E C T I O N 5.

ENDEAVOURS TO INCREASE THE YIELD OF LACTIC ACID.

In the previous section, lactic acid was shown to be a product of the electrolysis of calcium lactate. If this process is to have any industrial significance, however, it is essential to increase the yield of the acid. Some investigations were carried out, therefore, with this object in view.

The principal reason for the poor acid yield was, undoubtedly, the high electrical resistance of the solution which resulted in a low anode current. Semi-quantitative tests were performed to determine the total acidity of the anolyte after a definite anode current had been discharged. These results revealed that, although the total yield of acid was small, the efficiency of production was over 50%. As indicated previously, the conductivity of an aqueous solution of calcium lactate is limited by the poor solubility of this salt in the cold.

The following methods of reducing the electrical resistance between the electrodes were investigated:-

1) An increase in the electrode area.

2) An increase in the concentration of calcium lactate.

3) Means of preventing the formation of calcium carbonate in the cathode compartment.

1) An Increase in the Electrode Area.

Owing to the cost of the foil, the construction of platinum electrodes, larger than those already in use, was not entertained. Furthermore, the influence of electrode size could be gauged fairly accurately from a comparison of the yields of lactic acid for the two sizes of electrodes already constructed.

TABLE 1.

Current in mA.	Electrode Area in sq. cm.	Time of Electrolysis in mnts.	Vol. Anode Soln. in ml.	Acidity of Anode Soln.	Gram Equivs. Acid	Percentage Acid increase
40	2	300	344	0.0140	0.0048	
40	6	300	340	0.0159	0.0054	12.5%
50	2	420	338	0.0206	0.00706	
50	6	420	342	0.0224	0.00775	9.9%
60	2	270	348	0.0185	0.00643	
60	6	270	344	0.0209	0.00719	11.8%

Table 1 has been compiled at random from Table XIV, Section 7D and serves to illustrate that when the electrode area is increased from 2 sq. cm. to 6 sq. cm., there is an increment of approximately 10% in the total acidity of the anolyte. Cheaper electrode materials such as copper, aluminium, nickel, iron and lead were investigated, but in all cases the anode rapidly went into solution. There was invariably a large evolution of gas at the cathode. However, no tests were carried out using graphite as the electrode material. This substance may provide more promising results.

2) Increase in Electrolyte Concentration.

The solubility of calcium lactate in water increases markedly with temperature. By immersing the electrolysis vessel in a water bath maintained at a temperature of 60°C, it was possible to treble the concentration of the electrolyte, without causing precipitation.

For the purposes of this experiment, 115 grams of calcium lactate was dissolved in a litre of water. Gentle heat was applied to effect solution, and this 0.3 molar solution was employed as the electrolyte. Using the 6 sq. cm electrodes and an applied voltage of 12 volts, the initial current was found to be 280 mA. (It will be recalled that under the same conditions of applied voltage and electrode size, the 0.1 molar solution at room temperature gave an anode current of 60 mA.. (Section 2.))

Initially, the cathode was placed in the porous pot, but within minutes the cathode compartment had become choked with calcium carbonate and the anode current fell almost to zero. By placing the anode in the porous pot, it was possible to maintain the anode current at a more satisfactory value, although it did fall steadily due to the formation of a crystalline deposit on the cathode. The crystalline deposit was easily removed at regular intervals by scraping. The anolyte was replaced every two hours and was found to have a normality of 0.9 N with respect to acid. Thus the acidity of the anolyte was trebled approximately by increasing the molarity of the electrolyte threefold and thereby increasing the anode current.

The anode current could be increased further by using a pot of greater porosity, but this procedure resulted in an increased degree of streaming between the anolyte and catholyte. This, to a large extent, offset the improvement in the acid yield resulting from the higher anode current.

3) The Removal of Calcium Carbonate from the Catholyte.

A possible remedy to the fall of the anode current caused by the deposition of calcium carbonate on the cathode appeared to lie in the removal of the deposit by chemical means. It was decided to accomplish this by the addition of regulated quantities of dilute sulphuric acid to the cathode compartment in order to maintain the neutrality of the catholyte.

The electrolysis was carried out using the 0.1 molar solution. The anode was placed in the porous pot, while a piece of litmus paper was allowed to dip into the catholyte in order to indicate when the acid was required. The 6 N sulphuric acid, which was used for the purpose, was added drop by drop. When the catholyte became slightly alkaline, a deposit commenced to form on the cathode, but this was removed immediately on the addition of acid. In this manner the current was maintained between 300 and 400 milliamperes throughout the electrolysis. The anode solution was changed every 1½ hours and was retained for examination. A heavy white precipitate of calcium sulphate settled to the bottom of the cathode compartment.

The anode solution was found to be approximately 1.2 N with respect to acid. It was thus more acidic than any of the anode solutions hitherto obtained, but it was also found to contain a certain amount of sulphuric acid. This result was not unexpected, as some of the current was bound to have been carried by the sulphate ions which would naturally migrate to the anode compartment.

A portion of the anode solution was concentrated by vacuum distillation in the normal manner. Several millilitres of a viscous liquid remained undistilled which was highly acidic. However, any attempt at further distillation over a glycerine bath failed completely, even when the bath was heated to 240°C. There was no sign of

an oily distillate. It was observed, however, that when the glycerine bath reached a temperature of about 100°C, the colourless oil turned a dark brown and became viscous. It solidified into a hard brown cake on cooling. It is thus possible that, in the presence of sulphate ions, the lactic acid undergoes some form of polymerisation at this temperature. Lactide may even be formed. Although an attempt was made to remove the sulphuric acid as barium sulphate, it was still found impossible to effect a distillation.

There remained the possibility that the lactic acid was oxidised to acetic acid during the distillation process, but an examination of the aqueous distillate showed that acetic acid production was normal.

SUMMARY AND CONCLUSION.

1) Several methods of increasing the yield of lactic acid, resulting from the electrolysis of calcium lactate, have been investigated.

2) Of the electrode materials examined, platinum appears to be the only one which does not go into solution.

3) The production of acid is favoured by an increase in electrode area.

4) By maintaining the temperature of the electrolyte at 60°C, it was possible to increase the molarity threefold, and thereby increase the yield of acid by a corresponding amount.

5) Attempts to increase the acid yield by neutralising the catholyte proved unsuccessful.

CONCLUSION.

Under the most favourable conditions, using 6 sq. cm. electrodes and an applied voltage of 12 volts, a

maximum anode current of 0.5 amperes was attainable, but this current could not be maintained for any length of time.

With these limitations in mind, it appeared unlikely that this process could be employed profitably for the industrial manufacture of lactic acid.

S E C T I O N 6.

ANODE VOLTAGE AND CURRENT DENSITY DETERMINATIONS.

INTRODUCTION.

A tool frequently used to study electrolytic reactions is to plot anode voltage/current density curves. These, if properly interpreted, shed light on the actual reactions occurring at the anode.

The decomposition potentials of a number of normal solutions of mineral acids and alkalies were first studied by le Blanc (36). Using smooth platinum electrodes, the decomposition potentials were all found to be in the vicinity of 1.7 volts, with the exception of hydrochloric acid. From this evidence it was assumed that a fundamental electrolytic reaction occurred in each process. This was believed to be the discharge of hydrogen ions at the cathode and hydroxyl ions at the anode. From such evidence, it is the general belief today, that in the vast majority of electrolytic reactions in aqueous solution, no ions, other than hydroxyl ions, are discharged at the anode.

The Kolbe reaction has received a good deal of attention, particularly with regard to the electrolysis of acetates (37), (38), (39), (40), (41).

Preuner and Ludlam (37) plotted anode voltage current density curves for the electrolysis of mixtures of potassium acetate and acetic acid and found a break in the curve corresponding to an anode potential of 2.54 volts. They showed that at this voltage, ethane evolution commenced and oxygen evolution started to diminish. In other words, the Kolbe reaction commenced at this anode voltage.

Shukla and Walker (40) confirmed the existence of a definite potential for the commencement of the Kolbe

synthesis, but found the value to be 2.14 volts. The inflection of the curve is more pronounced if the anode voltage is plotted against the logarithm of the current density.

Hofer and Moest (42) found that in the presence of certain compounds, such as alkali bicarbonates, sulphates and perchlorates, the Kolbe reaction did not occur, and that methyl alcohol was the chief product of anodic oxidation when acetates were electrolysed.

The reaction is represented thus:-

$$CH_3.COOH + O \longrightarrow CO_2 + CH_3.OH$$

This is generally known as the Hofer-Moest reaction.

Glasstone and Hickling (41) studied electrode potentials in a number of acetate solutions, both with and without other compounds added. They found that, in the presence of compounds which inhibit the Kolbe reaction and bring about the Hofer-Moest reaction, there is a marked decrease in the anode potential. These workers consider that the anode potential is determined by the reactions occurring at the anode and not vice-versa.

For the purposes of the present investigation, it was decided to plot anode voltage/current density curves for the electrolysis of calcium lactate. It was hoped that curve inflections might be produced which would give some indication of the reactions occurring at the anode.

Further, a comparison would be made between the curves for the calcium lactate solution alone and containing added hydroxyl ion. It was hoped that this might provide some evidence for or against the hypothesis that the hydroxyl ion, only, is discharged at the anode.

EXPERIMENTAL.

The Apparatus.

The same cell and means of variable voltage application were employed as described in Section 2. The same two pairs of platinum electrodes were used for the electrolyses. (See Figure 2.)

A tube "S", containing the same solution as the electrolysis vessel, was pressed close to the anode, as shown, and was connected through a solution of saturated potassium chloride to a saturated calomel electrode. The end of "S" which dipped into the saturated potassium chloride was fitted with a porous plug to prevent diffusion. Bridge "S" was equipped with a side arm to facilitate filling by gentle suction.

A Cambridge potentiometer was used to measure the potential difference of the cell:-

$$^{+}Pt/(CH_3.CHOH.COO)_2Ca\ Soln./Satd.KCl/HgCl_2Satd.KCl/Hg^{-}$$

By adding 0.242 volts for the calomel half cell, the potential difference between the anode and solution was obtained with respect to the hydrogen zero. All recorded potentials refer to this scale.

The Cambridge potentiometer is only capable of reading voltages up to 1.8 volts. When the cell voltage exceeded this value, a standard Cadmium cell (1.0183 volts) was placed in the potentiometer circuit with its voltage in opposition. By this means voltages of 2.8 volts were capable of being read.

No correction was applied for liquid junction potentials, as, in consideration of the Henderson equation, this was found to be small.

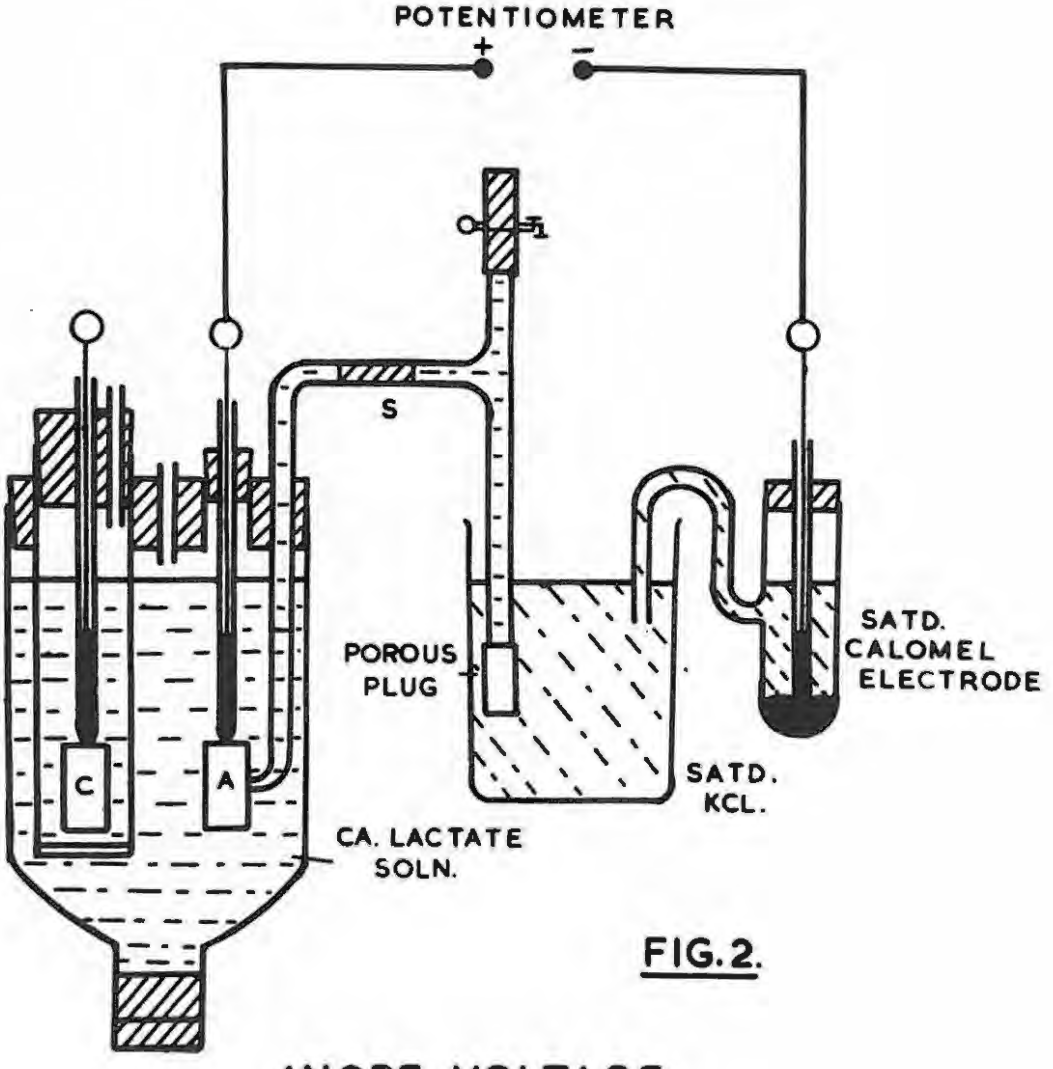


FIG. 2.

ANODE VOLTAGE MEASUREMENT

The anode currents were measured on a Cambridge Universal testing set (Pattern "U"), which is capable of measuring currents from 0.5μA to 1.5 amperes. The instrument was calibrated by carefully measuring the resistance of the coil for each scale; then passing a known current through the coil with the aid of a standardised accumulator and non-inductive resistance boxes. In this way the actual needle deflection was compared with the value of the current passing through the instrument. The error was less than 1% on all scales. A high degree of accuracy was not required for the anode voltage/current density determinations, but it was necessary to ensure that none of the meter scales was defective, in which case spurious curve inflections would occur.

General Experimental Procedure.

An aqueous solution of calcium lactate (32 grams per litre) was prepared and was used for all anode voltage/current density determinations.

A variable E.M.F. was applied across the electrodes and when conditions had become stable, readings of anode voltage and anode current were recorded.

A good deal of experimentation was necessary before reproducibility of readings was attained. Irregular fluctuations of voltage and current which may have been due to A.C. interference, were eliminated by earthing the negative of the accumulator to the water main.

In order to keep resistance errors to a minimum (see later), the tip of the bridge "S" should be pressed against the anode. It was found undesirable to place the tip against the flat side of the electrode as bubbles of gas were inclined to become entrapped in the orifice, resulting in unreliable anode voltage readings. A platinum wire anode would be most suitable for this purpose. This condition has been emulated, in the present investigation, by placing the tip of the bridge "S" in an "end

on" position to the anode (See Figure 2).

Considerable electrode polarisation was encountered during the electrolysis. This occurs particularly at voltages below that at which the evolution of gas takes place. At higher voltages, the stirring produced by the escaping gas was sufficient to keep the anode voltage and current constant. At low voltages, cathode polarisation appeared to be more serious than anode polarisation. The former resulted in a rapid drop in anode current and a corresponding drop in anode voltage, while polarisation in the anode compartment increased the anode voltage slowly, but had little effect on the anode current.

It was therefore decided to stir the cathode compartment with a thin glass rod, suitably shaped to encircle the electrode, in order to reduce the cathode polarisation to a minimum. The stirring was performed manually shortly before the anode voltage was due to be read. On the other hand, the anode was allowed to become fully polarised.

Readings.

Values of anode voltage and current density were obtained for the following electrolyses:-

1) Calcium lactate solution (32 grams per litre).

2) Calcium lactate solution made 0.01 N with respect to NaOH.

3) 0.01 N NaOH solution alone.

4) A calcium lactate solution (32 grams per litre) which had been electrolysed previously and was 0.02 N with respect to acid.

The readings have been tabulated as follows:-

TABLE II.

Curve 1, Figure 3.

Calcium Lactate Solution Alone.

Applied Voltage	Anode Current	Current Density	Anode Voltage on H_2 Scale
3.1 volts	6 mA.	1 mA/sq. cm.	1.882 volts
3.5 "	12 "	2 " " "	1.962 "
4.6 "	30 "	5 " " "	2.085 "
6.1 "	60 "	10 " " "	2.185 "
9.1 "	120 "	20 " " "	2.342 "

TABLE III.

Curve 2, Figure 3.

Calcium Lactate Solution (0.01 N with respect to NaOH).

Applied Voltage	Anode Current	Current Density	Anode Voltage on H_2 Scale
2.8 volts	6 mA.	1 mA/sq. cm.	1.681 volts
3.4 "	12 "	2 " " "	1.890 "
4.3 "	30 "	5 " " "	2.040 "
5.6 "	60 "	10 " " "	2.200 "
8.1 "	120 "	20 " " "	2.360 "
10.6 "	200 "	33.3 " " "	2.492 "

TABLE IV.

Curve 3, Figure 3.

0.01 NSodium Hydroxide Alone.

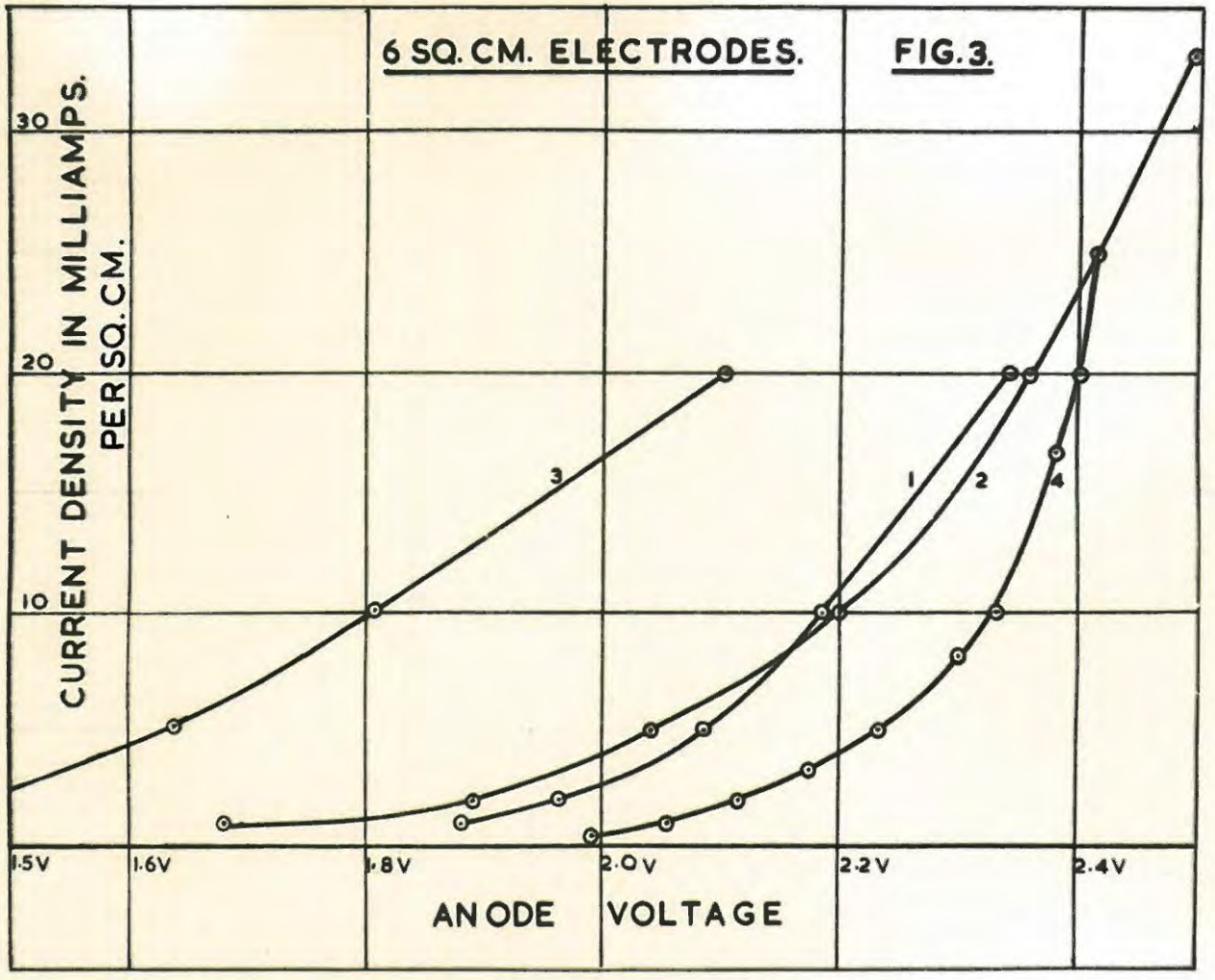
Applied Voltage	Anode Current	Current Density	Anode Voltage on H_2 Scale
3.0 volts	6 mA.	1 mA/sq. cm.	1.382 volts
4.0 "	12 "	2 " " "	1.448 "
6.2 "	30 "	5 " " "	1.638 "
9.5 "	60 "	10 " " "	1.810 "
14.1 "	120 "	20 " " "	2.102 "

TABLE V.

