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THE ELECTROLYSIS of a MIXTURE of the POTASSIUM SALTS of ACETIC and TRICHLORACETIC ACIDS

and

A NOTE on the NATURE of KOLBE'S ELECTROSYNTHESIS and ALLIED REACTIONS.

A THESIS

presented for the Degree of Ph.D.

by

RALPH EDWARD GIBSON, B.Sc.

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THE ELECTROLYSIS of a MIXTURE of the POTASSIUM SALTS of ACETIC and TRICHLORACETIC ACIDS.

INTRODUCTION.

Previous experiments on the electrolysis in aqueous solution of mixtures containing the salts of organic acids may be divided into three classes:-

(1) If the salts, or in the case of dibasic acids, the ester salts, of two different organic acids, which, when electrolysed singly, behave in the same way giving the normal KOLBE(1) or CRUM BROWN-WALKER(2) synthesis, are electrolysed together, the usual products from each salt are formed together with a mixed compound of exactly the same type. The nature and relative amounts of these products are such as would be expected from probability considerations. For example CARMICHAEL(3) obtained azelaic ester, succinic ester, and the ester, COOET.$(CH_2)_{12}$.COOET, by the electrolysis of a solution of the potassium ethyl salts of malonic and suberic acids.

$$COOET.CH_2.COOH + COOET.(CH_2)_6.COOH + O$$
$$= COOET.(CH_2)_7\ COOET + H_2O + 2CO_2.$$

2COOET/

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(1) Ann. 69 279 (1849)

(2) Ann. 261 107 (1891)

(3) Trans. Chem. Soc. 121 2545 (1922)

$$2COOET.CH_2.COOH + O = COOET.(CH_2)_2\ COOET + H_2O + 2CO_2$$

$$2COOET.(CH_2)_6\ COOH + O = COOET.(CH_2)_{12}.COOET + H_2O + 2CO_2$$

Other examples are to be found in the work of v. MILLER and HOFER (1) who produced the ethyl ester of butyric acid from potassium ethyl succinate and potassium acetate:-

$$CH_3COOH + COOET.CH_2.CH_2COOH + O$$
$$= CH_3.CH_2.CH_2\ COOET + H_2O + 2CO_2$$

and also in the researches of WURTZ (2) who produced various hydrocarbons from different fatty acids.

(2) If the salts of fatty acids are electrolysed in the presence of halogens or with alkali halides, halogen derivatives of hydrocarbons are found among the reaction products, only however, in very small amounts. HOFER and MOEST (3) prepared chloropentane from caproic acid and potassium chloride, and KAUFLER and HERZOG (4) shewed conclusively that traces of methyl iodide were formed when potassium acetate was electrolysed in the presence of iodine.

(3) When salts of fatty acids and certain inorganic oxygen salts are electrolysed together, these/

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(1) Ber. 28 2427 (1895)
(2) Jahresber. f. ch. 1855 P.575
(3) Ann. 323 286 (1902)
(4) Ber. 42 3858

these latter, by their presence in the electrolyte, modify considerably the anode reactions of the organic constituents without, however, participating in any reaction with them. HOFER and MOEST (1) added potassium perchlorate, potassium hydrogen carbonate, and other salts to solutions of potassium acetate and found that in each case the main product of electrolysis was methyl alcohol while the yield of ethane was very considerably diminished.

In the case of a mixture such as potassium acetate and trichloracetate new features are introduced. In the first place this mixture does not fall into class (1) because these salts, although of the same type, behave quite differently when electrolysed singly. From potassium acetate large quantities of ethane and only traces of methyl acetate are formed, but ELBS and KRATZ (2) have shewn that from potassium trichloracetate large amounts of a substituted methyl ester, trichlormethyl trichloracetate ($CCl_3COOCCl_3$) are formed and that no trace of the expected hexachlorethane can be detected. Secondly, it will be seen that, as both constituents are derivatives of organic fatty acids, this electrolysis does not, 'a priori' fall into classes (2) or (3).

Thus the object of the following work was to ascertain to which of the above classes this

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(1) op. cit.

(2) J. pr. chem. 55 502 (1897)
cp. Elbs. Zeit. Elektrochem. 18 662 (1912)

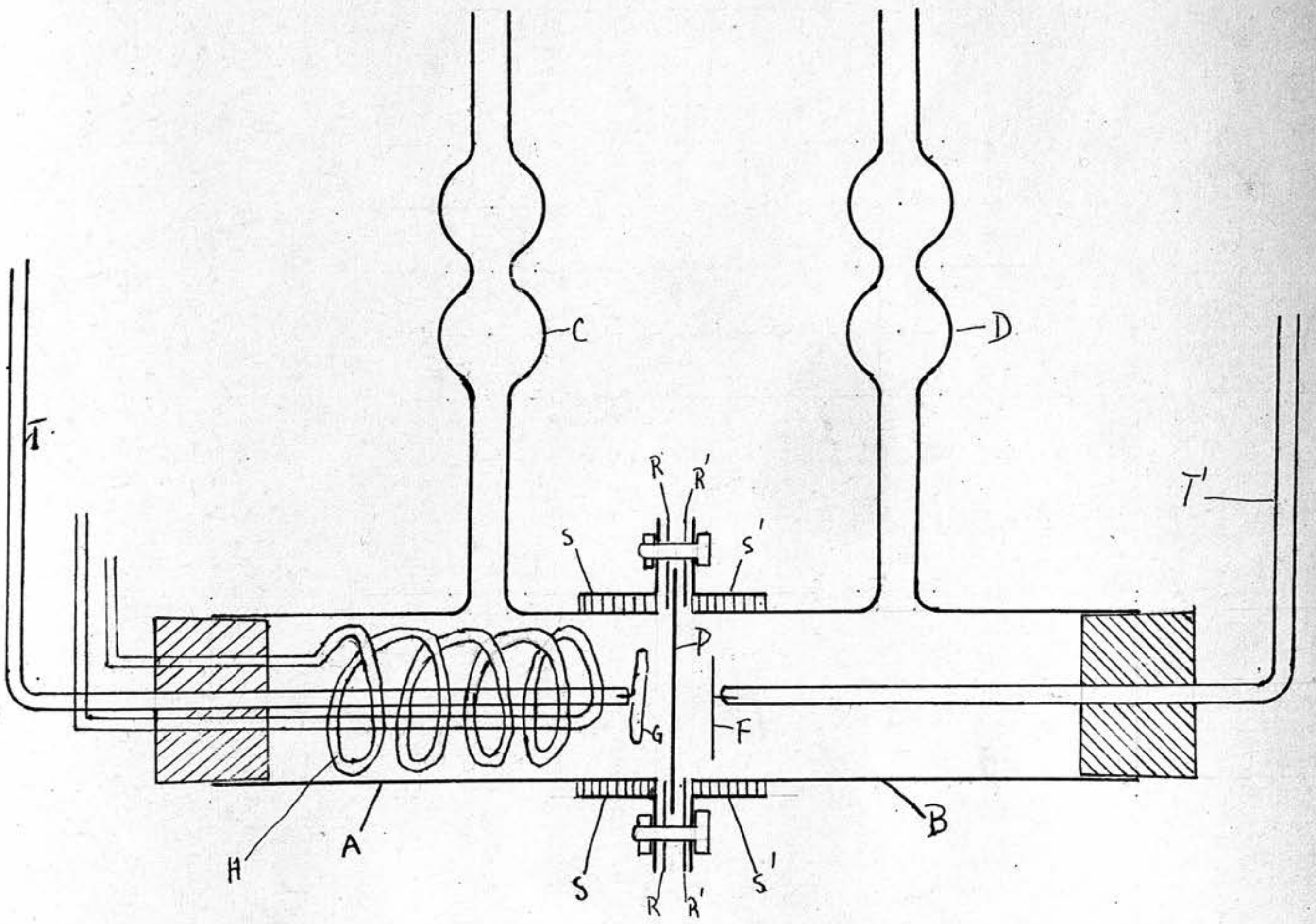
mixed electrolysis belonged, to see whether any mixed products, such as $CH_3COOCCl_3$, CCl_3COOCH_3 or $CH_3.CCl_3$, were to be found, and to determine whether the presence of either salt affected the reactions of the other in a manner analogous to the reaction of HOFER and MOEST.

EXPERIMENTAL.

As it had been found that during the electrolysis of potassium trichloracetate in a platinum crucible the salt itself and the highly chlorinated ester products were readily reduced at the cathode giving potassium acetate, methyl trichloracetate, and methyl acetate, a cell was used in which the anode and cathode were separated by a porous membrane. Such an apparatus possessed the additional advantages of preventing the destruction of esters formed at the anode by caustic alkalies liberated at the cathode, and of allowing the separate collection and examination of the gases evolved at either electrode. The cell is illustrated by Figure I.

The electrolytes were contained in the tubes A and B which were held together by the metal flanges//

Figure I.



flanges S and S' and were provided with side pieces C and D, widened to prevent loss by frothing, through which the gaseous products might be led away. Between the adjacent ends of A and B was placed a parchment membrane P, which was made from best filter paper by treatment with moderately concentrated sulphuric acid, and subsequent washing with water. The joint was made water tight by the rubber washers R and R'. The cathode F and the anode G, the latter being a spiral of platinum wire whose total surface area was 1.1 sq. cm., were fused into the glass tubes T' and T which contained mercury. The anode liquid was kept at a low temperature by the glass cooling spiral H. The cell, when in use, was supported on a mechanical rocker in a tank of water whereby its contents were agitated and cooled.

A 60 per cent. solution of potassium acetate was used as catalyte, while the analyte consisted of 20 cc. of a solution of potassium acetate containing 520 grams per litre, together with 15 cc. of a solution of potassium trichloracetate containing 670 grams per litre. The molecular proportions of potassium acetate to trichloracetate were therefore approximately two to one. When a current of 2-3 amps., making the anode current density 2-3 amps. per sq. cm./

cm., was passed through this mixture for three quarters of an hour at a temperature of 20°, 0.6 to 0.8 gram of an oil was produced. Although the experimental conditions, such as concentration and composition of the electrolyte, intensity and duration of the current, and temperature, were widely varied it was found impossible to obtain a larger quantity of the oil from one electrolysis in a cell of the dimensions of that described above.

The products of electrolysis were of three kinds:-

I those in the oil produced.
II those in the gases evolved.
III those in the residual electrolyte.

These were examined in turn.

I. EXAMINATION of the OIL.

The oily liquid was light yellow in colour and denser than water, in which it was insoluble. It decomposed at ordinary temperatures evolving a pungent gas. Immediately after preparation the oil was washed thoroughly with water to remove all traces of adhering acids, roughly dried and set aside for further investigation. As it was thought that the instability/

instability of the oil was due to its moist condition, about 5 grams of freshly prepared product were kept in a desiccator over phosphorus pentoxide. A comparatively stable liquid, still insoluble in water, resulted, but all attempts to separate its constituents by fractional distillation under reduced pressure or by fractional crystallisation at low temperature were abortive.

It was therefore decided to attack the problem by allowing the decomposition to proceed as far as possible, examining the resultant products, determining the course of the decomposition reactions, and thence arriving at the nature of the original components of the oil.

After the oil had been in contact with moisture for several days it became almost completely soluble in water, a fact which indicated that it might consist for the most part of readily hydrolysable esters which reacted with water to give soluble acids and alcohols. The gases evolved during the decomposition were passed into an ether solution of aniline. Diphenylurea, M.P. 235°, and aniline hydrochloride were formed in large amounts, shewing that the gases contained for the most part carbonyl chloride and hydrochloric acid. These two compounds arose in all probability from trichlormethyl esters which/

which are known to be hydrolysed readily as follows:-

$$R.COOCCl_3 + H_2O = COCl_2 + HCl + R.COOH.$$

This is illustrated by the behaviour of trichlormethyl trichloracetate (1) .

QUANTITATIVE ESTIMATION of TRICHLORMETHYL GROUPS in the oil.

The amount of chlorine evolved as carbonyl chloride and hydrochloric acid, and hence the percentage of the trichlormethyl group (CCl_3), in the oil was determined by allowing a weighed quantity of the oil to decompose in a confined space in the presence of a substance capable of absorbing the above mentioned gases. The oil was thoroughly washed immediately after preparation. A quantity (0.4-0.6 gram) was weighed into a small weighing bottle which was placed on a small glass triangle inside a wide-mouthed stoppered bottle containing 10cc. of a 40 per cent. solution of pure sodium hydroxide. The bottle was stoppered and set aside for one week. At the end of this time decomposition was complete and the chloride in the soda solution was estimated by VOLHARD'S method.

RESULTS./

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(1) Elbs and Kratz - Op.cit.

RESULTS.

Total Chlorine evolved as percentage of original oil = (1) 43 (2) 40, or an average of 41.5 per cent. which shewed that the chlorinated methyl group (CCl_3) formed about 46 per cent. of the total weight of oil and hence that most of the oil consisted of trichlormethyl esters.

QUALITATIVE EXAMINATION of the NON-VOLATILE PRODUCTS of DECOMPOSITION of the OIL.

Five cubic centimetres of the residue left after the decomposition of the oil were warmed under a reflux condenser with 10cc. of water. The main bulk dissolved at once but a small quantity remained which was quite stable even after being in contact with boiling water for twenty minutes. This stable portion was run off from the aqueous layer and on cooling it solidified as a white crystalline mass. The aqueous solution was decidedly acid, and was shewn to contain acetic acid by the ethyl acetate and cacodyl oxide reactions. It also contained trichloracetic acid, as chloroform was produced when it was warmed with caustic soda, and an ester boiling between 165° and 168° was prepared by warming the aqueous layer/

layer with ethyl alcohol and sulphuric acid. Ethyl trichloracetate boils at 167°. Five grams of the oil were made alkaline with sodium carbonate solution and the whole was then distilled to drive off any volatile constituents such as alcohols or aldehydes. 15c.c. of distillate were collected. A portion of this was shewn to contain formaldehyde by the MULLIKAN-SCUDDER TEST (1) and by the reduction of an ammoniacal silver solution. After treatment with silver oxide to destroy all formaldehyde, the remainder was oxidised with a hot oxidised copper spiral but this time no formaldehyde could be detected. Moreover, the copper spiral shewed no signs of reduction and, as a solution containing 1c.c. of methyl alcohol in 150c.c. of water reduced the spiral completely, it was concluded that not more than the slightest trace of methyl alcohol was present. A blank experiment shewed that silver oxide had no appreciable effect on methyl alcohol in aqueous solution.

QUANTITATIVE ESTIMATIONS.

In order to make certain that no important acid constituent had been overlooked in the quali-tative/

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(1) Amer. Chem. J. <u>21</u> 266.

qualitative examination and to obtain a rough idea of the proportions in which the various constituents were present, quantitative determinations of (a) total acid (b) acetic acid (c) trichloracetic acid (d) hydrochloric acid in the mixture left after the decomposition of the oil, were made.

(A) METHODS.