Curve 4, Figure 3.

Calcium Lactate Solution (approximately 0.02 N with respect to acid).

Applied Voltage	Anode Current	Current Density	Anode Voltage on H_2 Scale
3.4 volts	3 mA.	0.5 mA/sq. cm.	1.992 volts
4.1 "	6 "	1 " " "	2.054 "
5.1 "	12 "	2 " " "	2.116 "
6.5 "	20 "	3.33 " " "	2.175 "
7.8 "	30 "	6 " " "	2.234 "
9.2 "	40 "	6.67 " " "	2.274 "
10.5 "	50 "	8.33 " " "	2.306 "
11.8 "	60 "	10 " " "	2.332 "
14.5 "	80 "	13.33 " " "	2.351 "
17 "	100 "	16.67 " " "	2.380 "
20 "	120 "	20 " " "	2.402 "
24 "	150 "	25 " " "	2.416 "


6 SQ. CM. ELECTRODES.
FIG. 3.
CURRENT DENSITY IN MILLIAMPS. PER SQ. CM.
30
20
10
1
2
3
4
1.5V
1.6V
1.8V
2.0V
2.2V
2.4V
ANODE VOLTAGE

Analysis of Curves.

Curve 1, for the aqueous solution of calcium lactate, is perfectly smooth and thus gives no indication of any changes in reaction at the anode which might have resulted from a variation of the applied voltage. This may be a natural consequence of the small concentration of the electrolyte (40). The steep rise in the anode current corresponds with the evolution of gases at the electrodes. This occurs at the cathode slightly before the anode.

It was noted, further, that continued electrolysis is accompanied by a gradual increase in anode voltage. This is to be expected, as the pH of the solution increases with length of electrolysis. Curve 4 has been plotted merely to illustrate this trend, and is for a calcium lactate solution approximately 0.02 N with respect to acid.

As may be observed from Figure 3, curves 1 and 2 lie close together. On the assumption that it is the reaction at the anode which determines the anode voltage, the proximity of the curves may be taken as evidence that the processes occurring at the anodes in each case are similar. Further, it may be assumed that in the presence of sodium hydroxide (as in 2), the hydroxyl ions carry a large portion of the current and are discharged at the anode. Since the processes occurring at the anode in each case are similar, it appears probable that hydroxyl ions and not lactate ions are discharged at the anode during electrolysis 1 as well.

Curve 3 represents the electrolysis of 0.01 N sodium hydroxide. At first sight it might appear that the fact that curves 2 and 3 are widely separated is evidence against the "hydroxyl ion discharge" hypothesis. However, a fair comparison cannot be made between the two electrolyses because the secondary oxidation processes in each case are different.

(Glasstone and Hickling (41) encountered a similar situation when studying the electrolysis of 2 N potassium acetate, alone, and in the presence of 0.01 N sodium hydroxide. In both cases the anode voltage was found to be well above the evolution potential for oxygen. These workers suggested the formation of active acetate radicals near the anode which were capable of setting up a higher anode potential than that associated with oxygen evolution.)

Polarisation and Anode Voltage Measurement.

The importance of maintaining the tip of bridge "S" in contact with the anode, when anode voltages are being read, was demonstrated experimentally.

Using a constant anode current of 60 milliamperes, the distance between the tip of the bridge and the anode was varied and the corresponding readings for the anode voltage were measured. The readings are recorded in Table VI.

TABLE VI.

Current.	Gap Distance.	Anode Voltage Read.
60 mA.	0 mm.	2.184 volts
60 "	1 "	2.294 "
60 "	3 "	2.464 "
60 "	6 "	2.724 "
60 "	10 "	2.874 "

As may be seen from the table, the anode voltage increased by at least 100 millivolts when the tip of bridge "S" was moved 1 millimetre from the anode. However, the rate of anode voltage increment is not maintained as the gap distance is further increased. This

phenomenon is due to the electrical resistance of the solution between the anode and the tip of the bridge which causes a drop of potential equal to the product of the resistance and the anode current.

Glasstone and Hickling (43), (44), (45) maintain that there is an appreciable resistance error even when the tip of the bridge is in contact with the anode. In an endeavour to eliminate this effect, which is caused by polarisation, these workers use the commutator method of measuring anode voltages (45). An interrupter circuit is employed by means of which the anode current can be interrupted for any chosen period from 1×10^{-5} to 20×10^{-5} seconds at any desired frequency. By using a specially designed potentiometer circuit, the anode voltage may be measured at various intervals after the current has been interrupted. The anode voltages thus obtained are extrapolated to zero time and the anode voltage, free from the resistance effect due to polarisation, is obtained.

It is still open to conjecture whether the value of the anode voltage obtained by the cummutator method gives a more reliable indication of the reactions occurring at the electrode than the higher value obtained by the direct method. The latter method is still frequently used in spite of the aforementioned criticisms. In view of its simplicity, the direct method of anode voltage measurement has been employed throughout in the present investigation.

PYRUVIC ACID.

Carpeniseanu (9) obtained pyruvic acid when he electrolysed sodium lactate at low applied voltages and small anode currents. (Vide Section 1.) It was felt by the author that if pyruvic acid is liberated more abundantly over a particular range of current density,

the range might be evidenced by a study of anode voltage/current density determinations over a wide range of applied voltages.

Using both sets of electrodes, current densities ranging from 1 microampere to 10 milliamperes per square cm. were employed and the corresponding anode voltages were obtained. Some difficulty was experienced in keeping the current steady during the current range of 1 microampere to 1 milliampere. The cathode compartment required vigorous stirring. Furthermore, it was found that greater current and voltage stability was attained if a small potential was applied across the cell before the electrolysis. The voltage was of the order of 0.4 volts and resulted in a current of 1 or 2 microamperes.

(Hoar (46) encountered the same difficulty when studying oxygen overvoltage with smooth platinum electrodes. He found that preliminary prolonged anodic treatment was necessary before reproducible results could be obtained. It was suggested that the surface of the electrode may be converted to oxide during the treatment.)

It thus appears that some degree of electrode polarisation is necessary before reproducible results can be obtained.

The readings taken for the electrolyses, using the 2 and 6 sq. cm. electrodes, have been recorded in Table VII and Table VIII. Owing to the wider range of current densities employed, it was not possible to record the curves on one piece of graph paper. The logarithm of the current density was therefore utilised. (See Figure 4.)

TABLE VII.
Figure 4.

2 sq. cm. electrodes.

Applied Voltage (Volts)	Current in uA.	Current Density in uA/sq. cm.	Log. C.D.	Anode Voltage (Volts)
0.32	2	1	0.0000	0.661
0.4	4	2	0.3010	0.716
0.48	6	3	0.4771	0.771
0.68	10	5	0.6990	0.902
0.92	15	7.5	0.8751	1.139
1.08	20	10	1.0000	1.262
1.15	30	15	1.1761	1.326
1.25	40	20	1.3010	1.369
1.32	60	30	1.4771	1.418
1.45	100	50	1.6990	1.470
1.62	200	100	2.0000	1.539
2.10	300	150	2.1761	1.610
2.4	400	200	2.3010	1.648
2.63	600	300	2.4771	1.702
2.85	1,000	500	2.6990	1.793
3.1	1,500	750	2.8751	1.878
3.3	2,000	1,000	3.0000	1.935
3.6	3,000	1,500	3.1761	1.994
4.0	5,000	2,500	3.3979	2.111
4.6	8,000	4,000	3.6021	2.187
5.0	10,000	5,000	3.6990	2.235
5.4	12,000	6,000	3.7782	2.288
5.8	15,000	7,500	3.857	2.314
6.3	20,000	10,000	4.000	2.348

TABLE VIII.

Figure 4.

6 sq. cm. electrodes.

Applied Voltage (Volts)	Current in uA.	Current Density in uA/sq. cm.	Log. C.D.	Anode Voltage (Volts)
0.15	0			0.431
0.45	6	1	0.0000	0.670
0.60	12	2	0.3010	0.802
0.75	18	3	0.4771	0.918
1.0	30	5	0.6990	1.122
1.1	50	8.33	0.9206	1.215
1.15	70	11.66	1.0668	1.274
1.25	100	16.66	1.2217	1.319
1.33	150	25	1.3979	1.356
1.4	200	33.33	1.5228	1.388
1.5	300	50	1.6990	1.428
1.7	600	100	2.0000	1.508
2.2	1,250	208.3	2.3187	1.612
2.8	2,000	333.3	2.5228	1.682
3.2	3,000	500	2.6990	1.754
3.3	4,000	666.7	2.824	1.809
3.6	5,000	833.3	2.9208	1.860
3.8	6,000	1,000	3.0000	1.890
4.1	8,000	1,333	3.1249	1.930
4.2	10,000	1,667	3.2217	1.967
5.1	14,000	2,333	3.368	2.015
5.8	20,000	3,333	3.5228	2.086
7.2	30,000	5,000	3.6990	2.148
8.4	40,000	6,667	3.8241	2.192
9.6	50,000	8,333	3.9206	2.229
10.4	60,000	10,000	4.0000	2.260

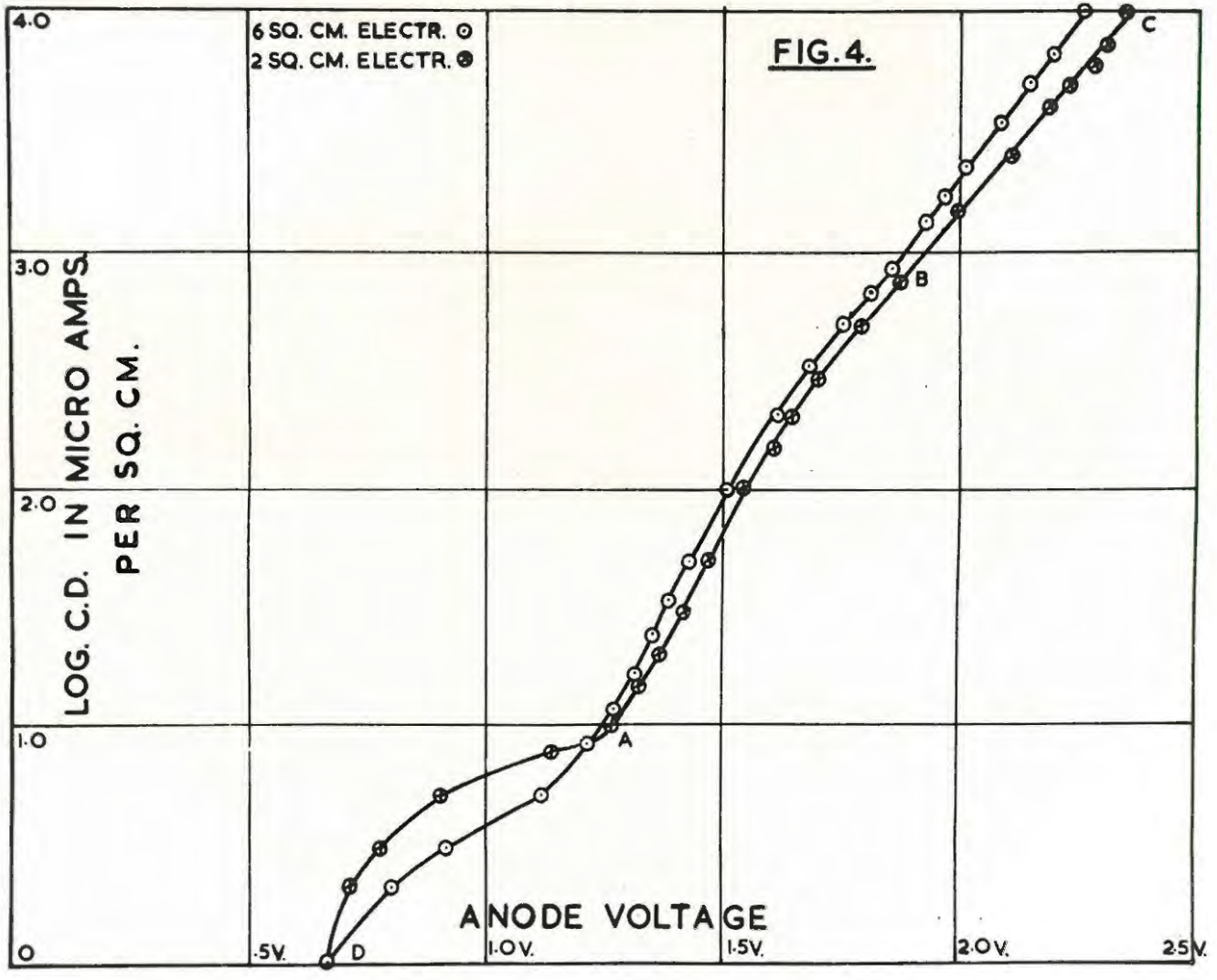


FIG. 4.
6 SQ. CM. ELECTR. ⊙
2 SQ. CM. ELECTR. ⊛
4.0
3.0
2.0
1.0
0
LOG. C.D. IN MICRO AMPS. PER SQ. CM.
.5V.
1.0V.
1.5V.
2.0V.
2.5V.
ANODE VOLTAGE
A
B
C
D

Analysis of Curves.

On inspection, the curves on Figure 4 may be divided into three distinct sections, viz. DA, AB and BC.

Along DA (i.e. for current densities of less than 10 μA. per sq. cm.) considerable polarisation was encountered with the result that reproducibility was not easily attained. Between AB, however, the graph was fairly smooth and slightly curved, whereas between B and C the graph was almost linear. The portion BC represents the electrolyses carried out at current densities of 1 mA. per sq. cm. and above, and corresponds to the curves recorded in Figure 3.

Points A and B correspond to applied voltages of 1.0 and 3.2 volts respectively. These two voltages approximate to the limits of the applied voltage used by Carpeniseanu (9) when looking for pyruvic acid. He electrolysed 0.01 N sodium lactate between platinum electrodes using applied voltages of 1.5 to 3.5 volts.

Thus the graph may be interpreted to indicate that pyruvic acid should be obtained between the limits of 1.0 to 3.0 volts applied to the electrodes. The most favourable applied voltage appeared to be approximately 3.0 volts, using the 6 sq. cm. electrodes.

Electrolysis at Small Current Density.

In order to determine whether pyruvic acid is produced more abundantly at these low applied voltages and current densities, 350 ml. of the 0.12 molar solution of calcium lactate was electrolysed for 290 hours at an applied voltage of 3.0 volts and an anode current of approximately 1 mA. The pair of 6 sq. cm. electrodes was used; the cathode being placed in the porous pot. There was a slight evolution of gas at the cathode but practically none at the anode. The cathode solution was renewed every 24 hours.

At the conclusion of the electrolysis, the anode solution was found to be 0.00156 N with respect to acid. 150 ml. of this solution was concentrated to a quarter of its original volume by vacuum distillation. To minimise any possible decomposition, the bath temperature was maintained below 50°C throughout the distillation.

The concentrated solution gave a strongly positive test for pyruvic acid, using the method of Carpeniseanu (9) described in Section 4. The concentration of the pyruvate ion in the concentrated anode solution was determined colorimetrically. The concentration in the undistilled anode solution was calculated to be 0.0014(6) N. The total acidity of the anode solution was found to be 0.00156 N. It therefore appears that, at low current densities, approximately 94% of the acid produced is pyruvic.

The efficiency of production is low, however, and was calculated to be of the order of approximately 0.047 gram equivalents per Faraday.

It will be recalled (Section 4) that the efficiency of pyruvic acid production for a current of 60 mA. using the 6 sq. cm. electrodes was found to be approximately 0.0084 gram equivalents per Faraday. Thus pyruvic acid is produced 5 times more readily at the lower current density.

SUMMARY OF SECTION 6.

1) The cell was modified to permit the measurement of anode voltages.

2) Anode voltage/current density determinations for the electrolysis of various solutions of calcium lactate, both with and without the addition of hydroxyl ion, have been made and graphically represented. These curves show no marked inflections.

(3) The close proximity of the curves for the electrolysis of calcium lactate, with and without added hydroxyl ion (Curves 2 and 1, Figure 3), is an indication that the processes occurring at the anode are similar in each case. Following from this, it seems probable that the hydroxyl ion, only, is discharged at the anode under the particular condition of the electrolysis.

(4) Anode voltage/log. current density curves have been plotted over a range of current densities from 1 microampere to 10 milliamperes in order to determine the most favourable range for pyruvic acid production. The most suitable applied voltage was approximately 3.0 volts using the 6 sq. cm. electrode.

(5) An electrolysis of long duration was performed at an applied voltage of 3.0 volts and an anode current of 1 to 2 milliamperes, using the 6 sq. cm. electrodes. Pyruvic acid was found to be present in the anolyte and was shown to be produced 5 times more efficiently than at an anode current of 60 mA.

S E C T I O N 7.

THE QUANTITATIVE ESTIMATION OF THE PRODUCTS OF ELECTROLYSIS.

INTRODUCTION.

Before any deductions could be made as to the reactions which occur at the anode, it was essential to perform a series of quantitative estimations of the products of electrolysis at various current densities. Such a survey would include gas analysis, and the estimation of acetaldehyde and the acids obtained.

A second electrolysis vessel, complete with porous pot, was constructed in the same manner as the first, so that two electrolyses could be conducted concurrently. The 6 sq. cm. electrodes were used in the one vessel while the 2 sq. cm. electrodes were used in the other. The two electrolysis vessels were placed electrically in parallel with each other as shown in Figure 5. A small variable resistor R_2 was placed in series with the vessel containing the 6 sq. cm. electrodes so that the currents passing through the cells could be equalised. As only one ammeter was available, a switching device was incorporated into the circuit so that the currents passing through the cells could be measured alternately. The currents were checked frequently throughout the electrolysis to keep the currents as constant as possible.

During the subsequent investigations many problems were encountered. These have been fully discussed under the various sub-sections concerned.

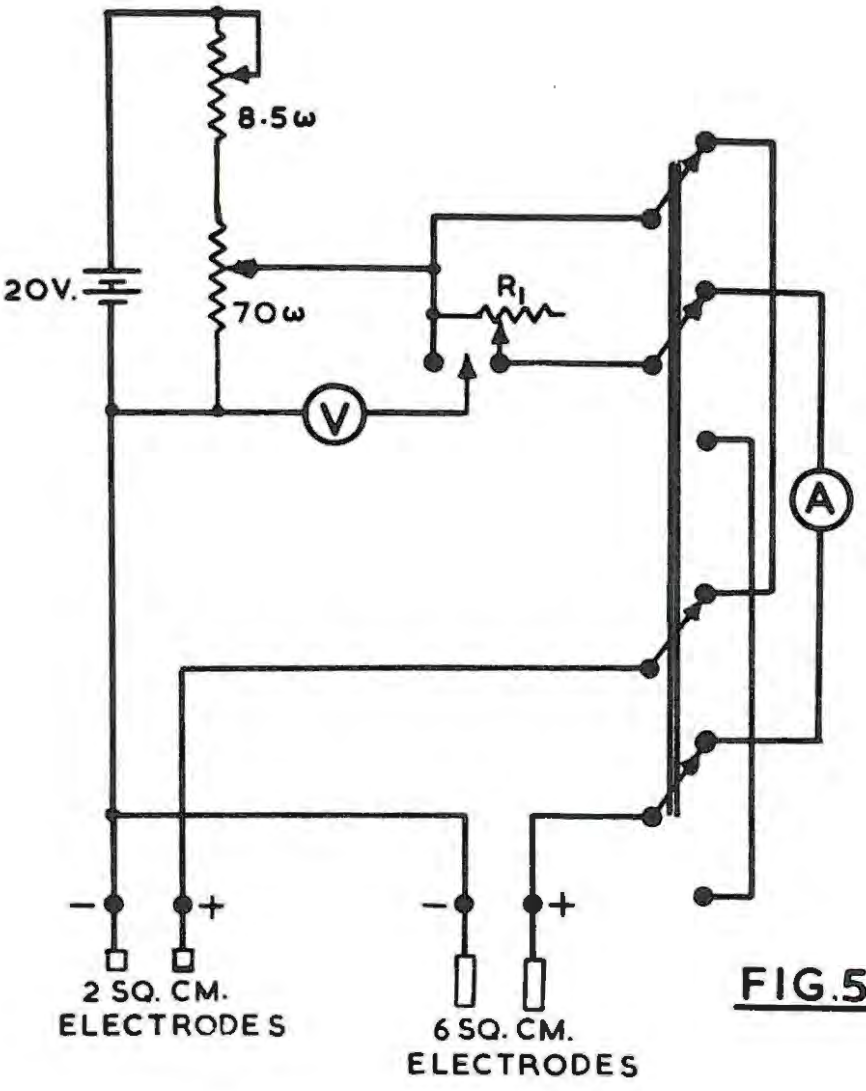


FIG.5.

CIRCUIT FOR BOTH
ELECTROLYSIS VESSELS

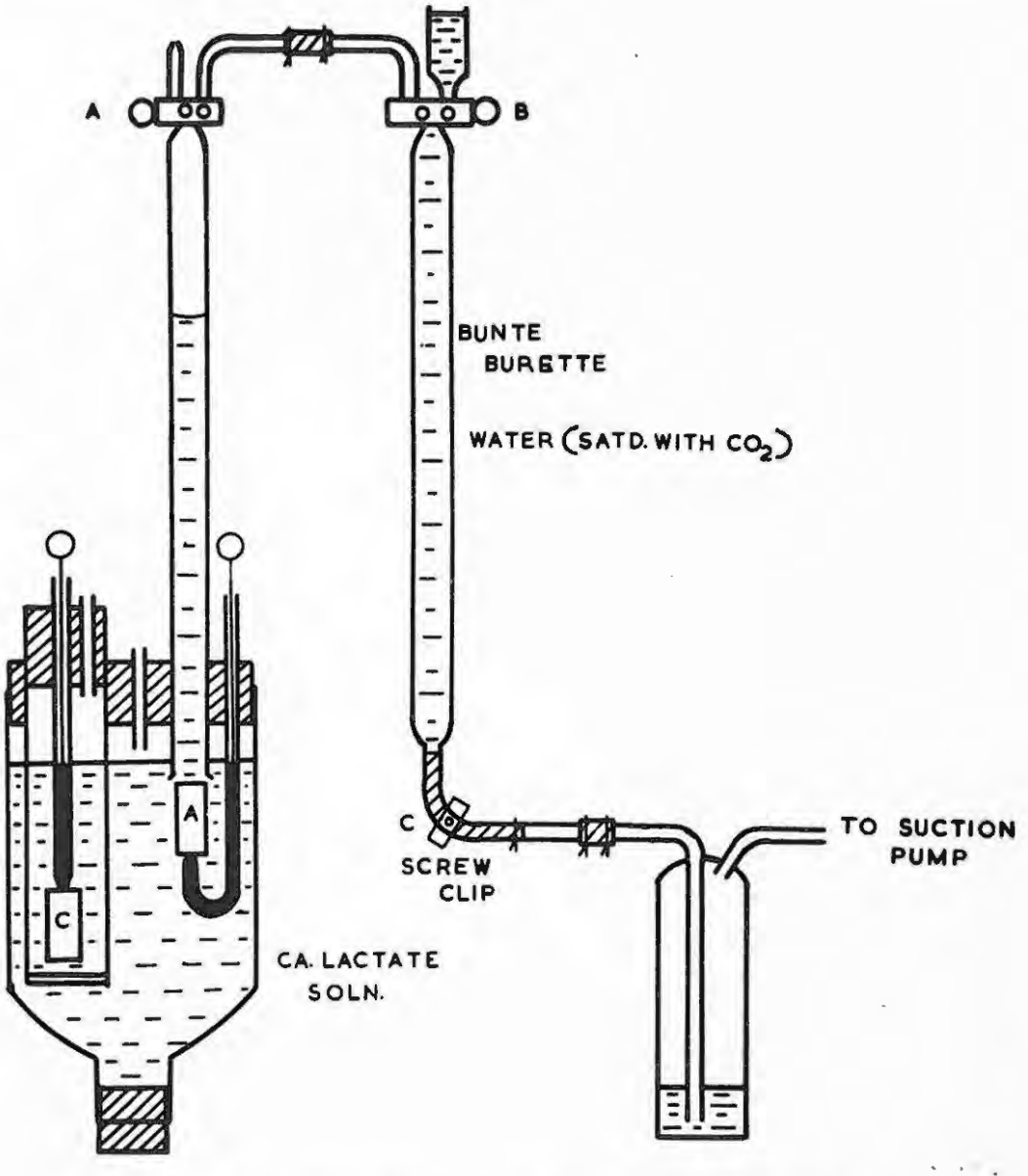
SUB-SECTION 7A.

GAS ANALYSES.

Unfortunately, with the limited apparatus available, the gas analyses could not be conducted with the accuracy which was at first hoped. The Orsat-Lunge apparatus which was available, is only suitable for measuring the constituents of a large quantity of gas and was quite useless for the present analyses. Two Bunte burettes of 50 ml. capacity were therefore employed for all gas analyses. The tube was of uniform bore and was graduated in 0.1 ml. divisions. The zero graduation mark was at the 3-way tap.

Owing to the constrictions at both ends, it was not possible to collect the anode gases directly into the Bunte burettes. After some experimentation, a suitable means of collecting the gas was devised as follows:- (See Figure 6.)

The tap of an ordinary burette was replaced by a 3-way tap with its capillary bent at 90° to the burette stem. (Tap A, Figure 6.) The capillary was strong enough to support rubber tubing. The open end of the burette was inserted through the hole in the large stopper which had been made for the anode stopper, and was placed over the end of the anode. The glass portion of the electrode had been bent through 180° and positioned to enable the gas to be collected without hindrance or loss. The collection and Bunte burettes were connected by means of rubber tubing, while the constricted end of the Bunte burette was



GAS COLLECTION APPARATUS FIG.6

joined to a water suction pump through a gas wash bottle. The latter join was made with rubber tubing and a short piece of glass tubing as shown in Figure 6. Ligatures of copper wire were employed to ensure that all rubber to glass joints were air-tight.

The procedure for a gas analysis was as follows:-

After the burettes had been clamped in position, the collection burette was filled with the electrolyte by applying suction to the bent capillary of the 3-way tap (A). In the same manner the Bunte burette was filled with water. The capillaries of the two burettes were then joined together; great care being taken that no air was introduced.

When a suitable quantity of anode gas had been collected, the gas was transferred to the Bunte burette as follows:-

Gentle suction was applied to the wash bottle and screw-clip C was opened. Cautiously, taps A and B were opened together. If the flow was from B to A, the suction was increased, otherwise, the gas in A was slowly transferred to burette B. B and C were closed as soon as all the gas had been transferred. The Bunte burette was then disconnected from the wash bottle and burette A; clip C was cautiously opened

under water to bring the gas in the burette to atmospheric pressure. Special care was taken to ensure that tap C contained no bubbles of air. The function of the piece of glass tubing near C was to facilitate this.

The Gas Absorbents.

1) Carbon Dioxide.

A 30% aqueous solution of potassium hydroxide was used as recommended by Bunte and Wunche (47).

2) Oxygen.

A 40% potassium hydroxide solution and a 25% aqueous pyrogallol solution were prepared. These were mixed in the ratio of 4:1 as required.

3) Carbon Monoxide.

The usual reagent was employed, namely, an ammoniacal cuprous chloride solution. This was prepared by adding 125 ml. of concentrated hydrochloric acid to 40 grams of cuprous chloride and was followed by the cautious addition of 130 ml. of concentrated ammonia solution. After cooling, a little more ammonia solution was added until the precipitate just dissolved, leaving a dark blue solution.

4) Hydrocarbons, Saturated and Unsaturated.

The most satisfactory absorbent appears to be fuming sulphuric acid containing 20% to 25% of free sulphur trioxide. However, this obviously could not be used in the present gas analysis, so a solution of bromine in 10% potassium bromide was employed.

Fortunately, none of the above gases was found, so the use of this unpleasant reagent was discontinued.

Experimental.

The preliminary experiments were conducted to find out qualitatively what gases were evolved at the anode. 350 ml. of the calcium lactate solution was electrolysed for approximately 8 hours at an anode current of 60 mA. About 50 ccs. of gas was collected and its volume was measured at atmospheric pressure by connecting C to a levelling reservoir containing water. As only a qualitative estimation was being made, the temperature and atmospheric pressure were not recorded. The remaining water in the Bunte burette was transferred, by suction, into the wash bottle. The latter was then carefully disconnected and the absorbent for CO_2 was sucked into the burette by dipping the glass tubing attached to C into a bowl containing the absorbent. C was closed, and the burette was well shaken by holding the tap in the one hand and the rubber tubing in the other. This procedure prevented undue heating of the gas. The tip of the burette at C was once more immersed in the absorbent and a little more of the solution was allowed to replace the gas absorbed. This procedure was repeated until no more of the absorbent was sucked into the burette. To remove the potassium hydroxide solution, the burette was connected to the wash bottle and filter pump once more. The absorbent was retained for further absorbtions. Water was once more sucked into the burette and with the aid of the levelling bottle the volume of the anode gas less CO_2 was obtained.

In a similar manner, using the pyrogallol solution as absorbent, the volume of oxygen was obtained. The absorbtion of CO_2 is rapid even if the potassium hydroxide has been used many times, but the absorbtion of oxygen is rapid only when the pyrogallol is fresh.

This particular gas mixture was found to contain 19.8% CO_2, 73.6% O_2 and about 1% of CO. No un-

saturated hydrocarbons were present. A residual gas of about 3.3 ccs. remained unabsorbed by any of the absorbents. It did not burn.

Examination of the Residual Gas.

Fourteen ccs. of the residual gas was admitted to a calibrated cylindrical tube standing over water. Near its upper end, the tube was equipped with a pair of sparking contacts, which were connected to a vibrator coil. Ten ccs. of pure oxygen was admitted to the tube and a continuous discharge was passed. There was no explosion, which might have occurred if hydrogen or some hydrocarbon was present, but the volume of the gas diminished slowly. A pale brown gas was generated which was thought to be NO_2. The sulphuric acid-diphenylamine test was applied to a little of the confining liquid, and resulted in a deep blue colour characteristic of nitrates and nitrites. This was taken as confirmation that the brown gas was NO_2.

The volume of the gas diminished until it stood at 8.5 ccs. A further 16 ccs. of oxygen was admitted and further sparking resulted in a further diminution of gas volume to 1 cc. The fact that 14 ccs. of residual gas combined with 26 ccs. of oxygen leaving 1 cc. of gas uncombined, seemed to indicate that the gas was entirely nitrogen.

$$N_2 + 2\ O_2 \longrightarrow 2\ NO_2$$

There is the possibility that hydrocarbons might have combined with oxygen, under the influence of the spark, to form CO_2, but there was no evidence of dissolved CO_2 when the lime water test was applied to the confining liquid.

The Origin of the Residual Gas.

Several electrolyses were performed and the quantity of the residual gas thus obtained varied between 6% and 10%. The quantity was thought to be excessive to say the least, and investigations were undertaken to find the source of this phenomenon.

In order to determine whether the nitrogen was introduced during the gas absorbtion process, or not, a mixture of O_2 and CO_2 was analysed. The mixture corresponded approximately with that encountered in an electrolysis and consisted of approximately 38 ccs. oxygen, (from cylinder) and approximately 12 ccs. of CO_2 (from a Kipp's apparatus). The operations for the gas analysis were identical with those carried out for a normal analysis of the anode gas. A residue of 1.3 ccs. remained which was equivalent to 2.6% of the total gas.

The possibility that the nitrogen was released when the confining liquids are subjected to reduced pressure, was also examined. The following columns of liquid were sucked from the Bunte burette and replaced by distilled water. The volume of gas released was recorded in each case.

Liquid.	Gas Released.
Boiled out distilled water	0.025 ccs.
Distilled water	0.4 ccs.
Pyrogallol	0.05 ccs.
Potassium hydroxide	0.1 ccs.
$CuCl_2.NH_3$ solution	0.1 ccs.

These experiments showed conclusively that the nitrogen was not released nor air admitted during the gas absorbtion process. The 2.6% residue from the absorbtion of

the O_2 and CO_2 mixture was shown to be impurity, which came from the oxygen cylinder principally. It was therefore concluded that the nitrogen was obtained during the electrolysis. The taps of the gas collection apparatus were subjected to reduced pressure for many hours and the taps were shown to be air-tight.

The air dissolved in the electrolyte was next examined.

At $15^{\circ}C$, one litre of water absorbs 13.83 ccs. of nitrogen at a pressure of 760 mms. of mercury, while at $20^{\circ}C$ one litre absorbs 12.76 ccs. (48). On the assumption that the calcium lactate solution is fully saturated with nitrogen, the 350 ml. in the electrolysis vessel could not contain more than 4.8 ccs. of nitrogen, while the 50 ml. of the solution in the gas collection burette could not contain more than 0.7 ccs. of dissolved nitrogen. In spite of this, up to 10% of nitrogen was always present together with the anode gases. (This amounted to approximately 4 ccs. for a normal electrolysis.)

Electrolyses were carried out with boiled out solutions of the electrolyte which had been saturated with oxygen and allowed to cool in an atmosphere of oxygen. A stream of oxygen was continually bubbled through the vessel during the electrolysis to prevent the electrolyte from coming in contact with air as far as possible. In this manner the gaseous residue was reduced to 3% of the total anode gases. The sample of calcium lactate was tested for nitrates, nitrites and organic nitrogen but these were absent.

A survey of a number of electrolyses indicated that the quantity of nitrogen obtained increased with the electrolysis time and with the total quantity of gas evolved. It decreased noticeably if a gas such as oxygen or carbon dioxide was bubbled through the electrolyte prior to the electrolysis.

It is undesirable to attempt to remove the dissolved nitrogen by boiling the electrolyte before the electrolysis, as the gases to be measured would be absorbed rapidly by the unsaturated solution. Thus for all the subsequent electrolyses the dissolved nitrogen was left undisturbed and the gaseous residue was ignored. In some cases the electrolyte was saturated with carbon dioxide from a Kipp's apparatus before electrolysis.

Nevertheless, it is interesting to contemplate the origin of so large a quantity of nitrogen among the anode gases. As pointed out before, the anode gases could not displace more than 0.7 ccs. of nitrogen from a saturated solution at 15°C contained in the collection burette. A possible explanation is that the dissolved nitrogen in the total solution is attracted towards the anode during the electrolysis. If this were the case, no nitrogen should be found among the cathode gases. Unfortunately, no suitable absorbent for hydrogen was available at the time, with the result that this test was not performed.

Shukla and Walker (40) obtained a residue, consisting of carbon monoxide and nitrogen, when analysing the anode gases evolved during electrolysis of acetates. The residue occurred to the extent of 10%, approximately. On the other hand, Glasstone and Hickling (41) do not refer to having obtained any residue at all when electrolysing potassium acetate in the presence of impurities. In this particular case the residue, after CO_2, O_2, CO and H_2 had been removed, contained methane and ethane. These gases were estimated by explosion with excess oxygen. Possibly, under these conditions, the presence of nitrogen would remain undetected. Furthermore, these electrolyses were conducted for about 40 minutes only.

The Origin of the Carbon Monoxide.

As mentioned previously, carbon monoxide was found present among the anode gases to the extent of approximately 1%. Unfortunately, alkaline pyrogallol, which was used for the absorbtion of oxygen, has a tendency to evolve carbon monoxide during the absorbtion process. Drakely and Nicol (49) have made an exhaustive study of the subject and claim that all solutions of alkaline pyrogallol evolve CO, and that the quantity evolved is proportional to the quantity of oxygen absorbed. The effect, however, is minimised by agitations of the solution during absorbtion.

It therefore was essential to determine whether the carbon monoxide found among the anode gases was truly a product of electrolysis or not.

This was simply determined by using alkaline sodium hydrosulphite ($Na_2S_2O_4$) as the absorbent for oxygen, as this solution does not liberate carbon monoxide.

The following solutions were prepared:-

1) 20 grams $Na_2S_2O_4$ in 100 ml. water.

2) 10 grams NaOH in 100 ml. water.

The solutions were mixed in equal quantities when required.

The absorbtion was considerably slower than when using pyrogallol, but the reaction rate was increased somewhat by the addition of 1 gram of sodium anthraquinone-β sulphonate to the absorbent. A thick precipitate formed which was removed. Eventually, after no further absorbtion of oxygen took place, it was shown that less than 0.1 ccs., or 0.2% of the anode gas, consisted of carbon monoxide. It was thus assumed that negligible quantities

of carbon monoxide are produced during the electrolysis of calcium lactate.

Alkaline pyrogallol was used in all subsequent gas analyses for the absorbtion of oxygen. The volume of carbon monoxide obtained was added to the measured volume of oxygen.

It will be recalled that both Carpeniseanu (9) and von Miller and Hofer (12) have reported the evolution of small quantities of carbon monoxide among the anode products during the electrolysis of lactates (vide Section 1). As no particular precautions appear to have been taken in either instance with regard to the choice of the absorbent for oxygen, the validity of their figures for carbon monoxide is questionable. According to the figures supplied by von Miller and Hofer for the composition of the anode gases (Section 1), the percentage carbon monoxide increased together with the percentage oxygen. This, according to Drakely and Nicol (49) and according to the observations of the author, is to be expected if alkaline pyrogallol was used as the absorbent for oxygen.

SUMMARY FOR SUB-SECTION 7A.

1) The apparatus and the techniques employed in the estimation of the anode gases have been fully described.

2) The principal constituents of the anode gas were found to be carbon dioxide and oxygen.

3) A residual gas of up to 10% always remained unabsorbed. This was shown to be nitrogen. Exhaustive attempts to eliminate the nitrogen before electrolysis were made with limited success. It was shown that the nitrogen origi-

nated from dissolved air in the electrolyte and was not introduced accidently. It is believed that the nitrogen dissolved in the electrolyte is attracted to the anode during the electrolysis and is not merely physically displaced by the escaping anode gas.

4) The 1% of carbon monoxide found among the anode gases was shown to be released by alkaline pyrogallol when it was used as the absorbent for oxygen.

SUB-SECTION 7B.

THE ESTIMATION OF ACETALDEHYDE.

Of several methods available for the estimation of acetaldehyde the following were investigated.

1) The polarograph.
2) Chemical methods including:-
    a) Parkinson's method.
    b) A modified Friedmann method.

The modified Friedmann method was finally adopted, but some of the work done on the other methods is worthy of mention.

1) THE POLAROGRAPHIC METHOD.

The polarograph has been used extensively for the quantitative analysis of aldehydes and, more particularly, mixtures thereof. This method therefore appeared to offer a simple and satisfactory way of estimating the acetaldehyde resulting from electrolysis of calcium lactate.

Using a weight burette and recently distilled acetaldehyde the following standard solutions were prepared:-

0.2 grams per litre, 0.3 grams per litre,
0.4 grams per litre and 0.5 grams per litre.

The preparation of so-called "standard" solutions of acetaldehyde presents several difficulties owing to its high volatility. The weight burette was discharged with its capillary under the surface of the liquid to minimise

this error. However, the concentration of the aldehyde could only be considered as approximate. From the above solutions, standard solutions, using 0.02 N lithium hydroxide as indifferent electrolyte, were prepared. These gave satisfactory polarograms but the accuracy was insufficient for the following principal reasons:-

a) The small vessels containing the solution were exposed to the atmosphere with the result that during the making of the polarogram there was a continuous evaporation of the acetaldehyde. In fact, if the vessel containing the acetaldehyde solution was allowed to stand for 30 minutes, the wave height decreased by 50%.

b) The wave for acetaldehyde is especially sensitive to temperature changes. The temperature should be controlled to within $0.1^{\circ}C$ for accuracy (50).

In view of the number of precautions required to attain a sufficient degree of accuracy, it was decided to seek a more convenient method.

However, the polarograph was used to demonstrate, qualitatively that no aldehydes, other than acetaldehyde are produced by the electrolysis of calcium lactate as this method is particularly suited for the purpose.

The procedure adopted was to compare polarograms for acetaldehyde and formaldehyde (both singly and together) in the presence of calcium lactate solution with the polarogram for the anode solution. According to

Whithack and Moshier (50), 0.1 N lithium hydroxide containing 0.01 N lithium chloride is a suitable indifferent electrolyte for aldehyde determinations, provided the pH is kept constant.

Experimental Details.

An acetaldehyde solution was prepared containing approximately 0.04 grams per litre.

The formaldehyde solution contained 4.0 ml. of formalin per litre.

The following four solutions were prepared:-

1) The Calcium Lactate Solution.
50 ml. N/5 LiOH, + 10 ml. N/10 LiCl + 10 ml. of calcium lactate solution. This was made up to 100 ml. in a measuring flask.

2) The Calcium Lactate Solution Containing Acetaldehyde.
50 ml. N/5 LiOH, + 10 ml. N/10 LiCl + 10 ml. calcium lactate solution + 10 ml. of the acetaldehyde solution. This was made up to 100 ml.