Acetic acid in the presence of trichloracetic acid was determined by evaporating a weighed quantity, 0.2-0.8 gram. of the decomposed oil to dryness with excess of caustic soda solution. This destroyed the last named acid producing chloroform, chloride, carbonate, and some formate. The residue, dissolved in a small quantity of water, was cautiously distilled with concentrated sulphuric acid and a trace of potassium permanganate, which oxidised the formic acid and prevented the formation of sulphurous acid. The total acid in the distillate was determined by titration with $\frac{N}{10}$ caustic soda, the chloride present estimated by VOLHARD'S method, and hence the acetic acid determined from the difference between these results. The distillate was tested in every case for traces of sulphuric acid and was rejected if such were found. By taking care that the temperature in the neck of the distilling flask did not rise above 110°, it was found possible to prevent all/

all volatilisation of sulphuric acid. Any chlorine evolved during the distillation was eliminated either by allowing the distillate to stand in sunlight in a stoppered flask for some time, or by aspirating it with air which removed the halogen but did not lead to any loss of acetic acid.

Two methods were employed for the estimation of trichloracetic acid. The first method depended on the fact that when trichloracetic acid was boiled with alkali it first split~~s~~ up giving chloroform and carbon dioxide as follows.

$$CCl_3COOH \rightarrow CCl_3H + CO_2$$

A determination of the amount of carbon dioxide formed by this process gave a measure of the trichloracetic acid present. A quantity of the substance under investigation was weighed into a small flask (100cc) provided with a reflux condenser. It was then treated with a boiling saturated solution of barium hydroxide for half an hour, during which time care was taken to exclude all atmospheric carbon dioxide by a soda lime trap. The reaction mixture was then diluted with an equal volume of boiling water and filtered hot. The precipitate of barium carbonate was thoroughly washed with hot water and then dissolved in a known volume of standard/

standard acid, the excess of which was determined by titration with alkali. Hence the amount of barium carbonate formed was calculated. Test experiments performed on pure trichloracetic acid shewed that the results obtained by this method were 6.5 per cent, too high as may be seen from table I.

TABLE I.

CCl_3COOH actually used.	CCl_3COOH found by Expt.	ERROR	Error per cent.
0.357	0.377	+0.020	+5.6
0.347	0.372	+0.025	+7.2
0.519	0.553	+0.034	+6.7 Av. 6.5 per cent.

The second method was founded on the fact that when trichloracetic acid is boiled for a prolonged period with sodium hydroxide or with sodium hydroxide and ethoxide it is hydrolysed completely with the formation of chloride, carbonate and formate:-

$$CCl_3COOH + 2NaOH = CCl_3H + Na_2CO_3 + H_2O$$

$$CCl_3H + 4NaOH = 3NaCl + HCOONa + 2H_2O.$$

If, therefore, all other sources of chloride are absent or at least accounted for, the amount of chloride produced by the above reaction should give a measure of the trichloracetic acid in the mixture. The results obtained by this method were in general a trifle low.

The/

The total acid was determined by titration with $\frac{N}{10}$ caustic soda solution, and the hydrochloric acid by Volhard's Method.

B. Results

Two samples of decomposed oil derived from different sets of electrolyses were examined. From sample(2) small crystals, afterwards identified as hexachlorethane had separated. In each case care was taken to remove all traces of carbonyl chloride from the substance before analysis. The figures given are averages from two experiments which differed by less than 1 per cent. and are expressed as percentages of the weight of decomposed oil taken.

(1) Total Acid as acetic acid = 38.7 per cent.

Free Hydrochloric Acid = 0.7 "

Trichloracetic Acid (by Chloride method) = 63 "

Acetic Acid = 11.3 "

Now 0.7 per cent. hydrochloric Acid = 1.3 per cent. acetic acid and 63 per cent. trichloracetic acid = 23.1 per cent. acetic acid.

Therefore, Total Acid accounted for = 35.7 per cent. This leaves a balance of 3 per cent., which is within the accuracy of the methods used.

(2) Trichloracetic Acid (by CO_2 method) = 86 per cent.

Corrected/

Corrected value = 80 per cent.

Acetic acid = 16 per cent.

As all the acids involved are extremely hygroscopic, and as the decomposed oil remained for a long time in contact with moist air, the absolute values of these results are insignificant, but the important feature is the comparatively close agreement between the values of the ratio, acetic acid to trichloracetic acid, which are 1: 5.5 and 1:5. From these ratios, together with the figures given previously for the percentage of trichlormethyl group in the oil, it is easily shewn that this latter contained 71 per cent. of trichlormethyl trichloracetate and 24 per cent trichlormethyl acetate. The remaining 5 per cent was probably for the most part adhering moisture. It is remarkable that no methyl acetate nor methyl trichloracetate could be found.

IDENTIFICATION of HEXACHLORETHANE.

The crystalline portion of the stable constituent of the oil, mentioned above, was found to be identical with a crystalline deposit which had separated from a quantity of the decomposed oil. It was a white solid, possessing a smell resembling that of camphor and having a very high vapour pressure at ordinary/

ordinary temperatures. The substance was volatile in steam and soluble in alcohol, ether and ligroin but not in water, acids nor alkalies, towards which it was very stable. It contained chlorine. The compound was purified by repeated distillation in steam, thorough washing with water, rough drying on a filter paper, and final desiccation by exposure to phosphorus pentoxide for three weeks. About 0.3 gram was so obtained. Five microcombustions after the method of DUBSKY (1) shewed that there was no hydrogen in the substance, and determinations of the chlorine content by the method of PREGL and DE CRINIS (2) gave the following results. Cl, found 90.1 and 89.6, Av. = 89.85. C_2Cl_6 requires 89.8 per cent. The substance melted in a sealed tube at 183-184°C. Hexachlorethane melts at 185°C. The molecular weight of the compound was determined by a micro-method described by BARGER (3), alcohol and ether being the solvents used. As the substance itself was very volatile, the results were only approximate, being 170-175 in alcoholic and 185-190 in ethereal solutions. As C_2Cl_6 requires a molecular weight of 237, it will be seen that the better result was obtained from the more volatile solvent. These results/

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(1) HOUBEN-WEYL - Die Methoden der organischen Chemie. Leipzig 1923 Vol 1 129-153.

(2) Ibid 165-166

(3) Trans. chem. Soc. <u>85</u> 286 (1904)

results shewed that the crystalline component of the oil was indeed hexachlorethane. This compound did not form more than 1-2 per cent. of the oil.

II. ANALYSIS of GASEOUS PRODUCTS.

The composition of the gas evolved at the anode was as follows:- Carbon Dioxide 87 per cent, Ethylene 8 per cent, Oxygen, Carbon Monoxide, Ethane and Methyl Chloride - 1 per cent. each, phosgene and chlorine - traces. These figures represent average values for a sample of the gas collected throughout the entire duration of normal electrolysis, namely three quarters of an hour. As table II shews, the composition of the Anode gas varied greatly as the experiment proceeded; in fact practically all the ethane formation took place at the beginning.

TABLE II

Time of sample in minutes t.	Ethane	Ethylene.	H_2 at Cathode	$\frac{\text{Ethane}}{\text{Hydrogen}}$	$\frac{\text{Ethylene}}{\text{Hydrogen.}}$
0 - 15	7.4cc.	17.3cc	280	0.027	0.062
23 - 39	<3.5cc.*	42.1cc	315	<0.01 *	0.134
39 - 53	<0.5cc *	28.0cc	280	<0.001*	0.100

* The volume of gas left after the various absorptions was too small for analysis but, as it contained ethane, methyl chloride and nitrogen, the actual amount of ethane was probably less than one half the value given.