3) The Calcium Lactate Solution Containing Formaldehyde.
50 ml. N/5 LiOH, + 10 ml. N/10 LiCl + 10 ml. calcium lactate solution + 10 ml of the formaldehyde solution. Made to 100 ml.

4) The Anode Solution.
50 ml. N/5 LiOH, + 10 ml. N/10 LiCl + 10 ml. anode solution which had been electrolysed for four hours at 60 mA. The solution was made up to 100 ml.

Thus each of the above solutions was made N/10 with respect to LiOH and N/100 with respect to LiCl. It was found important to mix the solutions in the correct order because calcium lactate forms a white precipitate with strong alkali. The procedure adopted was to mix

first all the components except calcium lactate; make the solution up to almost 90 ml. and then add the calcium lactate. In this way only a very slight turbidity was formed. Furthermore, it was found necessary to age solutions 1), 2), 3) and 4) for several hours before use, otherwise the resulting polarograms were invariably irregular. The formation of the white precipitate and the possibility of the solution not having attained equilibrium may have been responsible for the irregularity.

2.5 volts was applied across the wire-wound drum. This meant that each turn of the wire was equivalent to 0.125 volts. In each case the polarogram was started at an applied voltage of 1.375 volts, while the sensitivity was set at 1/30 th. The temperature of the liquid was 23.0°C.

The Polarograms (See Figure 7.)

Polarogram 1 (using Solution 1) The Calcium Lactate Solution.

The curve showed the complete absence of waves.

Polarogram 2 (using Solution 2) The Acetaldehyde and Calcium Lactate Solution.

The half-wave potential occurred at approximately 1.75 volts.

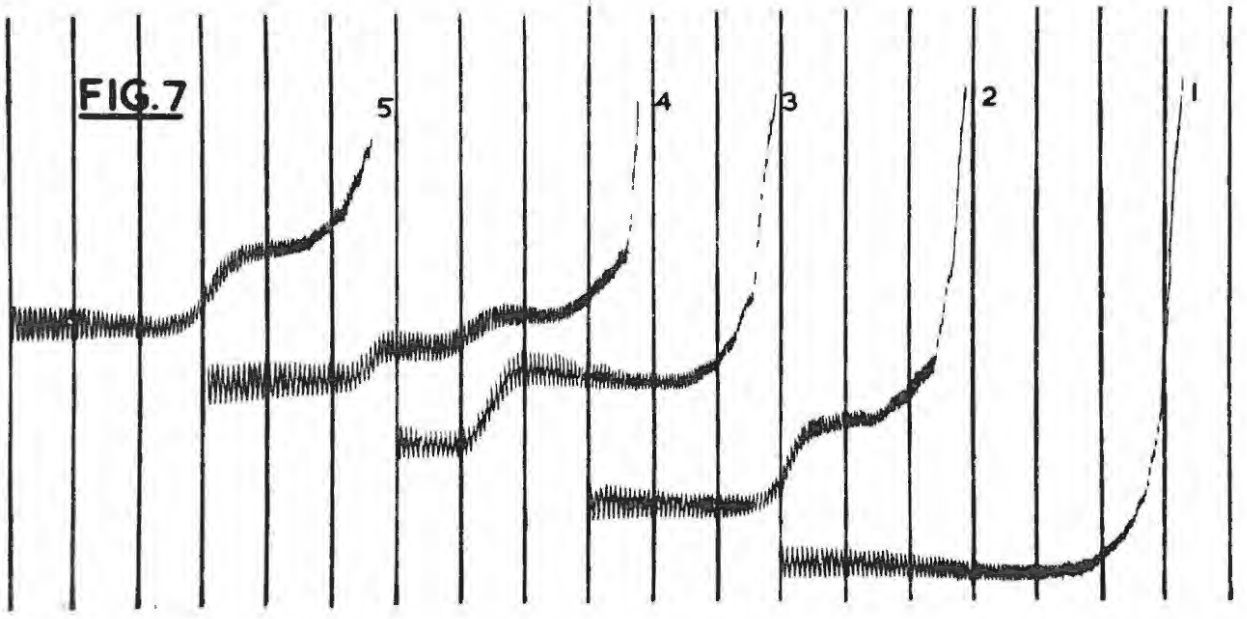
Polarogram 3 (using Solution 3) The Formaldehyde and Calcium Lactate Solution.

The half-wave potential occurred at approximately 1.56 volts.

Polarogram 4 (using a mixture of Solutions 2 and 3) Formaldehyde, Acetaldehyde and Calcium Lactate Solution.

This solution was prepared by mixing 4 ml. of Solution 3 with 4 ml. of Solution 2 in the capillary vessel. Hence the concentration of the individual aldehydes was half that used for Polarograms 2 and 3. The waves for

FIG.7



both acetaldehyde and formaldehyde were evident.

Polarogram 5 (using Solution 5) The Anode Solution.

The half-wave potential occurred at approximately 1.75 volts which is that for acetaldehyde. There was no evidence of other inflections. Thus formaldehyde and other aldehydes are not formed during the electrolysis of calcium lactate solution.

The aldehyde concentrations of the various solutions used were determined by chemical means. The concentration of the aldehyde in the capillary solutions used to make the polarograms was then calculated to be:-

Polarogram 2. Acetaldehyde 0.00041 gram equivalents per litre.

Polarogram 3. Formaldehyde 0.00044 gram equivalents per litre.

Polarogram 4. Acetaldehyde 0.0002 gram equivalents per litre.
Formaldehyde 0.00022 gram equivalents per litre.

Polarogram 5. Anode solution. Acetaldehyde 0.00035 gram equivalents per litre.

N.B. Owing to an oversight, Polarogram 4, Figure 7 was commenced at an applied voltage of 1.250 volts instead of 1.375 volts (i.e. one turn of the drum too soon). Unfortunately, the error was detected too late for a repeat series of polarograms to be made.

2) CHEMICAL METHODS.

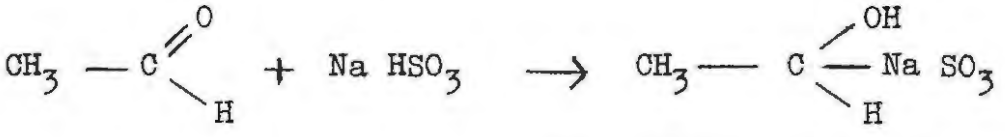
Gravimetric.

A useful survey of the methods for estimating

aldehydes has been made by Reynolds (51). Yoe and Reid (23) have utilised the reaction of dimedone with aldehydes to form the basis of a gravimetric method to estimate aldehydes. Great accuracy is claimed for the estimation of formaldehyde, provided the pH is carefully controlled, but the accuracy diminishes with higher aldehydes. At least 12 hours is required for complete precipitation. This method was not seriously considered here owing to its length. However, the reaction with dimedone was utilised in Section 3 to identify acetaldehyde as one of the products of electrolysis.

Volumetric.

The methods, which depend on the formation of an aldehyde-bisulphite by the addition of excess sodium bisulphite to the aldehyde, appeared to offer the best possibilities.



ACETALDEHYDE-BISULPHITE

The mixture of aldehyde and sodium bisulphite must be allowed to stand long enough for equilibrium to be attained.

According to the Ripper method (52), the excess bisulphite is titrated with standard iodine, but this method has disadvantages owing to the instability of the bisulphite. Koltoff (53) has calculated the inherent error which results from the dissociation of the addition compound.

Parkinson (54) endeavoured to overcome the errors in titrating bisulphite solutions with iodine by adding a measured excess of iodine and back titrating with a standard 0.1 N sodium thiosulphite solution. In this

way, using starch indicator, the end point colour change is from blue to colourless which is preferable to the reverse (53).

The Examination of the Parkinson Method.

This was thoroughly investigated to determine whether it was suitable for the measurement of acetaldehyde in dilute solution. A dilute acetaldehyde solution, of approximately the same aldehyde content as the anode solution, was prepared (i.e. approximately 0.002 molar). 20 ml. of this dilute solution was placed in a 50 ml. measuring flask. 20 ml. of 0.3 N sodium bisulphite solution was added and the flask was made up to the mark, corked, and allowed to stand for half an hour. A blank, containing no aldehyde, was prepared at the same time.

10 ml. aliquots of the aldehyde-bisulphite solution were transferred to conical flasks and 25 ml. of 0.1 N iodine was rapidly added to each. The excess iodine was rapidly titrated with standardised 0.1 N sodium thiosulphite. The thiosulphate equivalent of the aldehyde was of the order of 0.5 ml. N/50 sodium thiosulphate could have been used but this procedure was not considered to be of sufficient accuracy. The results obtained were inconsistent. Sodium bisulphite should be present in large excess to enable the aldehyde bisulphite compound to attain equilibruim (53). This immediately creates a difficulty, because sulphite should be titrated with iodine in dilute solution for accuracy (55). Furthermore, there is always a danger of loss of SO_2 by volatilisation and the sulphite may become oxidised to sulphate. Thus it appeared preferable to use a method which did not involve the estimation of excess bisulphite.

The Friedmann Method.

These difficulties are largely overcome by the method of Donnally (56) and more especially the method of Friedmann (57), for the estimation of lactic acid. The

latter method depends on the fact that at a pH of about 2 (i.e. the pH of a bisulphite solution) the dissociation constant of the aldehyde bisulphite compound is a minimum, while at pH 8 (the pH of a sodium bicarbonate solution) the dissociation of the addition compound is rapid. Thus if the aldehyde solution is allowed to stand at pH 2 in the presence of excess sodium bisulphite, and, after standing, the excess bisulphite is removed with iodine, the bound bisulphite may be released upon the addition of sodium bicarbonate, and titrated with dilute iodine. This gives a direct measure of the aldehyde in the solution.

Experimental Details.

The following solutions were prepared:-

1) Sodium Bisulphite Solution.

25 grams $NaHSO_3$ per litre. The flask was kept well corked.

2) Strong Iodine Solution.

20 grams iodine + 37 grams potassium iodide made to 1 litre. This gives a solution approximately 0.16 N with respect to I_2.

3) Standard Dilute Iodine Solution.

Made approximately 0.008 N and was prepared from Solution 2.

4) Standard Approximately 0.1 N Sodium Thiosulphate Solution.

25 grams $Na_2S_2O_7$ per litre. This was used to standardise the 0.1 N iodine daily.

5) Standard Approximately 0.1 N Potassium Bromate Solution.

2.784 grams A.R. K. bromate (dried at 120°C for 1 hour) made to 1 litre gives a 0.1 N

solution. This was used to standardise the sodium thiosulphate solution.

6) Saturated Sodium Bicarbonate Solution.

7) 10% Solution of Sodium Carbonate.
100 ml. is sufficient.

8) Starch Indicator.

After some experimentation, the following procedure was adopted which resulted in good precision and gave results for the "standard" aldehyde solutions which were in fairly good agreement with the theoretical.

20 ml. of the anode solution was pipetted into a 300 ml. conical flask. The acidity of the solution was neutralised rapidly with 0.1 NaOH using phenolphthalein as indicator. Roughly 20 ml. of the sodium bisulphite solution was added to the flask, which was then corked and allowed to stand at room temperature for about an hour and a half. The flask was then stood for 20 minutes in ice. It has been found that on lowering the temperature to $0^{o}C$ the period necessary to attain equilibrium is increased, but that the accuracy of the determination is also increased. Thus the most satisfactory procedure was to allow the reaction to approach equilibrium at room temperature and then to place the flask in ice to displace the reaction towards completion.

When the solution had become thoroughly cold, the excess bisulphite was removed by the addition of the strong KI- iodine solution. 1 ml. of fresh starch solution was added near the end point. The strong iodine solution was added to slight excess and this was then removed immediately by the addition of 0.1 N sodium thiosulphate. The walls of the flask were washed with distilled water and the end point was adjusted to faint blue with the aid of the dilute iodine solution. In

the presence of lactate, it was found that the blue colour was inclined to fade. A further drop or two of the dilute iodine was added to enable the end point colour to persist for 30 seconds. The flask was returned to the ice bath for 5 minutes whereupon the bound bisulphite compound was released by the addition of 15 ml. of the saturated sodium bicarbonate solution. The dilute iodine solution was run in at such a rate as to keep pace with the decomposition of the addition compound. Near the end point, 2 ccs. of the 10% sodium carbonate was added to ensure that the reaction had gone to completion. This usually resulted in the formation of a white precipitate which enabled the end point to be more clearly seen. The end point should persist for 30 seconds. The amount of dilute iodine solution required to react with the released bisulphite naturally gives a measure of the aldehyde in the original solution.

Each determination was performed in triplicate, together with two blanks using non-electrolysed calcium lactate.

The limitations of this method are as follows:-

1) The titration is from blue to colourless.

2) Considerable error may be introduced by air oxidation of the released sulphite after the addition of sodium bicarbonate.

Limitation 2) may be minimised by:-

a) The use of dilute solutions.

b) Titration of the bound sulphite as soon as it is released.

c) By keeping the system at $0^{o}C$.

The dilute iodine solution required standardisation every day as it was found that the concentration of this solution dropped daily by about 0.3%. On the other hand, the solutions of thiosulphate were found to remain fairly constant.

Reynolds (51), who has made a careful study of the rate at which the acetaldehyde-bisulphite reaction reaches equilibrium, has found that the r eaction reaches a constant maximum accuracy of 90% at 0°C. Thus all the results obtained in the present investigation have been increased by a factor of 100/90.

Correction for Acetaldehyde Vaporisation Losses.

A correction was applied to account for the loss of acetaldehyde due to volatilisation during the course of the electrolysis.

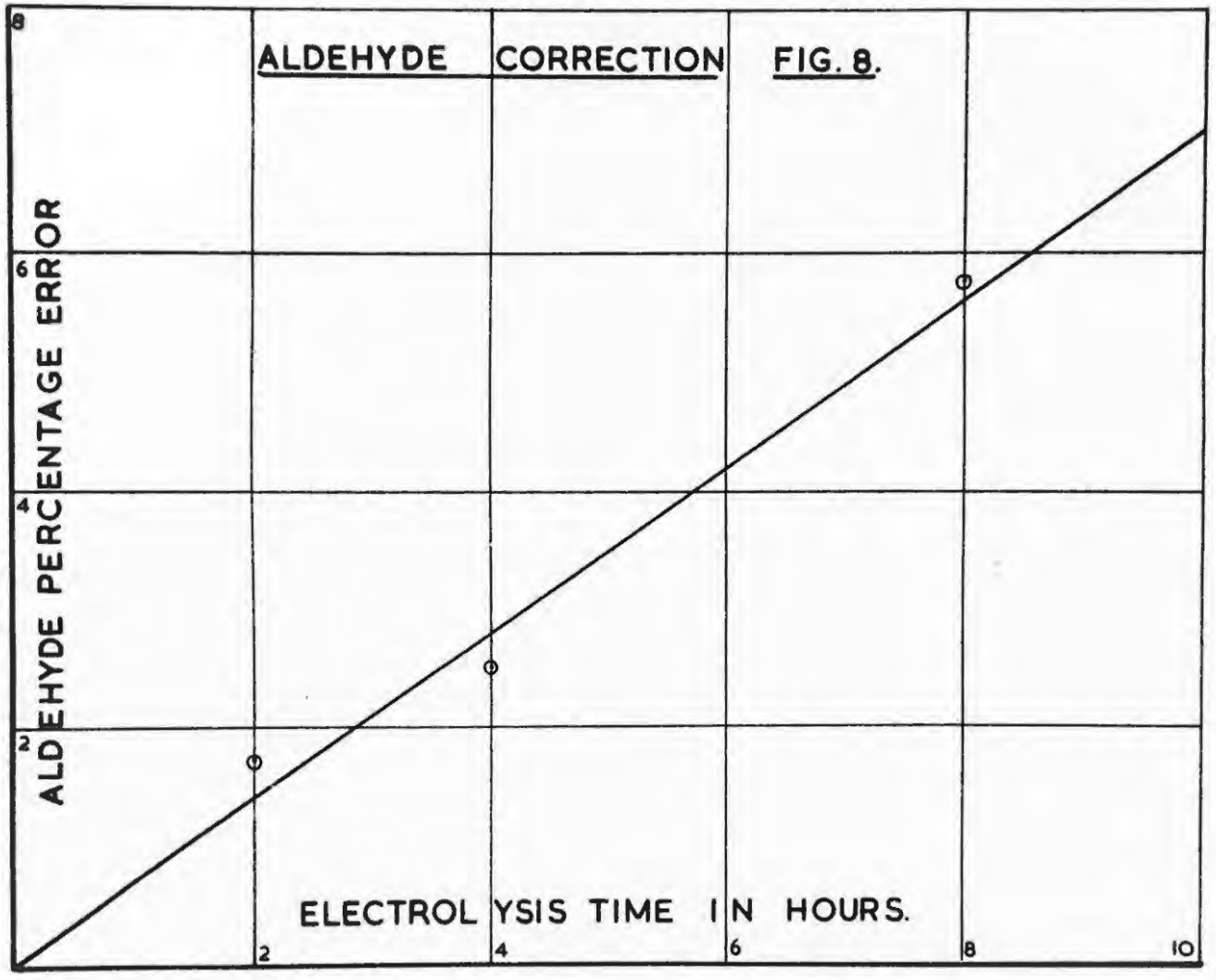
The correction was determined by electrolysing 350 ml. of calcium lactate solution at a current of 70 mA. for a period of 5 hours. The current was switched off and the apparatus was allowed to stand under the same conditions as had been encountered during the electrolysis. Aldehyde determinations were made every hour. The losses for the two cells were found to be almost identical.

TABLE IX.

Figure 8.

(Acetaldehyde Loss.)

Hours of Standing	Equivalent Electrolysis Time	Equivs. Aldehyde Found	Percentage Lost
0	0	0.001387	0
1	2	0.001363	1.73
2	4	0.001352	2.52
4	8	0.001308	5.77
17½	35	0.001156	16.65


ALDEHYDE CORRECTION FIG. 8.
ALDEHYDE PERCENTAGE ERROR
8
6
4
2
ELECTROLYSIS TIME IN HOURS.
2
4
6
8
10

The loss, calculated as a percentage of the original number of gram equivalents, was plotted graphically against time. (See Figure 8.) The points were found to lie on a reasonable straight line. The percentage loss after 5 hours standing was approximately 7%.

It was assumed that the loss of acetaldehyde during electrolysis occurred in a similar manner to the radiation of heat from a body which is being warmed. In other words a curve similar to Renault's cooling curve, would apply for the loss of acetaldehyde during an electrolysis.

Thus, according to this hypothesis, the loss of acetaldehyde for an electrolysis of x hours duration should be equivalent to the loss when allowing the apparatus to stand for $\frac{x}{2}$ hours after the current had been switched off.

This correction has been applied to all recorded acetaldehyde determinations.

SUMMARY OF SUB-SECTION 7B.

1) Various methods for the quantitative estimation of aldehydes have been investigated.

2) The polarographic method, although sensitive, is open to serious error due to the evaporation of the aldehyde and is very sensitive to temperature variation. This method was used, however, to confirm qualitatively that acetaldehyde only is produced by the electrolysis.

3) Of the various chemical methods investigated, a modified method of Donnally and Friedmann was finally adopted for the quantitative estimation of acetaldehyde.

4) A correction curve has been plotted for the evaporation of acetaldehyde during the electrolysis.

This has been based on Renault's cooling curve principle.

SUB-SECTION 7C.

THE ESTIMATION OF THE ELECTROLYSIS ACIDS.

1) The Total Acidity.

In the early stages of this work, some investigations were made into the efficiency of acid production at various current densities. It was also of interest to determine whether the level of efficiency was maintained during an electrolysis or not.

The procedure adopted was to electrolyse the calcium lactate solution at a particular current density and to withdraw 5 ml. portions of the anolyte every two hours for analysis. The titration was performed with standard sodium hydroxide using phenolphthalein as indicator. The end point was inclined to fade due to the presence of dissolved carbon dioxide, but, with experience, the correct end point could be determined without the necessity of boiling the solution. The total number of gram equivalents of acid was calculated from the normality and the volume of the solution when the titration was made. It was found necessary to measure the volume of the solution each time a calculation was made as there appeared to be a certain amount of electro-osmosis taking place. The volume of the anolyte diminished to a greater extent than could be accounted for by the removal of 5 ml. for each titration. The cathode solution (in the porous pot) was replaced every 2 hours of electrolysis, otherwise there was a marked drop in the efficiency of acid production. This may have been due to the diffusion of the alkaline solution into the anode compartment.