The current was first started at t = 0

IDENTIFICATION of ETHANE and METHYL CHLORIDE

The gaseous residue left after the absorption of the first four components was inflammable and contained combined chlorine. As the electrolyte was rich in potassium acetate, the presence of ethane in the anode gas was expected, and further consideration led to the conclusion that the only gas containing chlorine likely to survive the previous treatment was methyl chloride. On the assumption that these two gases, together with nitrogen, were the sole components, the residue was burned with pure oxygen over distilled water in a slow combustion pipette. From the total contraction after combustion and absorption of the CO_2 produced, and the volume of oxygen used, the relative amounts of the gases present were calculated with the help of the equations,

$$2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O$$

$$2CH_3Cl + 3O_2 = 2CO_2 + 2HCl + 2H_2O.$$

The value for the volume of methyl chloride obtained in this way was in fairly close agreement with that deduced from the chloride content of the water in the combustion pipette which had dissolved all the hydrochloric acid produced during the burning of the gas. The/

The following figures justify the assumptions made above.

	(a)	(b)
Volume of methyl chloride from Combustion Equations.	1.4cc.	1.2cc.
Volume of methyl chloride from chlorine content of water	1.2cc.	1.0cc.

III. EXAMINATION of the RESIDUAL ELECTROLYTE.

The residual electrolyte was found to contain comparatively large amounts of hydrochloric acid which was regarded as an ultimate decomposition product of trichlormethyl alcohol, formed at the anode as follows, to use the formulation of HOFER and MOEST.

$$CCl_3COO, + OH = CCl_3OH + CO_2$$

$$CCl_3OH + H_2O = CO_2 + 3HCL.$$

A certain proportion of this hydrochloric acid was probably derived from the hydrolysis of the unstable trichlormethyl esters already referred to, but the velocity of decomposition of these substances was only sufficient to account for a very small fraction of the chloride actually found. The hydrochloric acid was determined quantitatively immediately after several experiments and the results are incorporated in table IV.

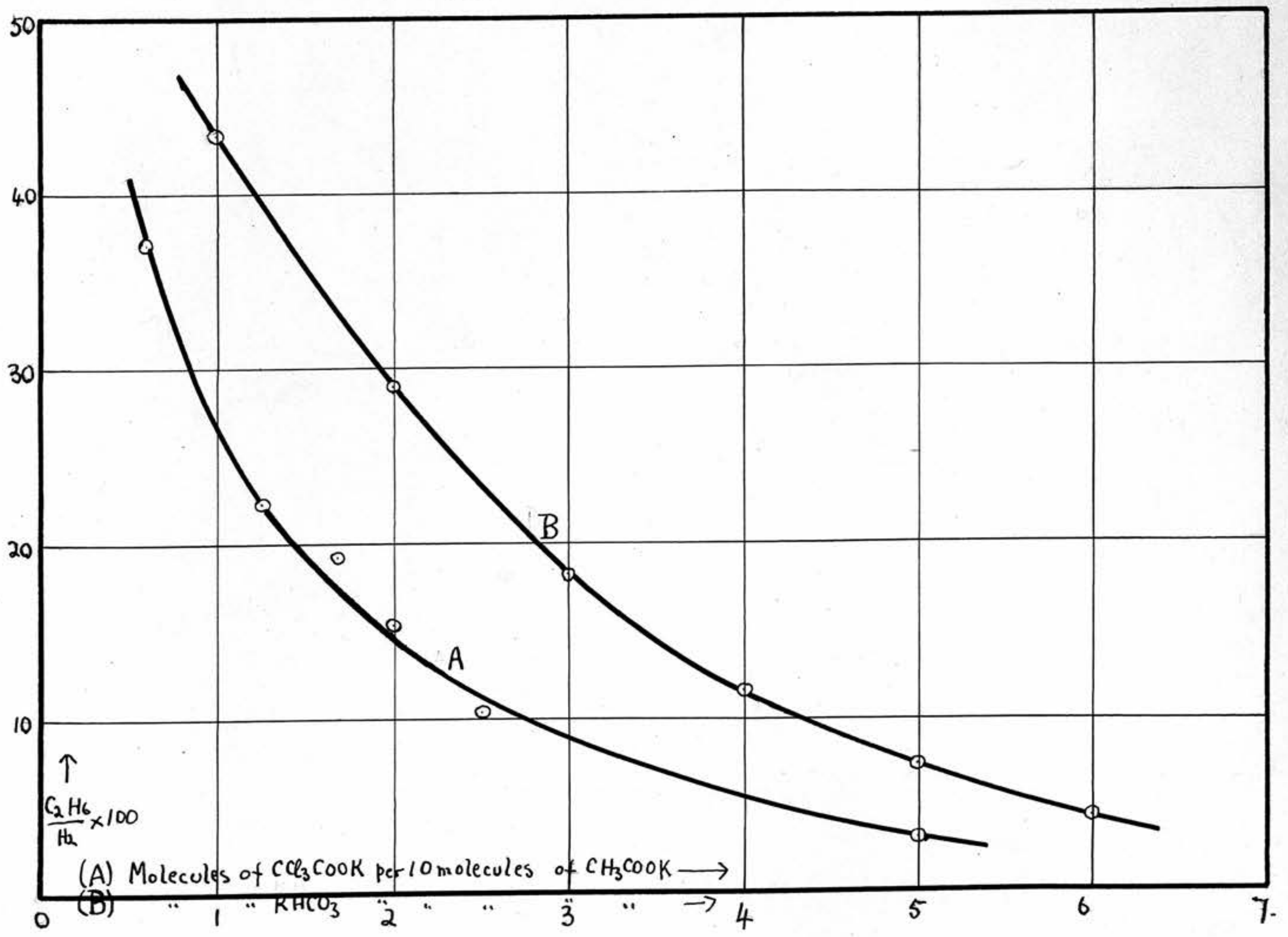
A quantity of the residual electrolyte was made/

made alkaline with sodium carbonate and distilled. The aqueous distillate was separated from a layer of chloroform which had also passed over, and was tested for formaldehyde and methyl alcohol in the way described on page 10. The presence of the former compound in considerable amounts was demonstrated, but despite prolonged search no appreciable quantities of methyl alcohol could be found.

THE EFFECT of VARIATION of the COMPOSITION of the ANALYTE on ETHANE PRODUCTION.

A remarkable feature of the results of the analysis of the anode gas was the comparatively small amount of ethane found. In order more closely to examine the influence of potassium trichloracetate on the anodic behaviour of potassium acetate, the molecular proportions of these salts in the electrolyte were altered and the resulting gases collected and examined with a view to determining the yield of ethane, and hence the ratio $\frac{\text{Ethane}}{\text{Hydrogen}}$. To ensure that the figures from the various experiments might be comparable, the gas for analysis was collected during the first fifteen minutes after the switching on of the current. All air was previously expelled/

Figure II


50
40
30
20
10
0
1
2
3
4
5
6
7.
A
B
↑
$\frac{C_2H_6}{H_2}\times 100$
(A) Molecules of CCl_3COOK per 10 molecules of CH_3COOK ⟶
(B) " " $KHCO_3$ " " " ⟶

expelled from the apparatus by a stream of carbon dioxide. The anode gas was collected in a SCHIFF'S azotometer over a concentrated solution of potassium hydroxide. The hydrogen evolved at the anode was collected and its volume measured. The concentrations of the solutions used as electrolytes were the same as those mentioned on page56. The quantity $\frac{\text{Ethane}}{\text{Hydrogen}} \times 100$ which represented the percentage of the current used in ethane formation was plotted against the varying number of gram molecules of potassium trichloracetate added to ten gram molecules of potassium acetate. Table III gives the results which are plotted on the accompanying graph (Figure II.). Curve A shews the results obtained in the present experiments, while curve B is taken from an experiment of HOFER and MOEST (1), in which potassium bicarbonate was added to the solution of potassium acetate under investigation. The similarity between the curves is obvious and lends support to the view that potassium trichloracetate influenced the course of the electrolysis of potassium acetate in the same way as did the inorganic admixtures used by HOFER and MOEST.

Table/

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(1) op.cit. p. 308.

TABLE III.

$\frac{CH_3COOK}{CCl_3COOK}$.	ETHYLENE	ETHANE	HYDROGEN.	$\frac{\text{ETHANE}}{\text{HYDROGEN}}$	$\frac{\text{ETHYLENE}}{\text{HYDROGEN}}$
10 : 0.6	3.1cc.	110.7cc	300cc	0.369	0.01
10 : 1.25	25.4"	69.0 "	300 "	0.230	0.08
10 : 1.7	41.2 "	57.8 "	300 "	0.193	0.14
10 : 2.0		46,5 "	300 "	0.155	
10 : 2.5	31.8 "	30.4 "	300 "	0.101	0.106
10 : 5	30.4 "	9.3 "	300 "	0.03	0.10

DISCUSSION of RESULTS.

It has been shewn in the foregoing that the following substances are produced when an aqueous solution of potassium acetate and trichloracetate, containing two molecules of the former salt to one of the latter, is electrolysed with high current density at a platinum anode:- Carbon dioxide, carbon monoxide, ethylene, ethane, methyl chloride, trichlormethyl trichloracetate, trichlormethyl acetate, hydrochloric acid (from trichlormethyl alcohol), hexachlorethane and formaldehyde, but no methyl alcohol nor methyl esters.

Such products may be classified as resulting from reactions involving.

(a) SINGLE MOLECULES of either ACID - ETHYLENE, FORMALDEHYDE, HYDROCHLORIC ACID.

CH_3COOH/

$$CH_3COOH + O = CH_2 + CO_2 + H_2O, \quad CH_2 + CH_2 = C_2H_4$$ (1).

$$CH_3COOH + 2O = CH_2O + CO_2 + H_2O.$$

$$CCl_3COOH + O = CCl_3OH + CO_2 \xrightarrow{H_2O} 3HCl + 2CO_2.$$

(b) TWO MOLECULES of either ACID-ETHANE, TRICHLORMETHYL TRICHLORACETATE, HEXACHLORETHANE.

$$2CH_3COOH + O = CH_3.CH_3 + 2CO_2 + H_2O$$

$$2CCl_3COOH + O = CCl_3.COOCCl_3 + CO_2 + H_2O$$

$$2CCl_3COOH + O = CCl_3.CCl_3 + 2CO_2 + H_2O.$$

(c) ONE MOLECULE of each ACID - TRICHLORMETHYL ACETATE.

$$CCl_3COOH + CH_3COOH + O = CH_3COOCCl_3 + H_2O + CO_2.$$

Carbon dioxide was formed in all the above reactions and also by destructive oxidation processes. The production of carbon monoxide has not yet been explained.

The/

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(1) The inclusion of ethylene in this group is justified on the following grounds. When fatty acids, other than acetic and formic acids, are electrolysed, unsaturated compounds which are obviously derived from single molecules of the acid are formed and appear in the final products. This is illustrated by the production of large amounts of ethylene during the electrolysis of potassium propionate, $CH_3CH_2.COOH + O = CH_2:CH_2 + CO_2 + H_2O$. No compounds of the type $CH_3CH:CH.CH_3$ have been isolated. In the case of potassium acetate the expected unsaturated compound is methylene (CH_2) which is, in all probability, first formed but, as it is incapable of a separate existence it appears in the end products as the polymerised compound, ethylene.

The hypothesis, that compounds produced at the anode result from the combination of discharged anion residues, would lead us to expect that the products mentioned in classes (b) and (c) should predominate, since in these experiments the conditions, such as anode current density, concentration of the electrolytes and temperature, were favourable to their formation, but this is not in agreement with the actual facts as a glance at table IV will shew. In fact the main products are those classified under heading (a)

TABLE IV.

Shewing the relative number of gram molecules of the various substances formed.

		a		b		c
HYDROGEN.	CARBON DIOXIDE	ETHYLENE	TRICHLORMETHYL ALCOHOL.	ETHANE	TRICHLORMETHYL TRICHLORACETATE.	TRICHLORMETHYL ACETATE.
100	125	10.7	29.2	1.5	3.3	1.9
100	122	8.7	29.0	1.2	3.8	2.3

The indications are, therefore, that the presence of either salt affects the reactions of the other in a very fundamental manner.

The close resemblance between the results of the electrolysis of a mixture of potassium acetate and/

and potassium trichloracetate and that of a mixture of, say, potassium acetate and potassium hydrogen carbonate or perchlorate has already been demonstrated. One difference is, however, to be noted, namely that, whereas methyl alcohol is the chief product from acetic acid in the latter case, ethylene is the main product in the former. HOFER and MOEST(1), who studied the latter reaction, based their explanation of the phenomenon on the assumption that the discharged perchlorate ions produced a large concentration of hydroxyl groups at the anode in consequence of the reaction.

$$ClO_4 + H_2O = HClO_4 + OH.$$

These hydroxyl groups were supposed to unite with the methyl residues from discharged acetanions to give methyl alcohol.

$$CH_3COO + OH = CO_2 + CH_3OH.$$

The discharged perchlorate residues (ClO_4) appear to be capable only of one type of reaction, namely that mentioned above, because no reactions such as

$$ClO_4 + ClO_4 \rightarrow (ClO_4)_2$$

are known, and products of the type CH_3ClO_4 although comparatively stable, have never been found even in traces in such experiments. Hence this explanation of/

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(1) op.cit.

of the formation of methyl alcohol at the expense of ethane seems quite plausible. The same argument applies to all cases where the admixtures are inorganic salts. The case under consideration differs from the above in that it involves two salts, both of which, when electrolysed singly under the same experimental conditions, readily form higher organic compounds (see p.3.). We have, therefore, no reason to assume that the concentration of the hydroxyl group will be any greater, relative to that of the other discharged ions, in the case of the mixture than in the case of the simple salts. Hence HOFER and MOEST'S theory does not apply with any great probability to the explanation of the enormous difference between the yields of ethane and trichlormethyl trichloracetate actually obtained during the electrolysis of a mixture of potassium acetate and trichloracetate, and those which would be expected from a consideration of the behaviour of the single salts under similar conditions.

It should be noted in passing that, owing to the liquid immediately around the anode being highly acid, the concentration of the hydroxyl <u>ion</u> is negligible in comparison with that of the other ions, and may be disregarded as a source of OH groups for/

for the reaction of HOFER and MOEST. Moreover, such a consideration shews that, what-ever view of the reaction one may take, the following equation is, strictly speaking, incorrect.

$$CH_3COO' + OH' + 2\oplus = CH_3OH + CO_2.$$

To explain the foregoing results we must enquire into the fundamental problem of electrosynthesis. It is known that the following conditions are necessary for the production of ethane in large yields from potassium acetate.

(1) High current density at an anode of polished platinum or iridium, together with low temperature of the electrolyte.

(1) As has already been pointed out these are the conditions necessary to secure a high anode potential and, therefore, electrolytic oxygen of high oxidising power. That a certain definite anode potential is necessary before electrosynthesis can begin has been demonstrated by PREUNER and LUDLAM (2) who found that this critical potential for acetic acid was 2.54 volts on the hydrogen standard.

(2) High concentration of acid at the surface of or inside the anode.