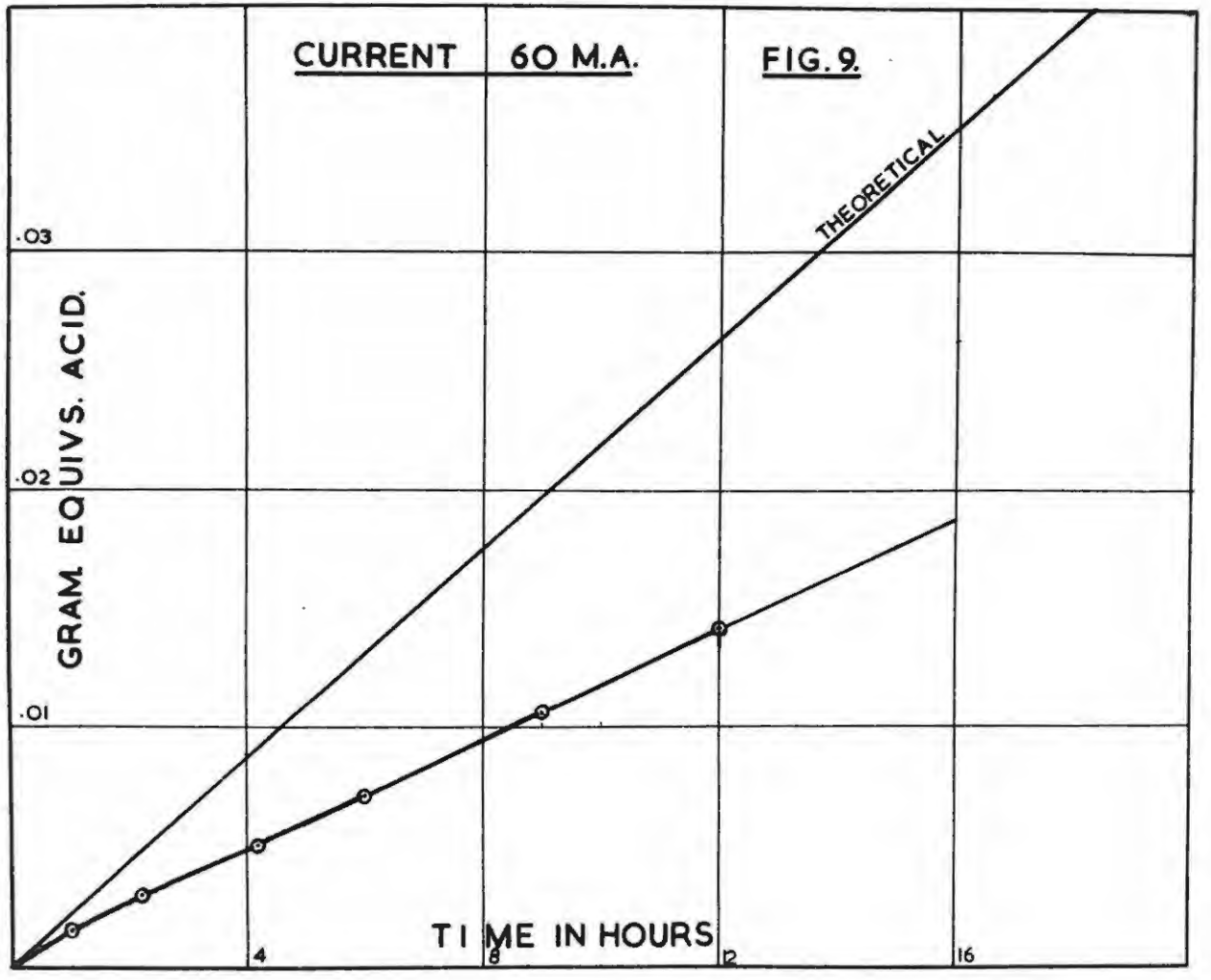

CURRENT 60 M.A.
FIG. 9.
THEORETICAL
.03
.02
.01
GRAM. EQUIVS. ACID.
4
8
12
16
TIME IN HOURS

TABLE X.

Figure 9.

Current 60 mA. (6 sq. cm. electrodes).

Time in hrs.	Vol. Anode Soln. in ml.	Normality Acid	Gram Equivs. Acid	Theoretical
1.0	268	0.0055	0.0014(8)	
2.2	260	0.0114	0.0029(7)	
4.2	253	0.0197	0.0050	
6.0	246	0.0287	0.0070(8)	
9.0	239	0.0445	0.0106	
12.0	231	0.0612	0.0142	0.0268

TABLE XI.

Figure 10.

Current 40 mA. (6 sq. cm. electrodes).

Time in hrs.	Vol. Anode Soln. in ml.	Normality Acid	Gram Equivs. Acid	Theoretical
1	275	0.0047(3)	0.0013	
2	270	0.0085(8)	0.0023(2)	
3½	262	0.0134	0.0035	
6	256	0.0243	0.0063	
8	248	0.0298	0.0073(9)	
11	242	0.0405	0.0097(9)	0.01642
14	234	0.0499	0.0116(8)	
16	227	0.0568	0.0129	

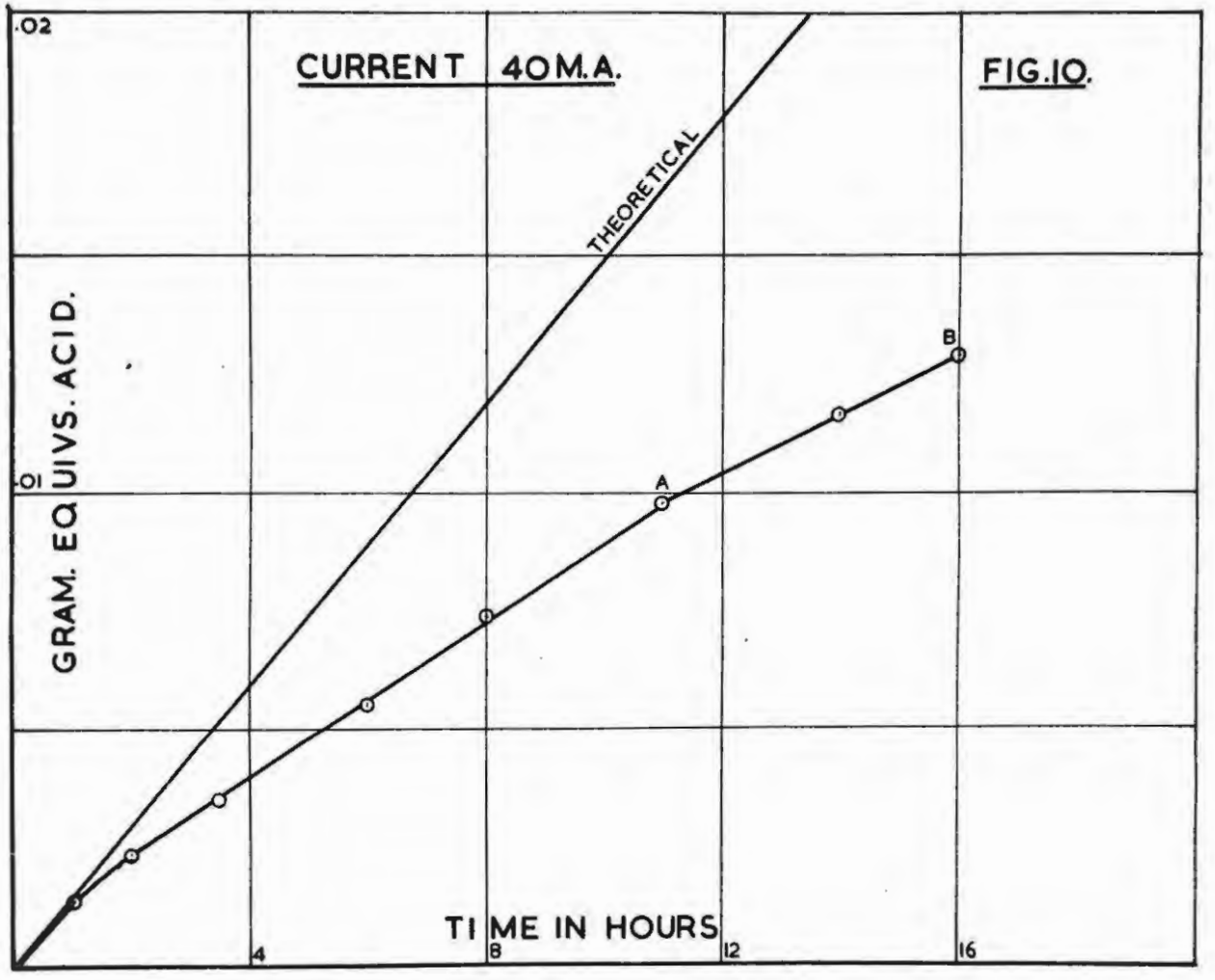

.02
CURRENT 40M.A.
FIG.10.
THEORETICAL
B
A
.01
GRAM. EQUIVS. ACID.
TIME IN HOURS
4
8
12
16

TABLE XII.

Figure 11.

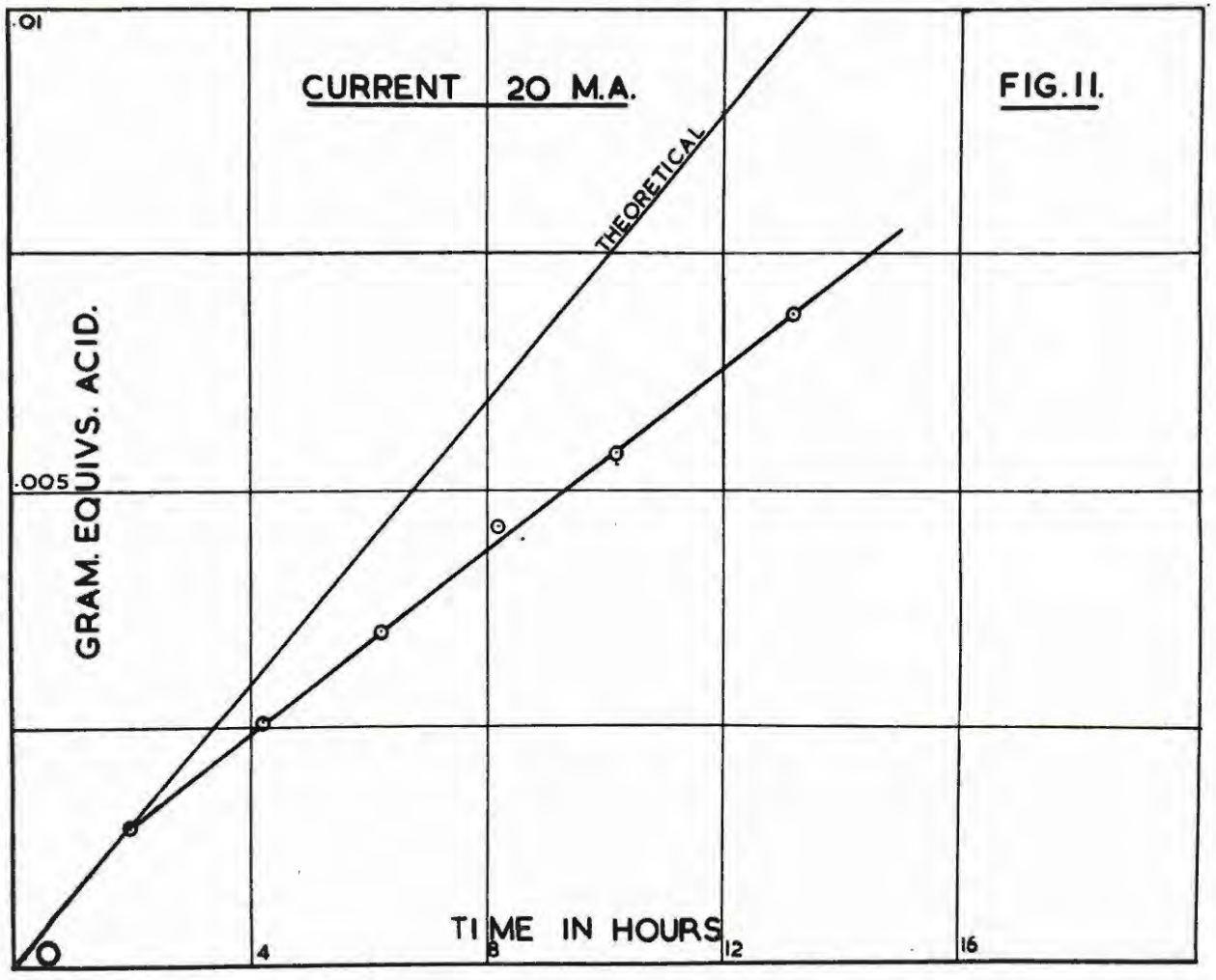
Current 20 mA. (6 sq. cm. electrodes).

Time in hrs.	Vol. Anode Soln. in ml.	Normality Acid	Gram Equivs. Acid	Theoretical
2.0	273	0.0053(8)	0.0014(7)	0.00149
4.2	266	0.0096	0.0025(6)	
6.2	260	0.0136	0.0035(3)	
8.2	255	0.0181	0.0046(3)	
10.2	247	0.0219	0.0054(1)	0.00758
13.2	241	0.0280	0.0067(5)	

The figures for the theoretical gram equivalents of acid have been calculated on the assumption that 1 gram equivalent of acid is produced by the passage of 1 Faraday. It is evident that the efficiency of acid production decreases with increased current density.

Current	Percentage Efficiency.
20 mA.	68%
40 mA.	56%
60 mA.	52.8%

It is also noticeable from the graphs that at the lower current densities the acid production approaches the theoretical during the first hour of electrolysis.


.01
CURRENT 20 M.A.
FIG. II.
THEORETICAL
GRAM. EQUIVS. ACID.
.005
TIME IN HOURS
0
4
8
12
16

THE ESTIMATION OF THE ACIDS INDIVIDUALLY.

Vacuum Distillation.

As has been indicated previously, three acids were found among the products of the anodic oxidation of calcium lactate; namely, lactic, acetic and a trace of pyruvic acid. Vacuum distillation was considered to be the most suitable means of separating acetic acid from lactic and pyruvic acids. Steam distillation was most undesirable, as it has been shown that there is a certain amount of decomposition of lactic acid to formic acid under the influence of steam (58). Furthermore, variable quantities of lactic acid are carried over with steam and up to 25% of the volatile acids may remain in the distilling flask.

Acetic acid has a boiling point of 118.2°C, so there appeared every hope that vacuum distillation would result in an efficient separation, provided the distillation was continued until the temperature of the distilling vapour had begun to fall.

The Accuracy of Separation.

This was checked by vacuum distilling calcium lactate solutions containing known quantities of lactic and acetic acids in approximately the same proportions as encountered in the anode solution.

The reduced pressure was adjusted so that most of the distillate came over at a temperature of 30°C. During this period, the bath was kept at a temperature of 40°C. Near the end of the distillation, the bath temperature was increased to a definite maximum and the distillation was continued until all the distillate had come over. This point was indicated by a fall in the temperature recorded by a thermometer placed in the path of the distilling vapour. For the sake of uniformity the distillation was discontinued when the temperature

had fallen to 22°C.

The aqueous fraction containing the acetic acid was made up to 200 ml. in a measuring flask, while the solid residue, containing the lactic acid was dissolved in water and made up to 250 ml. The acetic acid solution was titrated with standard approximately 0.005 N sodium hydroxide, while the lactic acid solution was titrated with approximately 0.01 N sodium hydroxide. Blank corrections were applied. The accuracy of the acetic acid separation did not come up to expectations. The large percentage error was due, principally, to the small quantity of this acid in the mixture.

Various maximum bath temperatures were employed in the subsequent distillations in order to determine what maximum bath temperature resulted in the best quantitative separation of the acids.

The results of these investigations have been recorded in Table XIII.

TABLE XIII.

Quantitative Vacuum Distillation.

	Max. Bath Temp.	Gram Equivs. Lactic Acid x10^5	Percentage Error	Gram Equivs. Acetic Acid x10^5	Percentage Error	Total Acid Gram Equivs. x10^5	Percentage Error
Theoretical		494		112		606	
	45°C	502	1.6	101	-10.0	603	-0.5
	45°C	501	1.5	102	-9.3	602(4)	-0.6
	50°C	494	0.0	107	-3.1	601(6)	-0.7
	50°C	491	-0.7	107(6)	-3.1	598	-1.3

TABLE XIII (Contd.)

	Max. Bath Temp.	Gram Equivs. Lactic Acid x10^5	Per-cen-tage Error	Gram Equivs. Acetic Acid x10^5	Per-cen-tage Error	Total Acid Gram Equivs. x10^5	Per-cen-tage Error
Theo-retical		427(9)		114(2)		542(1)	
	55°C	419(7)	-1.9	114(3)	0.0	534	-1.5
	55°C	418	-2.4	117(3)	2.7	535(3)	-1.2
Theo-retical		446(7)		618		508(5)	
	60°C	439(6)	-1.5	657	6.4	505(3)	-0.6

It appeared evident from a study of Table XIII that there is always a small loss of total acidity on vacuum distillation. It is possible that some of the lactic acid was oxidised to CO_2 and water by the continuous stream of air that was bubbled through the liquid (59).

The quantity of acid found in the aqueous distillate appeared to be very dependent on the maximum bath temperature. The most satisfactory distillations occurred at maximum bath temperatures between 50°C and 55°C. Below this temperature the yield of acetic acid was up to 10% low, while above this range the yield was high.

The estimation of the lactic acid fraction is far less dependent on the bath temperature due to the comparatively large amount of the acid present.

Unfortunately, due to a shortage of time, it was not possible to make a more comprehensive study of the factors affecting vacuum distillation. It is felt

that an investigation into the effects of bath temperature, vacuum pressure and bubbling rate on the accuracy of the separation of volatile from non-volatile acids would be of value, especially in the biological field where the methods used at present, namely, steam distillation, ether extraction and partition solubility, are not very accurate.

In view of the importance of bath temperature, a large water bath of 3 litres capacity was used for all subsequent vacuum distillations. By this means, a greater control of bath temperature was possible.

The following procedure was finally adopted as a result of these preliminary investigations:-

> The bath temperature was controlled at 40°C for the major portion of the distillation, whereupon the bath temperature was increased to 50°C and was maintained at this value until the temperature of the distillate had fallen to 22°C. The pressure was adjusted to enable the majority of the aqueous fraction to be collected at a vapour temperature of 30°C to 35°C.

The Partition Solubility Method.

The partition solubility method of Behrens (60) was also examined to see whether it could be applied with convenience to the quantitative estimation of the mixture of acetic and lactic acids. According to this method, the mixture of the two acids is shaken with 25 ccs. of ether and 75 ccs. of water. The two solvents are then separated and the acid content is determined with standard alkali. With a knowledge of the partition coefficients of lactic and acetic acids between ether and water, it is possible to estimate the concentration of each acid in

the mixture. Unfortunately, the presence of calcium lactate in the solution is a complicating factor, and the partition coefficient of this substance between ether and water would have to be known before calculations could be made. For this reason the method was abandoned.

SUMMARY OF SECTION 7C.

1) Tables and graphs have been prepared to determine the efficiency of total acid production at various anode currents using the 6 sq. cm. electrodes.

2) An investigation has been conducted to determine the most suitable procedure for a quantitative separation of the volatile and non-volatile acids in the anode solution by vacuum distillation.

3) The partition solubility method was also investigated but was found to be unsatisfactory under the present conditions.

SUB-SECTION 7D.

THE COMPLETE ANALYSIS OF THE PRODUCTS OF ELECTROLYSIS.

As a result of the work performed in the previous sub-sections, the procedure adopted for a complete analysis of the products of electrolysis was as follows:-

The calcium lactate solution and a quantity of distilled water were saturated with carbon dioxide for 2 hours prior to the electrolysis. The Bunte burette was filled with the distilled water saturated with CO_2, while the gas collection burette was filled with the electrolyte. The side arms of the two burettes were joined together, copper ligatures were applied, and the electrolysis was commenced. Two electrolyses were performed concurrently. In the first, the 6 sq. cm. electrodes were used, while the 2 sq. cm. electrodes were used in the other.

The current was checked at regular intervals and the cathode solution was replaced every 2 hours with the aid of a 100 ml. pipette. After the electrolysis had proceeded for a predetermined time, the anode gas was transferred to the Bunte burette with the aid of suction. As soon after as possible, the total volume of the gas was measured using the levelling bottle in order to prevent absorbtion of carbon

dioxide. The gas analyses were delayed for convenience.

In order to prevent diffusion, the cathode compartment was removed from the anolyte as rapidly as possible. Also, as rapidly as possible, 20 ml. portions of the anolyte were pipetted into conical flasks for the acetaldehyde determinations. These pipetted solutions were neutralised with 0.1 N NaOH, and 20 ml. of the $NaHSO_3$ solution was added to each. The flasks were firmly corked and set aside for 2 hours.

In the meantime, the total acidity of the anolyte was measured by titrating 10 ml. aliquots with standard 0.01 N sodium hydroxide. 150 ml. of the anolyte was measured out as accurately as possible, using measuring flasks, for the purposes of the vacuum distillation. The distillations took at least 4 hours, and during this period the gas analyses were performed. A regular check was kept on atmospheric pressure and room temperature for the purposes of the gas analyses.

After standing at room temperature for 1½ hours, the flasks, set aside for the acetaldehyde determination, were placed in ice for ½ hour. The acetaldehyde determinations were then performed in the manner previously described.