This is brought about by the anions being discharged/

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(1) FICHTER and KRUMMENACHER (Helv. chim. acta I 146 1918)

(2) Zeit. phys. chem. 59 682. (1907)

discharged at the anode and forming the corresponding acids by interaction with water. As long as platinum anodes are used with moderate current densities, condition (1) is fulfilled completely, but condition (2) is subject to alteration in two ways, (a) by dilution of the electrolyte with water, (b) by introduction into the electrolyte of a second ion. Case (a) was investigated by MURRAY (1) who found that the production of ethane decreased as the concentration of the potassium acetate in the electrolyte decreased, and that within fairly wide limits this effect was not very large, but that in dilute solutions ethane formation was almost completely stopped. This result is not unexpected as it is simply the concentration of the acid in the immediate vicinity of the electrode which matters, and in the solutions ordinarily used, this is kept to a high value by the rapid discharge of ions. In case (b) an extra carrier for the electricity is provided and so the number of original ions congregating round the anode is diminished. Moreover, the acid molecules produced from the second ions may be regarded as exerting a diluent or separative influence on the acid molecules produced/

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(1) Trans. chem. Soc. 61 10 (1892)

produced from the original anions. We see then that the addition of a second anion strikes right at the very centre of reaction.

Let us apply these ideas to the results already given, the anode reactions being regarded as oxidation phenomena.(1) When, in the electrolysis of potassium acetate, the concentration of acetic acid at, or in, the anode is great owing to the large congregation of acetanions thereat and the subsequent reaction,

$$2CH_3COO + H_2O = 2CH_3COOH + O.,$$

the main oxidising action is one in which two molecules of acid are attacked by one atom of oxygen as follows:-

$$\begin{array}{l}CH_3COOH\\CH_3COOH\end{array} + O = CH_3.CH_3 + 2CO_2 + H_2O$$

while the reaction, $CH_3COOH + O = CH_3OH + CO_2$, only proceeds to a relatively slight extent. If, however, we add to the solution of potassium acetate a second salt, be it potassium perchlorate or potassium trichloracetate, the acid produced from the discharged anions is no longer pure acetic acid but contains, in addition, perchloric or trichloracetic acids which, by their presence alone, reduce considerably the probability that two molecules of acetic/

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(1). Cp. Jahn Wied. Ann. 37 420. or Bunge J. Russ chem. Soc. 21 525-557.

acetic acid and one atom of oxygen will be in a position to react. In these circumstances, one molecule of acid is attacked by one atom of oxygen and such reactions take place as;-

$CH_3COOH + O = CO_2 + CH_3OH$ (HOFER and MOEST)

$CH_3COOH + O = CO_2 + H_2O + CH_2$ (Ethylene Formation)

As the same argument may be applied to the behaviour of trichloracetic acid and, in fact, of any organic acid, we see that the theory explains in a simple manner why, in the case before us, the chief products should be those described under class (a) and not as formerly expected, those in classes (b) and (c).

There is, moreover, a second factor which governs the nature of the products of electrolysis, namely, the tendency of the acids formed at the anode to give mixed compounds by the reaction of one molecule of each acid with one atom of oxygen. In the cases just quoted this influence is negligible as is shewn by the small quantity of trichlormethyl acetate produced, but at times it becomes so important that it determines the whole result, as in the case already mentioned of the preparation of azelaic acid.

The above theory shews clearly the relation between the alcohol formation of HOFER and MOEST and/

and the ethylene formation observed here. Further, it explains to some extent the diminution in ethane evolution after the electrolysis had proceeded for some time, for a third anion, the chloride ion, made its appearance thereby rendering even more improbable the encounters appropriate to ethane formation. The non-appearance of methyl alcohol is in accordance with an observation of HOFER and MOEST (1), that in an experiment where sodium chlorate was added to sodium acetate, a small quantity of chlorine was given off at the anode, and that oxidation of methyl alcohol to formaldehyde took place to a large extent. In the present case chlorine was found in the anode gas and formaldehyde was detected in the residual electrolyte.

The Production of hexachlorethane in these experiments also calls for some remark, as it appears that hitherto no investigator has observed its presence in the products of the electrolysis of trichloracetic acid. Only a very small amount was found but sufficient to shew that the difference in behaviour between trichloracetic acid and acetic acid in electrolysis is merely one of degree. In fact, while in the former case much ester and little hydrocarbon derivatives are formed, in the latter case the/

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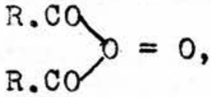
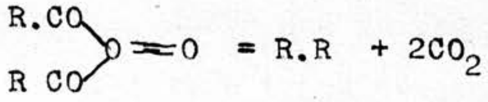
(1) op. cit. p. 303.

the opposite is the characteristic feature. Furthermore, this throws a light on a theory of KOLBE'S electrosynthesis of hydrocarbons etc. recently propounded by FICHTER and KRUMMENACHER (1) who from a study of the thermal decomposition of acid peroxides of the type  $\begin{matrix}R.CO\\R.CO\end{matrix}>O = O$, postulate these as necessary intermediate compounds in the synthesis of hydrocarbons from fatty acids. Such compounds are alleged to be produced by oxidation of acid anhydrides formed at the anode and are shewn to decompose as follows:-



$$\begin{matrix}R.CO\\R\ CO\end{matrix}>O = O \quad = R.R \; + 2CO_2$$

Lately FICHTER, FRITSCH and MULLER (2) have drawn attention to the fact that the anyhdride of trichloracetic acid is extremely unstable to water, and, moreover, conclude from their researches that the peroxide of trichloracetic acid is incapable of existence. These facts reinforce each other in indicating that trichloracetic peroxide cannot be formed during the electrolysis of that acid or its salts. Hence in hexachlorethane we have an example of the formation of a hydrocarbon derivative by KOLBE'S Reaction without the possibility of an intermediate acid peroxide being formed.

Summary/

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(1) op. cit.
(2) Ibid 6 502 1923.

SUMMARY

When potassium acetate and trichloracetate are electrolysed together, mixed compounds are formed but only to a very slight extent. A small quantity of trichlormethyl acetate is to be found among the reaction products. No appreciable amounts of methyl trichloracetate nor of the compound $CH_3.CCl_3$, are formed. The presence of either salt affects the reactions of the other by diminishing the yields of the normal products and by promoting the production of substances like trichlormethyl alcohol, ethylene, and formaldehyde which result from the oxidation of single molecules of each acid. A short explanation of this phenomenon has been given. No methyl alcohol appears among the final products but formaldehyde is found in considerable quantities. This oxidation is connected with the production of an oxidising agent such as chlorine at the anode. Hexachlorethane and methyl chloride are also produced during the electrolysis of this mixture., and the theoretical importance of the formation of the former compound has been emphasised.

PART II.

NOTE on the MECHANISM of KOLBE'S ELECTROSYNTHESIS and ALLIED REACTIONS.

PART II.

NOTE on the MECHANISM of KOLBE'S ELECTROSYNTHESIS and ALLIED REACTIONS.

INTRODUCTORY

In the first part of this thesis it was assumed that the processes taking place at the anode during the electrolysis of a concentrated solution of a salt of an organic acid might be regarded as oxidation phenomena.(1) As, however, this is by no means the only, nor the most widely accepted view of this reaction, it cannot be advanced without some reasons for its tenure being appended, and it is the object of this second part to shew, mainly from electrochemical considerations, that such a view is justifiable, and indeed that it represents the experimental facts more completely than any of the other theories.

Historical/

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(1) In this paper the term oxidation will be used in a restricted sense to denote the direct action of oxygen on a molecule or residue.

HISTORICAL DEVELOPMENT of the CONCEPTIONS of the MECHANISM of ELECTROSYNTHESIS.

KOLBE,(1) himself, who had observed the very high oxidising power of a platinum anode during his researches on the electrolytic oxidation of trichlormethane sulphonic acid, regarded electrosynthesis merely as a process of oxidation in which the acid liberated at the anode was oxidised to hydrocarbons, unsaturated hydrocarbons, esters, carbon dioxide, and water. He formulated the behaviour of acetic acid as follows:-

$$HO\ (C_2H_3)\ C_2O_3 + O = C_2H_3 + 2CO_2 + HO$$

This view was supported by JAHN(2) from thermochemical experiments and also by the work of **BUNGE.**(3)

Prior to the work of these last two investigators, KÉKULÉ,(4) had advanced the hypothesis that acid anhydrides were first produced at the anode by the combination of residues from discharged anions with the elimination of oxygen. These anhydrides, he said, were then oxidised to hydrocarbons, carbon dioxide etc. by electrolytic oxygen. Thus:-

$2CH_3/$

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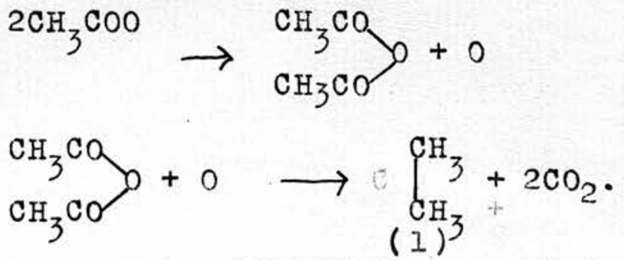
(1) Ann. <u>69</u> 279 (1849)
(2) Wied. Ann. <u>37</u> 420.
(3) J. Russ. chem. Soc. <u>21</u> 525.
(4) Ann. <u>131</u> 79.



$$2CH_3COO \longrightarrow \begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!>O + O$$

$$\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!>O + O \longrightarrow \begin{matrix}CH_3\\|\\CH_3\end{matrix} + 2CO_2.$$

Four years later BOURGOIN(1) carried this theory a step further by assuming that the anhydride was oxidised at the anode in precisely the same manner as SCHUTZENBERGER(2) had shewn acetic anhydride to be oxidised to ethane and carbon dioxide by barium peroxide. The view that anhydrides were temporarily produced during the reaction was further supported by LOEB(3) from his researches on the electrolysis of acetates in the presence of hydrogen sulphide, and from the formation of large amounts of phthalic anhydride during the electrolysis of salts of phthalic acid. This second view, while involving the idea of oxidation also introduced the notion which formed the basis of the second great theory, namely, that of reaction between the residues of discharged anions.

In 1891, CRUM BROWN and WALKER(4) propounded a simple explanation of the phenomenon, founded on the Ionic Theory. Discharged anions of an organic acid could, according to these authors, react in/

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(1) C. R. 65 892 (1867); A.ch. [4] 14 162 (1868)
(2) C. R. 61 487
(3) Zeit. Elektrochem. 3 43.
(4) Ann. 261, 107 (1891).

in either of two ways:-

(a) If the solution were dilute, or the current density at the anode small, or, in fact, if conditions were such that the concentration of discharged anions was very small, then these last reacted with the surrounding water, generating the original acid and oxygen. This was called the Faraday Reaction.

(b) If experimental conditions were such that a large concentration of anions at the anode could be obtained, then the discharged ion residues reacted with each other, producing the various compounds characteristic of electrosynthesis as follows:-

(i) $2CH_3COO' + 2\oplus = CH_3.CH_3 + 2CO_2$.

(ii) $2CH_3COO' + 2\oplus = CH_3COOCH_3 + CO_2$

(iii) $2CH_3COO + 2\oplus = CH_2 + CH_3COOH + CO_2$.

This theory presented a simple picture of the process. It explained most of the known reactions of this kind, and was successfully applied to predict new ones.

The experimental conditions such as strength of current, concentration of electrolyte, size of electrodes, acidity or alkalinity of the electrolyte, and temperature, under which the maximum yields/

yields of ethane might be obtained from potassium acetate, were studied by MURRAY(1) and found exactly to fulfil the requirements of this hypothesis. Moreover, the same investigator electrolysed a mixture of 10 per cent. acetic and 10 per cent. sulphuric acids and found that no appreciable oxidation of acetic acid took place. This fact, together with the extreme stability of acetic acid towards ordinary oxidising agents, remained for many years one of the chief arguments against the oxidation theory.

An attempt to penetrate more deeply into the mechanism of these reactions by inserting an intermediate step into the theory of CRUM BROWN and WALKER was made in 1896 by SCHALL,(2) who alleged that primarily the discharged acetanions united to give an acid peroxide which thereafter decomposed into the usual products. His formulation was

$$R.COO' + R.COO' + 2\oplus \rightarrow \begin{array}{l} R.COO \\ R.COO \end{array} \rightarrow R.R + 2CO_2$$

This formed the foundation of the Peroxide Theory of Electrosynthesis which was upheld by FOERSTER and PIGUET(3) who noted that there existed a high transition resistence between an anode producing ethane and the electrolyte. They concluded that this fact argued the formation of a poorly conducting intermediate/

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(1) Trans. Chem. Soc. 61 10 1892.
(2) Zeit. Elektrochem. 3 83 (1896)
(3) Ibid. 10 727 (1904)

intermediate compound on the anode and supposed this to be acetyl peroxide. KAUFLER and HERZOG (1) dealt with this view, shewing that such transfer resistances were by no means limited to anodes in solutions of organic salts, and also indicated the danger of assuming the presence of a particular compound from so general a phenomenon.

In 1902 HOFER and MOEST (2) found that, in addition to hydrocarbons and esters, alcohols could be produced by the electrolysis of organic acids. As their ideas have been fully discussed in Part I, it is sufficient to say that their discovery was taken as further support of the truth of the Discharged Ion Combination Hypothesis. The simple equation

$$CH_3COO + OH = CH_3OH + CO_2$$

seemed to fulfil all the requirements, and it was also observed that if, for any reason, the concentration of OH, or OH producing, groups increased, the yield of alcohol also increased. In an article published in 1904 (3) these authors stated their belief in the Discharged Ion Combination Theory with great clearness. The experiments on the electrolysis of/

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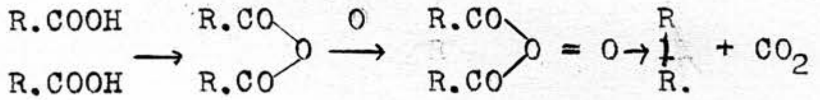
(1) Ber. 42 3858 (1909)
(2) Ann. 323 284 (1902)
(3) Zeit. Elektrochem 10 833 (1904)

of mixtures were all taken as supporting this theory and, in fact, by 1910 it was accepted by almost all chemists. Still further support was added when HOPFGARTNER (1) shewed that the electrolytic behaviour of the salts of fatty acids dissolved in the corresponding anhydrous acids was the same as in aqueous solution.

The oxidation and peroxide theories received new life from a paper published by FICHTER and KRUMMENACHER (2) in 1918 wherein, as a result of an examination of the thermal decomposition of acid peroxides and peracids the following theory was set forth:-

It was assumed that at a working anode the anhydride of the acid was first formed but not necessarily by the combination of discharged ion residues, that this anhydride was oxidised to an acid peroxide which, at the temperature of the working anode, alleged by FICHTER and KRUMMENACHER to be high, decomposed to give hydrocarbons, carbon dioxide and the other products, in the following way:-



$$\begin{matrix}R.COOH\\R.COOH\end{matrix} \longrightarrow \begin{matrix}R.CO\\R.CO\end{matrix}\!>O \xrightarrow{O} \begin{matrix}R.CO\\R.CO\end{matrix}\!>O = O \rightarrow \begin{matrix}R\\|\\R.\end{matrix} + CO_2$$

Thus if an organic acid is to take part in electrosynthesis/

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(1) Monatsh. für chem. <u>32</u> 523 (1911)
(2)) Helv. Chimica. Acta I 146 (1918)

electrosynthesis it must have the power:-

(a) of yielding an anhydride at the anode,

(b) of forming an acid peroxide.

(c) of itself withstanding the attack of oxygen.