When the vacuum distillations were complete, the residue containing the lactic acid was made to 250 ml. while the distillate containing the acetic acid was made to 200 ml. These solutions were then estimated with standard sodium hydroxide.

A Specimen Electrolysis and Analysis.

A specimen electrolysis and analysis has been included to give some indication of the calculations involved and the manner in which the results in Table XIV, Section 7D have been obtained.

Electrolysis No. 9.

Electrode size - 6 sq. cm.

Volume of calcium lactate solution - 350 ml.

CO_2 bubbled through electrolyte for 1 hour before electrolysis.

Initial applied voltage - approximately 13 volts.

Total current - 60 mA.

Duration of electrolysis - 270 minutes.

Volume of anode solution after electrolysis - 344 ml.

Gas Analysis.

Room temperature - 18.5°C.

Atmospheric pressure - 713.9 mms. mercury.

Water vapour pressure - 15.97 mms. mercury.

Meniscus correction for gas tube of 11 mms. diameter (from Tables) - 0.2 ml.

Total volume of gas at atmospheric pressure - 41.9 - 0.2

= 41.7 ccs.

Volume after CO_2 removed - 25.6 - 0.2

= 25.4 ccs.

Volume after O_2 removed - 4.0 - 0.2
= 3.8 ccs.

Volume after CO removed - 3.1 - 0.2
= 2.9 ccs.

Total volume at N.T.P. - $\frac{41.7 \times 697.9 \times 273}{760 \times 291.5}$

= 35.8(7) ccs.

Volume after CO_2 removed at N.T.P. = 21.8(9) ccs.

Volume after O_2 + CO removed = 2.50 ccs.

Thus volume of CO_2 at N.T.P. - 13.98 ccs

Volume of O_2 at N.T.P. - 19.39 ccs

Gram equivalents CO_2 = $\frac{13.98}{22414}$

= 0.000624

Gram equivalents O_2 - $\frac{19.39 \times 4}{22414 \times 1}$

= .00346

(1 gram equivalent of O_2 occupies $\frac{22414}{4}$ ccs.)

Acetaldehyde Determination.

20 ml. aliquots pipetted into conical flasks.

20 ml. $NaHSO_3$ added after acid neutralised.

Normality of dilute I_2 solution - 0.006722 N

Volume of dilute I_2 required

1) 22.80 ml.
2) 22.72 ml. Blank 1.3 ml.
3) 22.75 ml.

Mean volume - 22.75 - 1.3 = 21.45 ml.

Number of gram equivalents - $\frac{21.45 \times .006722 \times 344 \times 103.8}{1000 \times 2 \times 20 \times 90}$

(Correction for aldehyde loss after 4.5 hours electrolysis is 3.8%.)

Number of gram equivalents = 0.001446

Total Acidity.

10 ml. portions of anode solution titrated with 0.009992 N sodium hydroxide.

1) 21.2 ml.
2) 21.5 ml.
3) 20.9 ml. Blank 0.3 ml.
4) 21.1 ml.

Normality of anode solution - $\frac{20.9 \times .009992}{10}$

= 0.02088 N

Number of gram equivalents = $\frac{0.02088 \times 344}{1000}$

= 0.007185 gram equivalents

Individual Acids.

Volume anode solution vacuum distilled - 150 ml.

Solid residue containing lactic acid made to 250 ml.

Distillate containing acetic acid made to 200 ml.

Lactic Acid. (including a trace of pyruvic acid).

25 ml. portions titrated with 0.00999 N NaOH

1) 25.3 ml.

2) 25.3 ml. Blank 0.3 ml.

3) 25.2 ml.

Gram equivalents lactic

$$\frac{25.0 \times .009992 \times 250 \times 344}{25 \times 1000 \times 150}$$

$$= \underline{0.00573} \text{ gram equivalents}$$

Acetic Acid.

25 ml. pipetted and titrated with 0.004996 N NaOH

1) 11.8 ml.

2) 11.6 ml. Blank 0.5 ml.

3) 11.8 ml.

Gram equivalents acetic

$$\frac{11.3 \times .004996 \times 200 \times 344}{25 \times 1000 \times 150}$$

$$= \underline{0.00104} \text{ gram equivalents}$$

The results for 34 electrolyses and analyses at various anode currents have been recorded in Table XIV. Paired electrolysis numbers indicate that the two electrolyses were conducted concurrently.

S E C T I O N 8.

A DISCUSSION ON THE REACTIONS INVOLVED IN THE ELECTROLYSIS OF CALCIUM LACTATE.

INTRODUCTION.

The electrolysis of potassium acetate and the Kolbe reaction have been studied in great detail. It was felt that a consideration of the various general theories, which have been advanced to explain this electrolysis, might be of assistance in elucidating the reactions which occur during the electrolysis of calcium lactate.

The Discharged Ion Theory.

According to this theory, which was proposed by Brown and Walker (61), and followed the development of of the Theory of Ionic Dissociation, the anions of the organic acid are discharged at the anode. The resulting radicals may react with each other, if they are present in sufficient concentration, to give the Kolbe reaction.

$$2\ CH_3.COO^- \longrightarrow 2\ CH_3.COO^{\cdot} + 2e$$

$$2\ CH_3.COO^{\cdot} \longrightarrow C_2H_6 + 2\ CO_2$$

If the current density is low and the concentration of the discharged radicals is small, the reaction with water takes place in preference.

$$2\ CH_3.\ COO^{\cdot} + H_2O \longrightarrow 2\ CH_3COOH + O$$

The Hofer-Moest reaction is due to the simultaneous discharge of an acetate and a hydroxyl ion.

$$CH_3COO^- + OH^- \longrightarrow CH_3OH + CO_2 + 2e$$

One of the main pieces of evidence in support of this theory is the fact that there is a critical potential of 2.14 volts in a number of acetate solutions below which the Kolbe reaction does not take place (40). Hence, here the voltage is a primary factor in determining what reaction occurs.

However the critical potential at which the Kolbe reaction occurs is much higher than that for the evolution of oxygen at the same current density and pH. The theory is unable to explain why the evolution of oxygen does not occur in preference, unless the deposition of the hydroxyl ion is prevented in some way. It is an experimental fact, however, that the evolution of oxygen ceases entirely when ethane is evolved strongly.

A further phenomenon, which could not be explained by the Discharged Ion Theory, is the fact that certain catalysts, such as lead, silver, manganese, etc., completely inhibit the Kolbe reaction (41). In addition, the reaction does not occur at platinised platinum, gold, iron or nickel electrodes (41).

The Hydrogen Perioxide Theory.

In view of these difficulties, Glasstone and Hickling (41) have proposed the Peroxide Theory to explain the phenomena encountered. The origin of the theory lies in the observation that the catalysts which inhibit the Kolbe reaction are also catalysts for the decomposition of hydrogen peroxide.

Hydrogen peroxide is first formed at the anode by the irreversible union of two hydroxyl radicals.

$$2\ OH^- \longrightarrow 2\ OH^{\cdot} + 2\ e$$

(OH· : radical)

$$2\ OH^{\cdot} \longrightarrow H_2O_2$$

The hydrogen peroxide, if present in sufficient concentration will react with the acetate ions to give the Kolbe reaction.

$$H_2O_2 + 2\ CH_3COO^- \rightarrow C_2H_6 + 2\ CO_2 + 2\ OH^-$$

If the acetate concentration is small, or if the hydrogen peroxide concentration is low due to decomposition, the Hofer-Moest reaction takes place. Peracetic acid is formed first which decarboxylates to form methyl alcohol as follows:-

$$CH_3.COOH + H_2O_2 \longrightarrow H_2O + CH_3COOOH$$

or

$$CH_3.COOH + O \longrightarrow CH_3COOOH$$

$$CH_3COOOH \longrightarrow CH_3OH + CO_2$$

The failure of the Kolbe reaction to occur at electrodes of platinised platinum, iron, gold, etc. is explained by the fact that these metals, or the oxides thereof, are the catalysts for the decomposition of hydrogen peroxide. Glasstone and Hickling, from the evidence of anode potential/current density curves, do not entertain the possibility ofthe acetate ion being discharged at the anode, and maintain that the hydroxyl ion is the only ion that is discharged in any electrolysis.

The Peroxide Theory has been used to offer reasonable explanations for a number of electrolytic

reactions which had proved difficult hitherto.

However the theory was unable to explain the occurrence of the Kolbe reaction in non-aqueous solutions and in fused electrolytes. A further blow was dealt to this theory by Haissinsky and Cottin (62), who electrolysed solutions of potassium carbonate in the presence of hydrogen peroxide. It was found that the presence of the peroxide actually inhibited the formation of percarbonate. Haissinsky believes that it is impossible to admit a general mechanism for electrolytic reactions at different electrodes under widely different conditions, and feels that it is preferable to formulate a suitable mechanism from experimental data in each particular case.

Thus, the present position seems to be that most of the existing general theories of electrolysis have been discredited. The problem therefore is to determine what causes the oxygen overvoltage to be so high in the presence of certain ions, such as acetate and malonate, that, using a smooth platinum electrode, reactions demanding a high potential are permitted. It has been suggested (63) that the Kolbe reaction occurs at a potential far above that for the evolution of oxygen, because the hydroxyl ions are prevented from discharging for some reason or other. This may be due to the formation of a surface film of acetate ions on the anode, sufficiently compact to prevent the majority of the hydroxyl ions from getting through. The acetate ions would then be discharged in preference.

THE ELECTROLYSIS OF CALCIUM LACTATE.

In consideration of the various theories and electrolytic reactions referred to in the introduction to this section, two series of possible reactions have been worked out for the electrolysis of calcium lactate which

have been based on:-

a) The discharge of the hydroxyl ion only.

b) The discharge of the lactate ion only.

From a critical examination of the products of electrolysis it was hoped to determine which of the series of reactions is more likely to apply.

The Hydroxyl Ion Discharge.

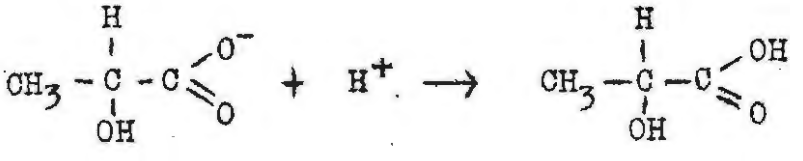
The reactions which may occur are as follows: The hydroxyl ion may discharge to form a hydroxyl radical. Two radicals then combine to form oxygen and water.

$$2\ OH^- \longrightarrow 2\ OH^{\cdot}\ (\text{radical}) + 2\ e$$

$$2\ OH^{\cdot} \longrightarrow H_2O + \tfrac{1}{2}\ O_2 \quad \text{(Equation 1)}$$

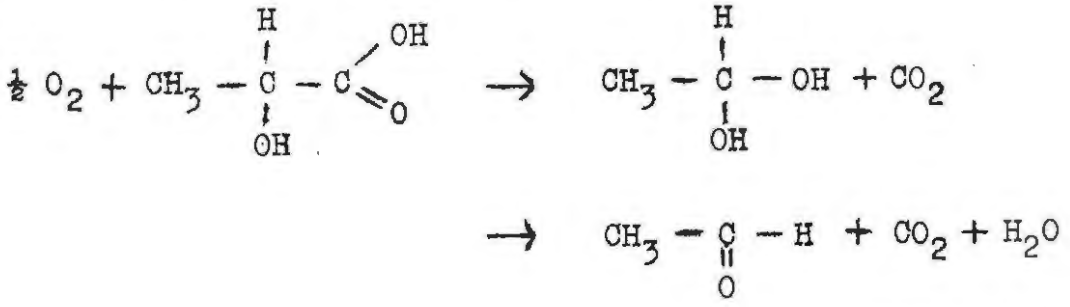
This process is similar to that postulated by the Peroxide Theory except that water and oxygen are formed here instead of hydrogen peroxide. The oxygen is available for further oxidation.

The discharge of the hydroxyl ions results in an excess of hydrogen ions in the anode compartment. These combine with lactate ions in the solution to form lactic acid.



(Equation 2)

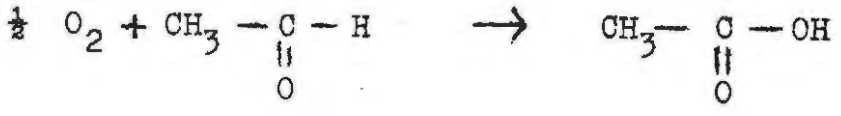
In the presence of excess lactate ions, the lactic acid will remain largely undissociated. Oxidation of the lactic acid may then take place.



(Equation 3)

This process may be compared with the Hofer-Moest reaction for acetates.

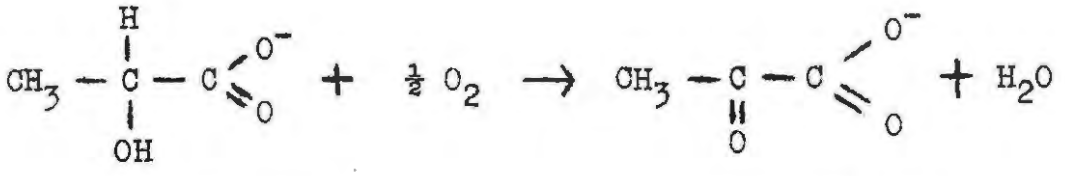
The acetaldehyde so formed may be further oxidised to acetic acid.



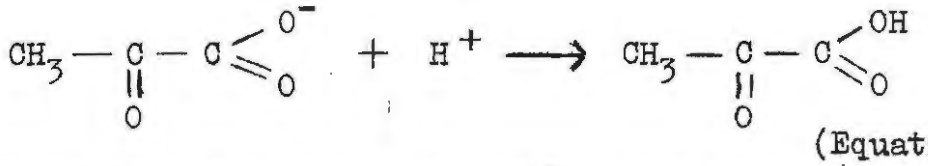
(Equation 4)

Thus, according to this formulation, two equivalents of oxygen are required to produce one equivalent of acetaldehyde, and four equivalents of oxygen are required to produce one equivalent of acetic acid.

The lactate ion may be oxidised to the pyruvate ion, which, in turn, undergoes the same reaction as Equation 2 to form pyruvic acid.

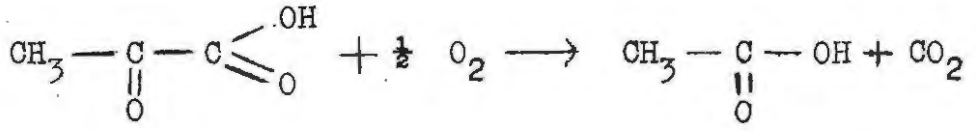


LACTATE ION PYRUVATE ION



(Equation 5)

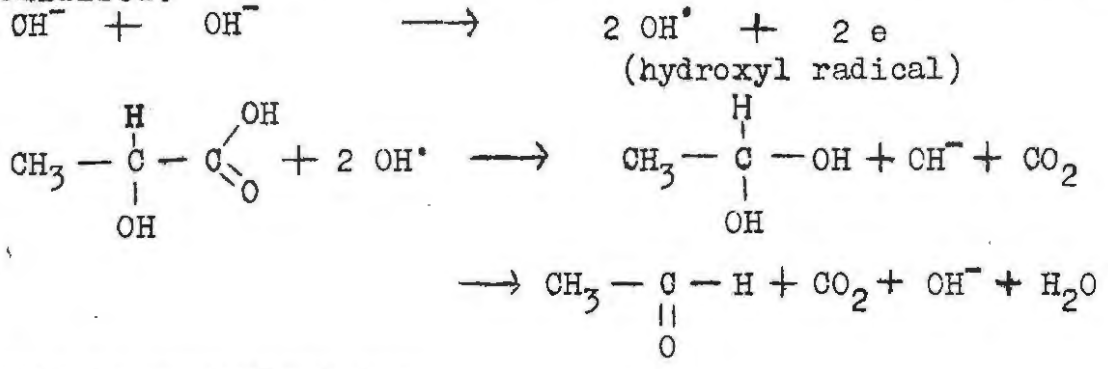
Further oxidation would produce acetic acid and carbon dioxide without passing through the intermediate stage of acetaldehyde.



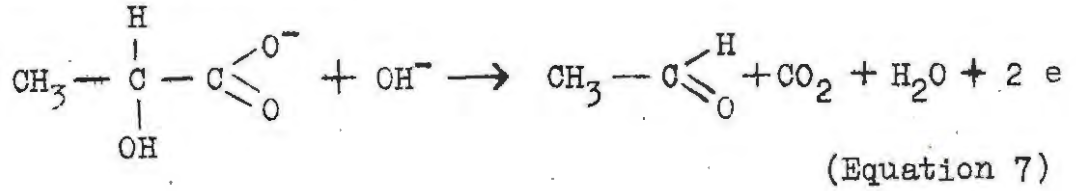
(Equation 6)

(Hofer electrolysed pyruvic acid and found the products to be acetic acid, carbon dioxide and a little diacetyl. No acetaldehyde was produced (64).)

In the preceeding formulations, it has been assumed that the oxidation process has been achieved by nascent or gaseous oxygen. However, it is possible that the oxidation may be accomplished by the hydroxyl radical, in which case, the lactate ion and not lactic acid would be oxidised.



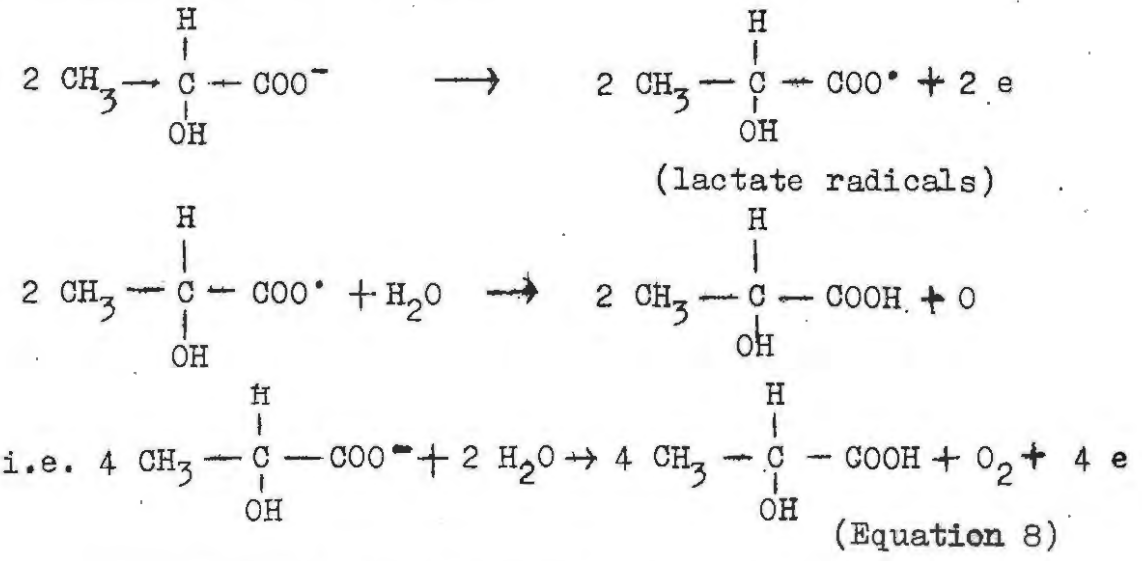
This is equivalent to:-



(Equation 7)

Lactate Ion Discharge.

If the lactate ion only is discharged, as envisaged by the Discharged Ion Theory, the following reactions may be expected:



(lactate radicals)

(Equation 8)

Some of the liberated oxygen would then be consumed in oxidation processes as represented by Equations 3, 4, 5 and 6.

Thus, from Equation 8, the passage of one Faraday produces one equivalent of lactic acid and one equivalent of oxygen.

INFORMATION FROM THE RESULTS OF THE QUANTITATIVE ANALYSES

In order to make a comparative examination for the various electrolyses, the products of electrolysis have been expressed in terms of gram equivalents per Faraday. These figures have been recorded in columns, A, B, C, D, E and F of Table XV, Section 8 and have been graphically represented (against total current) in Figures 12 and 13. (The letter describing the curve represents the particular column in Table XV, while the

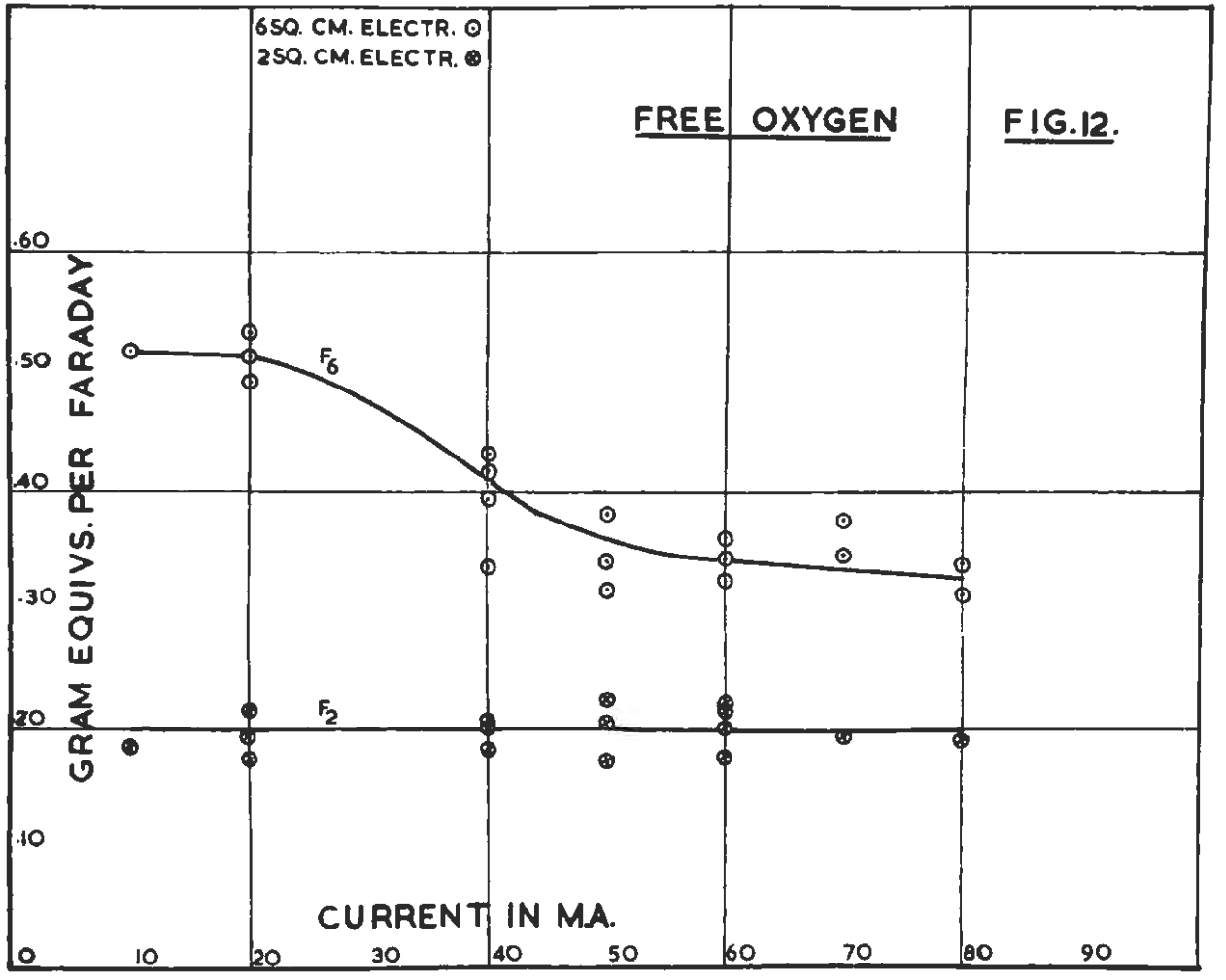
numerical suffix represents the electrode area.)

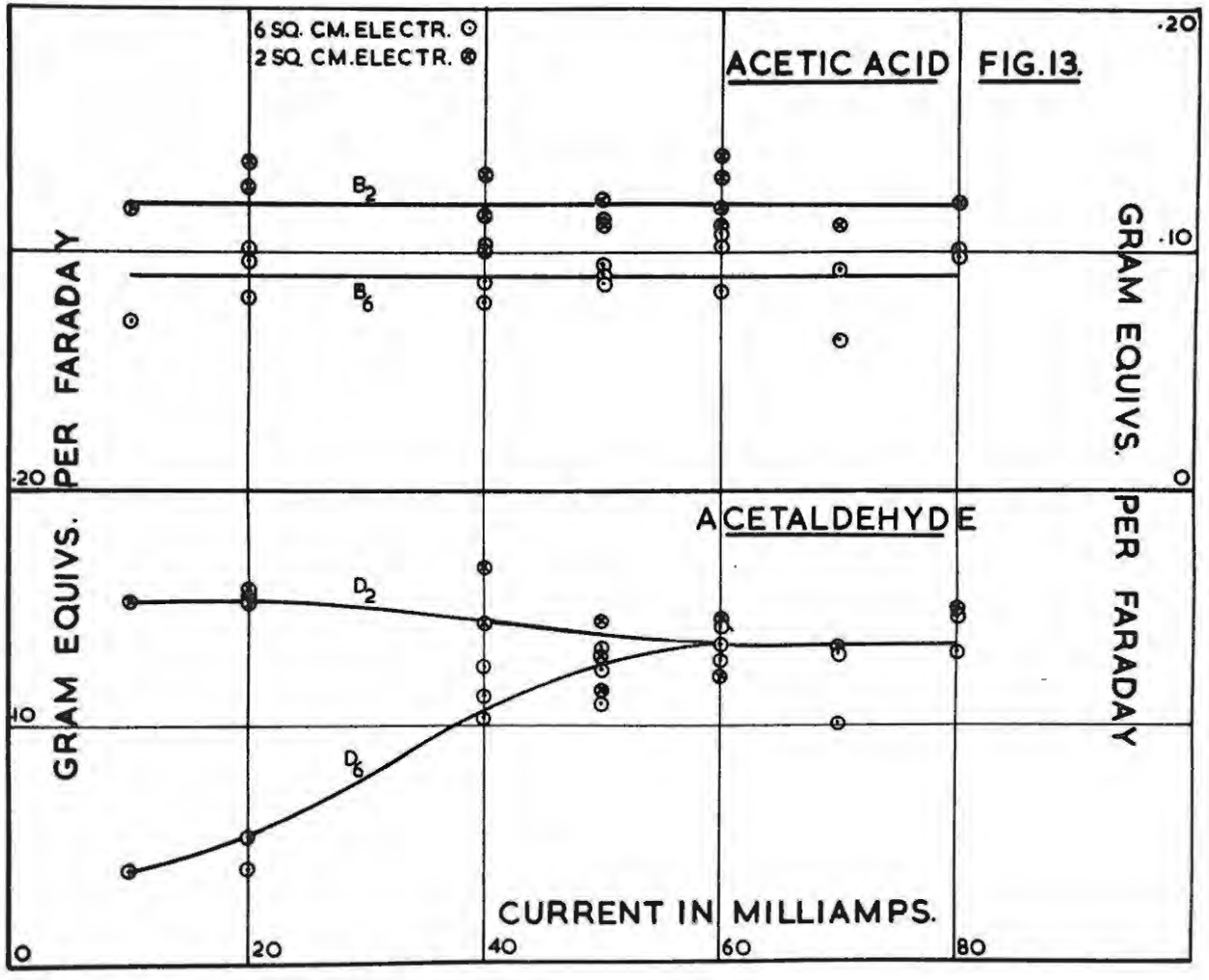
An examination of Figures 12 and 13 shows that, for the 6 sq. cm. electrodes, there is a falling off of aldehyde production (Curve D_6) and a corresponding increase in oxygen evolution (Curve F_6) at low anode current densities. On the other hand the acetic acid production remains reasonably constant at all current densities.

Since two equivalents of oxygen are consumed in the production of one equivalent of acetaldehyde, (Equation 3) it was considered to be of greater interest to compare the oxygen value (gram equivalents per Faraday) with twice the acetaldehyde value. (See Curves F_6 and $2D_6$ in Figure 14 for the 6 sq. cm. electrodes, and Curves F_2 and $2D_2$ in Figure 15 for the 2 sq. cm. electrodes.) The sum of these two quantities, $F + 2D$, has been recorded in Column G, Table XV and gives a reasonably constant value for a particular set of electrodes. G_6 (i.e. $F_6 + 2D_6$) gives an average value of approximately 0.6 gram equivalents per Faraday while G_2 gives a value of approximately 0.5 gram equivalents per Faraday. G_6 and G_2 have been graphically represented in Figures 14 and 15 respectively. A certain degree of convergence of values of G for the two sets of electrodes at equivalent current densities was expected, but this does not appear to be born out by experiment.

Oxygen Equivalence.

According to Equations 3, 4, 5 and 6, two equivalents of oxygen are required for each equivalent of acetaldehyde and four equivalents of oxygen for each equivalent of acetic acid, regardless of the mechanism of production. On the assumption that one equivalent of oxygen becomes available for oxidation with the passage of one Faraday, the following relationship should hold.


6SQ. CM. ELECTR. ⊙
2SQ. CM. ELECTR. ⊛
FREE OXYGEN
FIG.12.
.60
.50
.40
.30
.20
.10
GRAM EQUIVS. PER FARADAY
F_6
F_2
CURRENT IN MA.
0
10
20
30
40
50
60
70
80
90


6 SQ. CM. ELECTR. ⊙
2 SQ. CM. ELECTR. ⊗
ACETIC ACID FIG.13.
.20
.10
0
B_2
B_6
GRAM EQUIVS. PER FARADAY
.20
ACETALDEHYDE
D_2
D_6
.40
GRAM EQUIVS. PER FARADAY
CURRENT IN MILLIAMPS.
0
20
40
60
80

$$F + 2D + 4B = 1$$

where

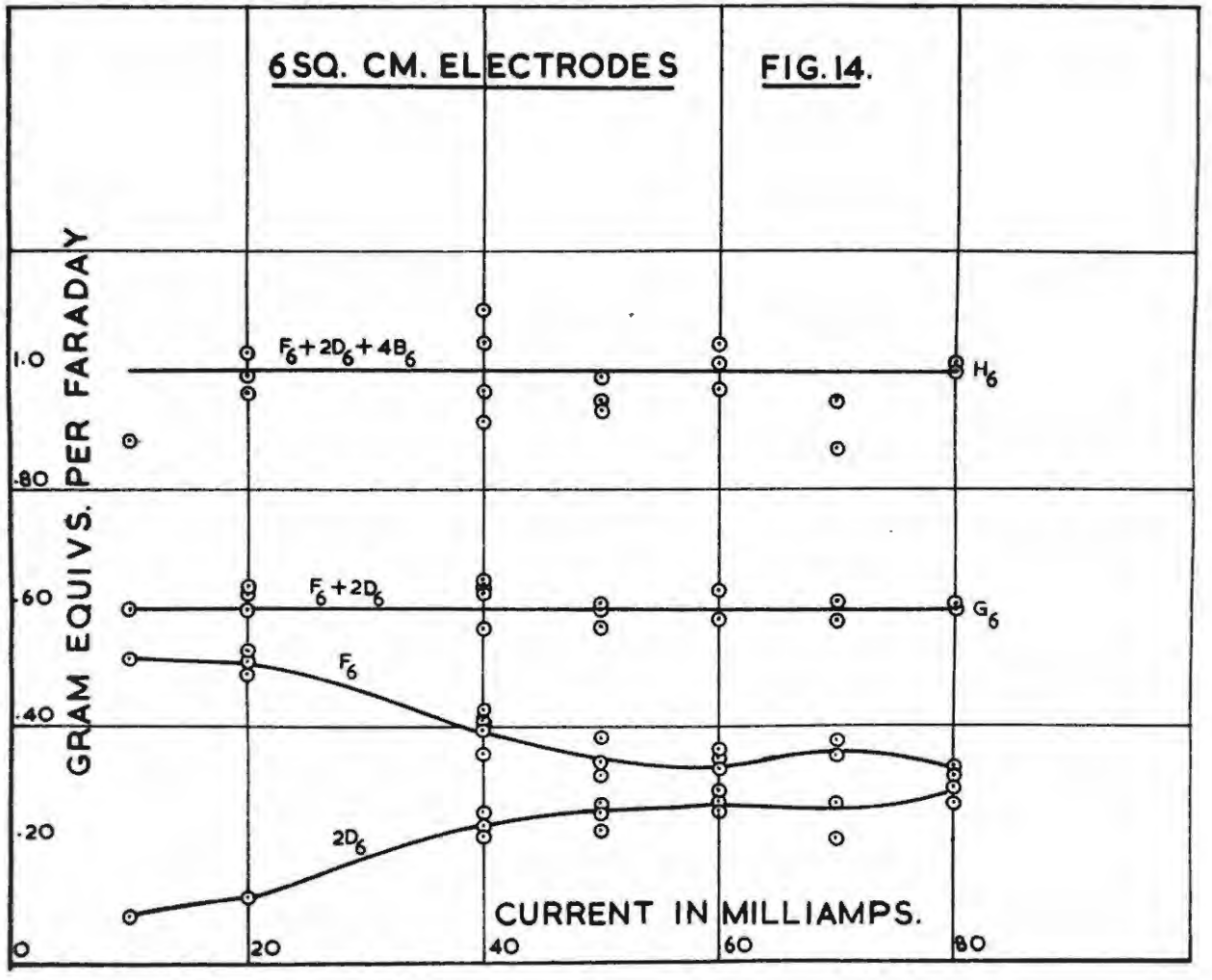
F = number of gm. equivs. of free oxygen per Faraday

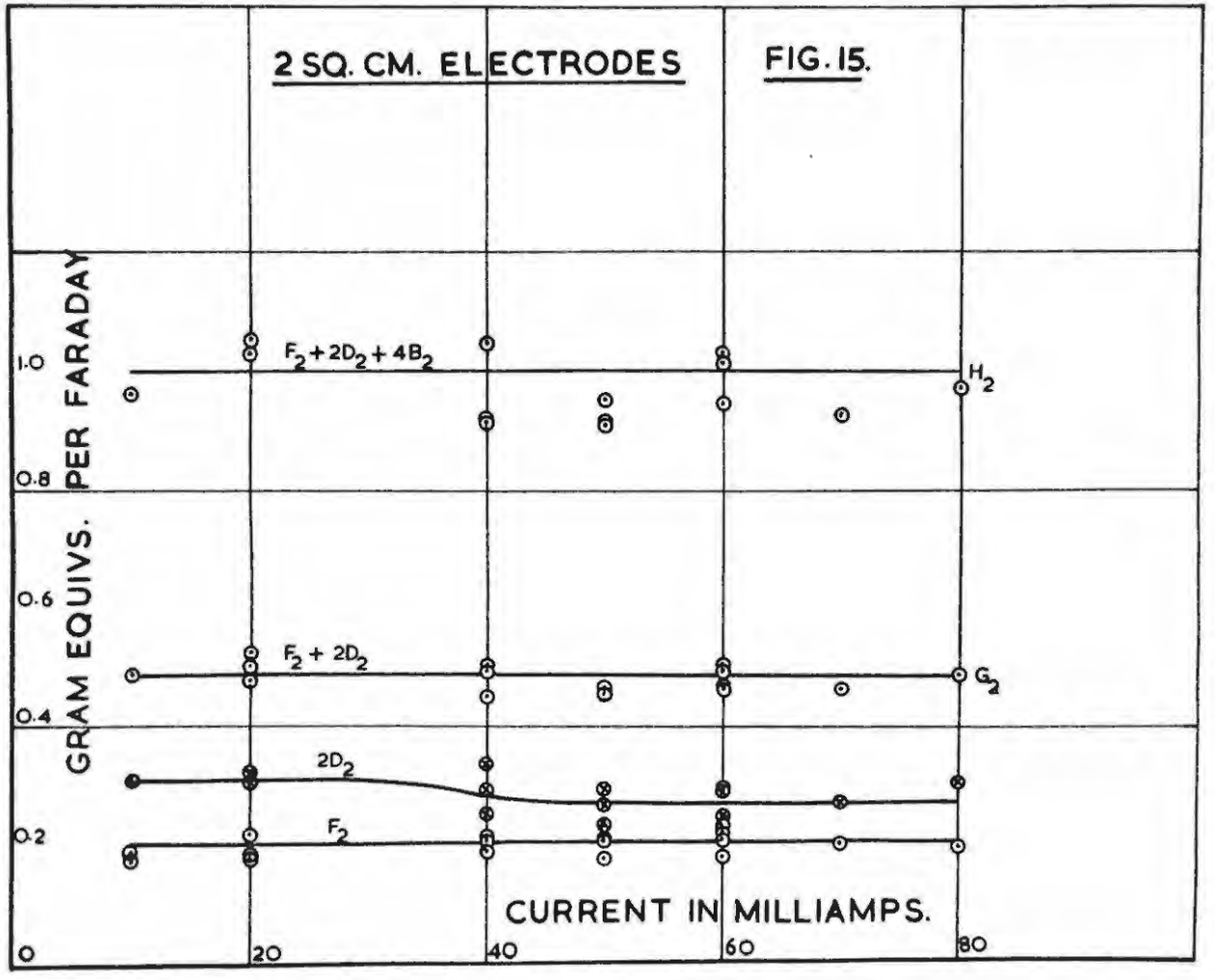
D = " " " " " acetaldehyde " "

B = " " " " " acetic acid " ".

The numerical evaluation of this relationship for each electrolysis has been recorded in Column H of Table XV, (Section 8) and represented graphically by Curves H_6 and H_2 on Figures 14 and 15. It is readily observable that, allowing for experimental error, the relationship does hold. The points on the graph are scattered about a mean value of unity for both sets of electrodes. The relative inaccuracy of the acetic acid determination is born out by a comparison of the points on lines G and H for both electrodes. (Figures 14 and 15.) The points on G lie much nearer to a mean value than do the corresponding points on H. It must be born in mind, however, that any error in the acetic acid determination is magnified by four when calculating the oxygen equivalent.

It may be observed from Figure 14, that the point on H_6 corresponding to an anode current of 10 milliamperes is low. (0.88 instead of 1.0.) This oxygen difficiency was very probably due to the formation of pyruvic acid, which would be determined as lactic acid and therefore, would not be accounted for among the products of oxidation. As was shown in Section 4, the yield of pyruvic acid falls off to a large extent at higher current densities. No explanation can be offered for the low value of H_6 obtained for a current of 70 mA. This may have resulted from an incomplete separation of acetic and lactic acids by vacuum distillation (giving a


6 SQ. CM. ELECTRODES
FIG. 14.
GRAM EQUIVS. PER FARADAY
1.0
.80
.60
.40
.20
0
$F_6+2D_6+4B_6$
H_6
F_6+2D_6
G_6
F_6
$2D_6$
CURRENT IN MILLIAMPS.
20
40
60
80


2 SQ. CM. ELECTRODES
FIG. 15.
GRAM EQUIVS. PER FARADAY
1.0
0.8
0.6
0.4
0.2
0
$F_2 + 2D_2 + 4B_2$
H_2
$F_2 + 2D_2$
G_2
$2D_2$
F_2
CURRENT IN MILLIAMPS.
20
40
60
80

low value for acetic acid) although the same procedure was employed as in the other distillations. Unfortunately, due to a shortage of time, confirmatory electrolyses could not be performed.

The Discharge of Lactate or Hydroxyl Ions.

If the lactate ion, only, is discharged at the anode, as envisaged by the Discharged Ion Theory, the passage of one Faraday would produce one equivalent of lactic acid. (See Equation 8.) However, an examination of the products of electrolysis shows that a good deal less than one equivalent of lactic acid is produced even if all the other products of electrolysis are assumed to result from the oxidation of lactic acid. Column J, Table XV, Section 8, represents the algebraic sum of the gram equivalents of lactic acid, acetic acid and acetaldehyde per Faraday. (i.e. J = B + C + D.) As may be seen from the table, the quantity J never exceeds the value 0.82, while the mean value is approximately 0.75 gram equivalents per Faraday.

While it cannot be said from this evidence that the lactate ion is definitely not discharged at the anode, it can be said that the Discharged Ion Theory is not adequate to explain this particular electrolysis. Other ions, namely hydroxyl ions, must be discharged at the anode also.

The hydroxyl ion hypothesis, in which the lactic acid is formed by the union of a hydrogen ion and a lactate ion (Equation 2), can explain the situation, on the other hand. The fact that the value of J is less than unity may be explained by the migration of some hydrogen ions from the anode compartment to the cathode compartment.

Although the above evidence cannot be described as absolutely conclusive, if the information gleaned from the anode voltage/current density determinations is also taken into account, it seems very probable that hydroxyl

ions are discharged at the anode when calcium lactate is electrolysed at the particular dilution employed during these experiments.

The Oxidation of Lactic Acid and (or) Lactate Ions.

The next question to be considered is whether lactic acid (as in Equation 3) or the lactate ion (as in Equation 7) is oxidised to acetaldehyde and acetic acid. If lactic acid is oxidised, there should be a correlation between the yield of this acid on the one hand and the yield of acetaldehyde and acetic acid on the other, whereas if the lactate ion only is oxidised, the yield of lactic acid should be independent of the yield of oxidation products.

A comparison ofthe yields of lactic acid for the two electrode sizes, under the same electrolysis conditions, (TableXV, Section 8) shows that in every case the yield of acid, when using the 6 sq. cm. electrodes, is larger than when using the smaller electrodes. At the smaller currents, the difference is as much as 30%. On the other hand, larger yields of acetaldehyde and acetic acid result from the use of the smaller electrodes. Thus, when the yield of acetic acid and acetaldehyde is low, the yield of lactic acid is relatively high and vice-versa. It is therefore believed that lactic acid, and not the lactate ion is oxidised directly to acetaldehyde and acetic acid.

The Oxidation of the Lactate Ion to the Pyruvate Ion.

There appears to be every indication that this oxidation does occur, as represented by Equation 5. The pyruvate ion then combines with a liberated hydrogen ion to form pyruvic acid, which in turn is very probably oxidised directly to acetic acid, according to Equation 6, without the formation of acetaldehyde as an intermediate stage. The evidence for this statement is derived from

a comparison of the yields of acetaldehyde and acetic acid at low current densities. The yield of acetic acid per Faraday is almost double that of acetaldehyde for currents of 10 mA. and 20 mA., using the 6 sq. cm. electrodes. (See Figure 13.) It is therefore unlikely that the acetic acid here is derived from the oxidation of acetaldehyde, otherwise a similar situation should apply at higher current densities when the oxidation process is more vigorous. An examination of the end products at higher current densities shows that the yield of acetaldehyde is generally slightly higher than that of acetic acid.

Further, it has been shown in Section 4 that the yield of pyruvic acid increases at the expense of lactic acid at low current density. In fact at a current of 1 mA., using the 6 sq. cm. electrodes, the acid produced in the anode compartment is practically all pyruvic. Since the yield of acetaldehyde falls rapidly at low current densities and yield of acetic acid remains reasonably constant, it follows that the acetic acid is derived largely from the oxidation of pyruvic acid and the acetaldehyde from oxidation of lactic acid. Of course, at higher current densities, a certain amount of acetaldehyde is bound to be oxidised to acetic acid.

Incidently, the falling off of the yield of acetaldehyde at low current density is additional confirmation that lactic acid and not the lactate ion is oxidised to acetaldehyde, since the yield of lactic acid is known to diminish at low current density.

The Evolution of Carbon Dioxide.

It was hoped that the yield of carbon dioxide would show a correlation with the sum of the yields of acetic acid and acetaldehyde in accordance with Equations 3, 4 and 6. Even though the electrolyte was saturated for one

to two hours with CO_2 prior to the electrolysis, the yield of CO_2 was found to be well below that expected, and did not appear to have any relationship with the other products of electrolysis.

It was observed, however, that if the cathode solution was not replaced frequently enough, a white precipitate of calcium carbonate formed under the porous disc which was no doubt due to the diffusion of calcium hydroxide. Under these conditions the yield of carbon dioxide increased considerably. The oxidation processes may be facilitated in the presence of added hydroxyl ions.

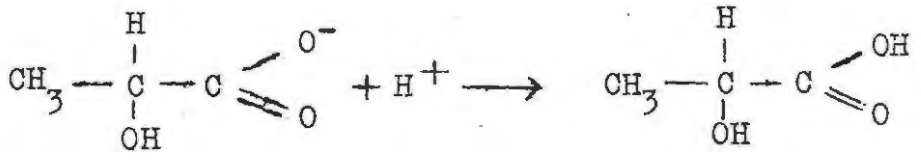
In order to obtain an estimate of the amount of carbon dioxide which is dissolved in the electrolyte during the course of an electrolysis, some electrolyses were conducted with calcium lactate which had not been saturated with carbon dioxide previously. After the electrolysis, aliquot portions of the electrolyte were treated with fresh clear calcium hydroxide solution and allowed to stand for some time in corked conical flasks. The fine precipitate of calcium carbonate which formed was filtered through asbestos pads and estimated by difference with 0.01 N hydrochloric acid. Blanks were carried out with non-electrolysed calcium lactate solutions.

The results varied a good deal, but did indicate that a large proportion of the evolved carbon dioxide dissolves in the electrolyte even when carbon dioxide is bubbled through the electrolyte prior to the electrolysis. It is thus apparent that unless carbon dioxide is evolved in very large quantities in an electrolysis, any attempt to estimate it is valueless.

However, a curious observation did emerge from these investigations; namely, that when the electrolyte was saturated with carbon dioxide prior to the electrolysis, the yield of lactic acid was found to increase

markedly. In some cases the yield of lactic acid was 20% higher than when using an unsaturated solution. It was at first thought that when the electrolyte is saturated with carbon dioxide, the decarboxylation process, which accompanies oxidation, is retarded. However, the production of acetaldehyde and acetic acid was normal or even increased.

Thus it would appear that in the presence of excess bicarbonate, the process



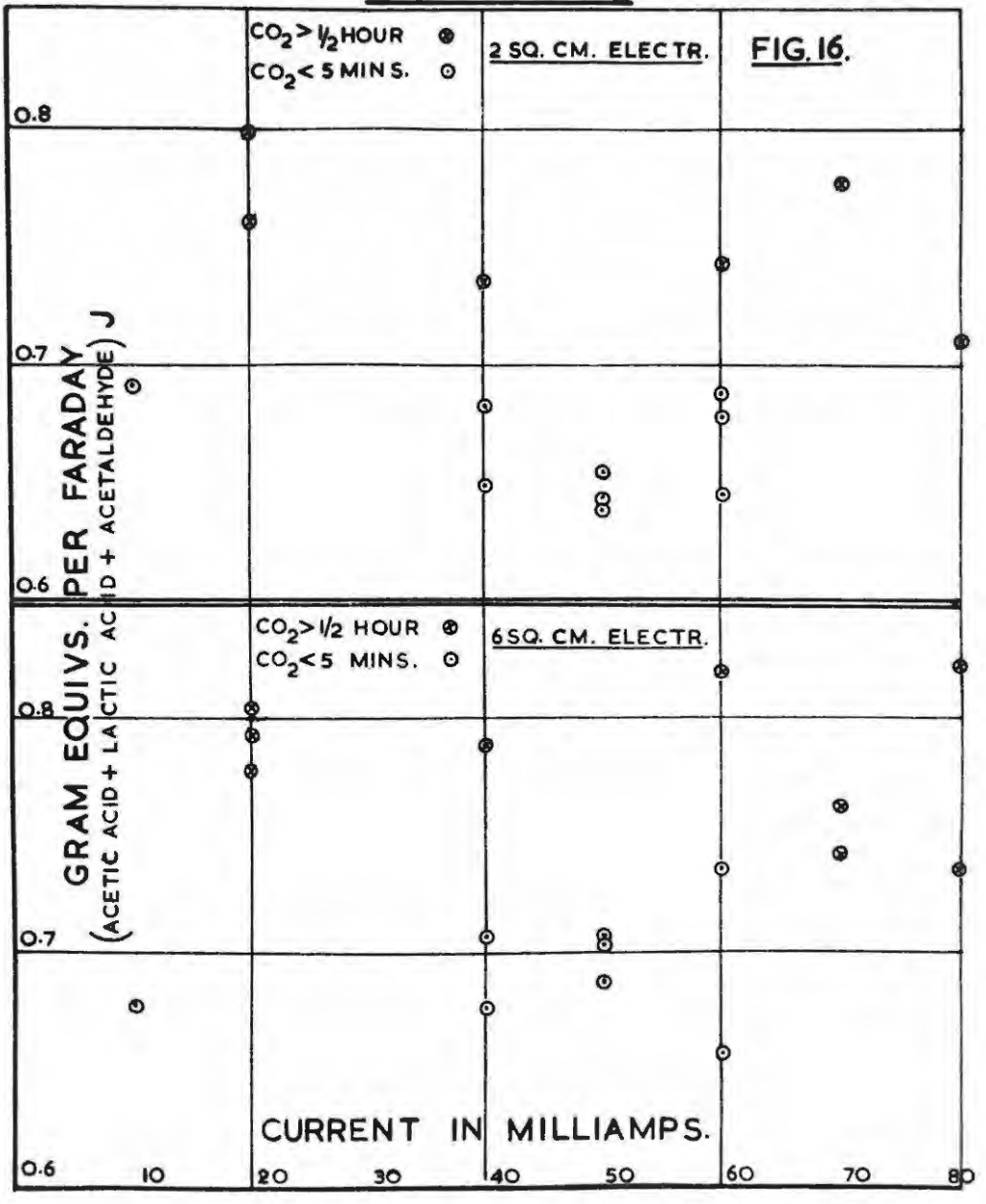
is facilitated.

This could only be due to an increase in the hydrogen ion concentration, which, of course, is expected when an aqueous solution is saturated with carbon dioxide.

(The possibility of the electrolyte being contaminated with mineral acid from the Kipp's apparatus used for generating the carbon dioxide was born in mind. The carbon dioxide was washed by passing it through Dressler tubes containing water before use.)

In order to demonstrate the influence of dissolved carbon dioxide, the algebraic sum of the yield of lactic acid, acetaldehyde and acetic acid (in gram equivalents per Faraday) has been evaluated and recorded in Column J, Table XV, Section 8. The figures in Column J for the two sets of electrodes have been graphically represented in Figure 16.

EFFECT OF CO_2



It is clearly observable that when carbon dioxide has been bubbled through the electrolyte for half an hour or more before the electrolysis, the quantity J is increased to a large extent.

Although no mention of this method has been made in Section 5, where methods of increasing the yield of lactic acid were discussed, the passage of carbon dioxide through the electrolyte is indeed a means of increasing the yield of lactic acid.

SUMMARY OF SECTION 8.

1) A brief introductory discussion on the general theories, which have been advanced to explain the electrolysis of acetates, has been made in order that the reactions which occur during the electrolysis of calcium lactate may be elucidated in a similar manner.

2) For comparison purposes, the end products of the two electrodes for various anode currents and periods of electrolysis, have been reduced to a common unit; namely, the yield in gram equivalents per Faraday. These quantities have been recorded in Table XV, Section 8.

3) From a quantitative consideration of the end products of electrolysis, the following are believed to be the reactions which occur at the anode during the electrolysis of an aqueous 0.1 molar solution of calcium lactate.

$$OH^- + OH^- \longrightarrow \tfrac{1}{2}\ O_2 + H_2O + 2\ e$$

(Equation 1)

$CH_3.CHOH.COO^- + H^+ \longrightarrow CH_3.CHOH.COOH$

LACTATE ION — LACTIC ACID (Equation 2)

$CH_3.CHOH.COOH + \frac{1}{2} O_2 \longrightarrow CH_3.CHO + CO_2 + H_2O$

ACETALDEHYDE (Equation 3)

$CH_3.CHO + \frac{1}{2} O_2 \longrightarrow CH_3.COOH$

ACETIC ACID (Equation 4)

$CH_3.CHOH.COO^- + \frac{1}{2} O_2 \longrightarrow CH_3.CO.COO^- + H_2O$

LACTATE ION — PYRUVATE ION

$CH_3.CO.COO^- + H^+ \longrightarrow CH_3.CO.COOH$

PYRUVIC ACID (Equation 5)

$CH_3.CO.COOH + \frac{1}{2} O_2 \longrightarrow CH_3.COOH + CO_2$

ACETIC ACID (Equation 6)

At very low current density (current 1 mA. using the 6 sq. cm. electrodes), the oxidation of the lactate ion to the pyruvate ion (Equation 5) appears to be the principal process, while at higher current density, all the reactions represented appear to take place.

4) The estimation of carbon dioxide was found to be impracticable due to the solubility of the gas in the electrolyte. This seems to occur

even when carbon dioxide is passed through the electrolyte for two hours before the electrolysis.

5) If the electrolyte is saturated with carbon dioxide prior to the electrolysis, an improved yield of lactic acid was found to result.

TABLE XV SECTION 8

Electrolysis No.	Current in M.A.	Electrode Area in sq.cms.	No. of Faradays A	gm. Equivs. Acetic Acid per Faraday B	gm. Equivs. Lactic Acid per Faraday C	gm. Equivs. Acetaldehyde per Faraday D	gm. Equivs. CO_2 per Faraday E	gm. Equivs. O_2 per Faraday F	1 Equiv. O_2 + 2 Equivs. Acetaldehyde G = F + 2D	1 Equiv. O_2 + 2 Equivs. Acetal. + 4 Equivs. Acetic H = F + 2D + 4B	1 Equiv. Lactic + 1 Equiv. Acetic + 1 Equiv. Acetal. J = B + C + D	CO_2 Bubbled
1	40	6	0.0097	0.100	0.502	0.105	0.024	0.418	0.628	1.028	0.707	0
2	40	2	0.0119	0.115	0.446	0.122	0.020	0.205	0.449	0.909	0.683	0
2	40	6	0.0119	0.080	0.485	0.126	0.025	0.395	0.647	0.967	0.691	0
3	40	2	0.0106	0.104	0.401	0.144	0.022	0.209	0.497	0.913	0.649	0
3	40	6	0.0103	0.088	0.479	0.114	0.018	0.337	0.565	0.917	0.681	0
4	40	2	0.0075	0.133	0.435	0.168	0.078	0.182	0.518	1.050	0.736	*
4	40	6	0.0075	0.117	0.576	0.105	0.132	0.430	0.640	1.108	0.798	*
5	50	2	0.0131	0.113	0.414	0.116	0.035	0.227	0.459	0.911	0.643	0
5	50	6	0.0131	0.087	0.489	0.110	0.036	0.381	0.601	0.949	0.686	0
6	50	2	0.0131	0.123	0.370	0.146	0.020	0.171	0.463	0.955	0.639	0
6	50	6	0.0131	0.092	0.486	0.125	0.018	0.318	0.568	0.936	0.703	0
7	50	2	0.0131	0.111	0.414	0.130	0.032	0.205	0.465	0.909	0.655	0
7	50	6	0.0131	0.095	0.487	0.134	0.033	0.341	0.609	0.989	0.716	0
8	60	2	0.0101	0.111	0.424	0.143	0.065	0.215	0.501	0.945	0.678	0
8	60	6	0.0101	0.084	0.516	0.135	0.076	0.361	0.631	0.967	0.735	0
9	60	2	0.0101	0.131	0.470	0.146	0.050	0.201	0.493	1.017	0.747	*
9	60	6	0.0101	0.103	0.573	0.144	0.062	0.344	0.632	1.044	0.820	*
10	60	2	0.0101	0.140	0.426	0.122	0.029	0.222	0.466	1.026	0.688	0
11	60	2	0.0101	0.119	0.380	0.146	0.025	0.176	0.468	0.944	0.645	0
11	60	6	0.0101	0.108	0.420	0.128	0.023	0.326	0.582	1.014	0.656	0
12	70	2	0.0118	0.116	0.525	0.134	0.049	0.195	0.463	0.927	0.775	*
12	70	6	0.0118	0.093	0.569	0.101	0.046	0.378	0.580	0.952	0.763	*
13	70	6	0.0109	0.064	0.544	0.132	0.056	0.349	0.613	0.869	0.740	*
14	80	2	0.0080	0.121	0.440	0.150	0.121	0.190	0.490	0.974	0.711	*
14	80	6	0.0080	0.099	0.504	0.132	0.140	0.340	0.604	1.000	0.735	*
15	80	6	0.0089	0.102	0.573	0.147	0.053	0.313	0.607	1.015	0.822	*
16	20	2	0.0063	0.127	0.478	0.156	0.046	0.216	0.528	1.036	0.761	*
16	20	6	0.0063	0.081	0.645	0.052	0.068	0.533	0.637	0.961	0.778	*
17	20	2	0.0063	0.137	0.502	0.159	0.046	0.192	0.510	1.056	0.798	*
17	20	6	0.0063	0.097	0.654	0.054	0.056	0.492	0.600	0.988	0.805	*
18	20	2	0.0063	-	-	0.152	0.056	0.175	0.479	-	-	-
18	20	6	0.0063	0.103	0.637	0.054	0.092	0.514	0.622	1.034	0.794	*
19	10	2	0.0075	0.118	0.422	0.153	0.019	0.185	0.491	0.963	0.693	0
19	10	6	0.0075	0.071	0.573	0.040	0.018	0.519	0.599	0.883	0.684	0

* 30 minutes

0 5 minutes

TABLE XIV SECTION 7D

Electrolysis No.	Current in m. amps.	Electrode Area in sq. cms.	Time in Mins.	Vol. Anode Solution in ml.	Total Acidity of Anode Soln.	gm. Equivs. Total Acid.	gm. Equivs. Acetic Acid	gm. Equivs. Lactic Acid	gm. Equivs. Acetaldehyde.	Total Vol. of gas at N.T.P.	Vol. CO_2 N.T.P.	Vol. O_2 N.T.P.	gm. Equivs. CO_2	gm. Equivs. O_2
1	40	6	390	344	0.0170	0.00584	0.00097	0.00487	0.00102	31.2	5.2	22.7	0.00023	0.00406
2	40	2	470	403	0.0158	0.00636	0.00109	0.00509	0.00137	20.3	4.9	12.8	0.00022	0.00228
2	40	6	450	330	0.0199	0.00656	0.00089	0.00542	0.00141	33.9	6.3	24.7	0.00028	0.00441
3	40	2	428	370	0.0151	0.00558	0.00111	0.00427	0.00153	20.2	5.2	12.5	0.00023	0.00222
3	40	6	415	334	0.0181	0.00604	0.00091	0.00494	0.00118	26.4	4.1	19.5	0.00018	0.00348
4	40	2	300	344	0.0140	0.00480	0.00099	0.00324	0.00126	24.2	13.1	7.6	0.00056	0.00136
4	40	6	300	340	0.0159	0.00542	0.00087	0.00430	0.00078	42.0	22.1	18.0	0.00098	0.00321
5	50	2	420	308	0.0223	0.00696	0.00148	0.00540	0.00152	29.5	10.2	16.6	0.00046	0.00291
5	50	6	420	320	0.0243	0.00777	0.00114	0.00638	0.00144	41.3	10.5	27.9	0.00047	0.00497
6	50	2	420	348	0.0192	0.00668	0.00160	0.00483	0.00190	20.6	5.8	12.5	0.00026	0.00223
6	50	6	420	352	0.0216	0.00772	0.00120	0.00634	0.00163	31.5	5.3	23.2	0.00024	0.00415
7	50	2	420	338	0.0206	0.00706	0.00145	0.00540	0.00170	27.0	9.5	15.0	0.00042	0.00268
7	50	6	420	342	0.0224	0.00775	0.00124	0.00636	0.00175	37.9	9.7	25.0	0.00043	0.00445
8	60	2	270	325	0.0179	0.00581	0.00112	0.00427	0.00144	28.5	14.7	12.1	0.00065	0.00216
8	60	6	270	330	0.0197	0.00650	0.00085	0.00521	0.00136	40.1	17.6	20.3	0.00078	0.00363
9	60	2	270	348	0.0185	0.00643	0.00132	0.00473	0.00147	24.5	11.3	11.4	0.00050	0.00202
9	60	6	270	344	0.0209	0.00719	0.00104	0.00577	0.00145	35.9	14.0	19.4	0.00062	0.00346
10	60	2	270	344	0.0174	0.00598	0.00141	0.00429	0.00123	20.9	6.2	12.5	0.00028	0.00223
11	60	2	270	340	0.0149	0.00505	0.00120	0.00382	0.00147	17.6	5.6	9.9	0.00025	0.00177
11	60	6	270	342	0.0156	0.00532	0.00118	0.00433	0.00129	26.2	5.1	18.4	0.00023	0.00082
12	70	2	270	356	0.0217	0.00770	0.00136	0.00617	0.00158	27.9	12.8	12.8	0.00057	0.00229
12	70	6	270	336	0.0229	0.00771	0.00109	0.00669	0.00119	39.8	12.1	25.0	0.00054	0.00445
13	70	6	250	338	0.0194	0.00655	0.00130	0.00490	0.00136	31.9	15.5	14.3	0.00069	0.00259
14	80	2	160	349	0.0136	0.00475	0.00096	0.00350	0.00119	31.3	21.5	8.5	0.00096	0.00151
14	80	6	160	348	0.0140	0.00487	0.00079	0.00401	0.00105	41.6	24.9	15.2	0.00111	0.00270
15	80	6	180	346	0.0165	0.00569	0.00091	0.00510	0.00131	29.0	10.6	15.6	0.00047	0.00279
16	20	2	510	349	0.0114	0.00399	0.00080	0.00301	0.00098	16.2	6.6	7.6	0.00029	0.00136
16	20	6	510	330	0.0146	0.00461	0.00051	0.00406	0.00033	31.0	9.7	18.8	0.00043	0.00336
17	20	2	510	348	0.0125	0.00434	0.00086	0.00316	0.00100	14.6	6.5	6.8	0.00029	0.00121
17	20	6	510	352	0.0138	0.00487	0.00061	0.00412	0.00033	27.4	7.8	17.4	0.00035	0.00310
18	20	2	510	342	0.0121	0.00415	-	-	0.00096	15.3	7.8	6.2	0.00035	0.00110
18	20	6	510	340	0.0142	0.00481	0.00065	0.00401	0.00034	33.1	13.0	18.2	0.00058	0.00324
19	10	2	1200	348	0.0120	0.00417	0.00088	0.00314	0.00114	13.0	3.1	7.8	0.00014	0.00138
19	10	6	1200	344	0.0140	0.00480	0.00053	0.00427	0.00030	27.4	3.0	21.7	0.00013	0.00387

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