To account for HOFER and MOEST'S reaction the authors add a second clause to the effect that when agents which "favour saponification"(1) (such as sulphates, bicarbonates, perchlorates) are present, acid peroxides are either not formed at all or are rapidly decomposed. In either case, the product is a per-acid of the formula $R.CO_3H$ which splits up giving carbon dioxide, alcohols, and unsaturated hydrocarbons. This theory which is really an amplification of the simpler ideas of KOLBE &JAHN will be referred to later.

It will be seen from the foregoing that the theories propounded to explain KOLBE'S Electrosynthesis involve only two essentially different ideas:-

(1) The idea of Oxidation (KOLBE)

(2) The idea of Combination of Discharged Anion Residues. (CRUM BROWN and WALKER)

As all other explanations of the reaction under consideration are either modifications or amplifications of these two main theories, hereinafter referred to as/

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(1) "die Verseifung erleichtern".

as the Oxidation Theory and the Discharged Ion Theory, we shall confine our attention to determining which of the two gives the more complete representation of the experimental evidence.

Either theory is capable of accounting in a simple and adequate manner for most of the known electrosynthetic and allied reactions, and no evidence on one side or the other can be gathered from qualitative or quantitative studies of the products of the various reactions. The following observations shew that there is still a strong case for the oxidation theory, and that, although the work of previous investigators does not altogether establish the truth of the theory, there is no cause to believe that its tenure is impossible or unreasonable.

(1) A platinum anode evolving oxygen has an extremely high oxidising power, and oxidations which are almost impossible by purely chemical means may be carried out with its aid (1).

(2) It has been demonstrated (2) that acetic acid or potassium acetate is readily oxidised by potassium persulphate to ethane, ethylene, carbon dioxide, and carbon monoxide. This shews conclusively that fatty acids can be oxidised to hydrocarbons, a fact which has been subject to grave doubts since the experiments/

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(1) KOLBE - loc. cit.

(2) M.A.Gordon J. phys. chem. 18 55 (1914).

experiments of MURRAY.

(3) Although solutions of potassium benzoate contain large concentrations of benzoate ions, it has been found impossible to prepare diphenyl from this salt by electrolysis. The same applies to all other aromatic acids. The chief products in all cases are carbon dioxide and other products of oxidation.

(4) The Discharged Ion Theory leaves practically unexplained the production of unsaturated hydrocarbons, such as ethylene from propionic acid, for the equation.

$$2CH_3.CH_2COO = CH_2 = CH_2 + CH_3COOH + CO_2,$$

is at best a formal presentation of the reaction and is extremely improbable. It has been shewn in Part I that the oxidation theory accounts very well for this reaction.

(5) Passing to the work of KAUFLER and HERZOG, v. MILLER and HOFER, and others on the electrolysis of mixtures, it should be noted that the yields of mixed compounds, such as alkyl halides, were only very small and might, with as much justification, have been attributed to the action of halogen acids on the alcohols which were also produced. as to the reaction between discharged anions.

(6)/

(6) The experiments of MURRAY may be interpreted as supporting both theories, in fact Part I shews that his results are in harmony with the oxidation hypothesis, although they were originally taken as strong proof of the correctness of the discharged ion theory.

THE SIGNIFICANCE of ANODE POTENTIAL in a STUDY of ELECTROSYNTHESIS.

PREUNER and LUDLAM (1) have shewn that a platinum anode in a solution of acetate must acquire a certain definite potential, 2.54 volts, before any appreciable amounts of ethane are formed, and also that, at the point 2.54 volts on the curve shewing the relation between current and anode potential, a "knickpunkt" or sharp increase in the gradient is to be observed.

This may mean either of two things,

(a) that at 2.54 volts the acetate ion is discharged at the anode, in which case strong evidence in favour of the discharged ion theory would be obtained.

(b) that at 2.54 volts the anode has acquired an oxidising potential high enough to allow the reaction,

$2CH_3COOH$/

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(1) Zeit. phys. chem. 59 682 (1907).

$2CH_3COOH + O = CH_3CH_3 + 2CO_2 + H_2O$,

to proceed, or, in other words, that at anode potentials above 2.54 volts acetic acid acts as a depolariser. If such were true the oxidation theory would be proved. Although it has been generally assumed (1) that interpretation (a) is the correct one, this is by no means proved, and it was thought that an investigation of the electrochemical behaviour of the anode and the electrolyte in the neighbourhood of this critical point would throw some light on the problem under consideration.

SCOPE of EXPERIMENTS.

The reaction to be studied is the production of trichlormethyl trichloracetate by the electrolysis of a solution of trichloracetic acid, and it is our purpose to show:-

(1) That within very wide limits the process is independent of the anode current density.

(2) That a certain definite potential at a polished platinum anode is necessary before the reaction can begin.

(3)/

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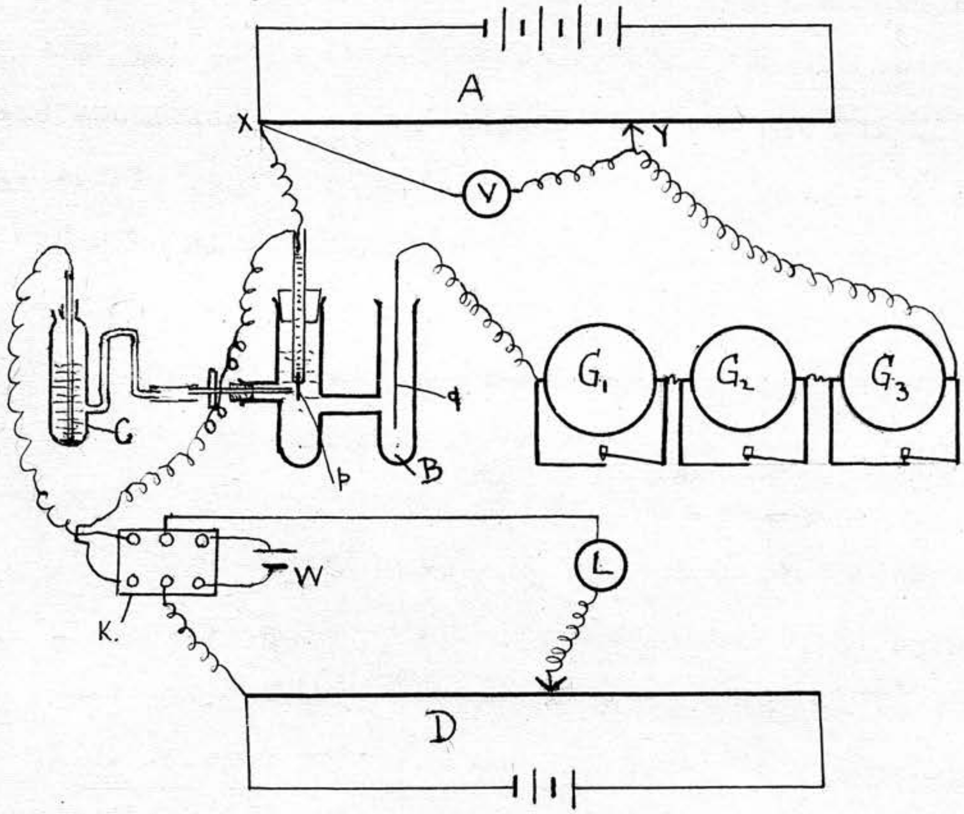
(1) See Nernst. Theoretische Chemie 8-10th Edition p.849.

(3) That this potential does not correspond to the discharging potential of the trichloracetate ion.

(4) That the actual potential of the anode is not sufficient to cause the reaction, but that the nature and state of the anode play a large part.

(5) That non-ionised acetic acid is oxidised by electrolytic oxygen at a platinum anode.

Figure I.



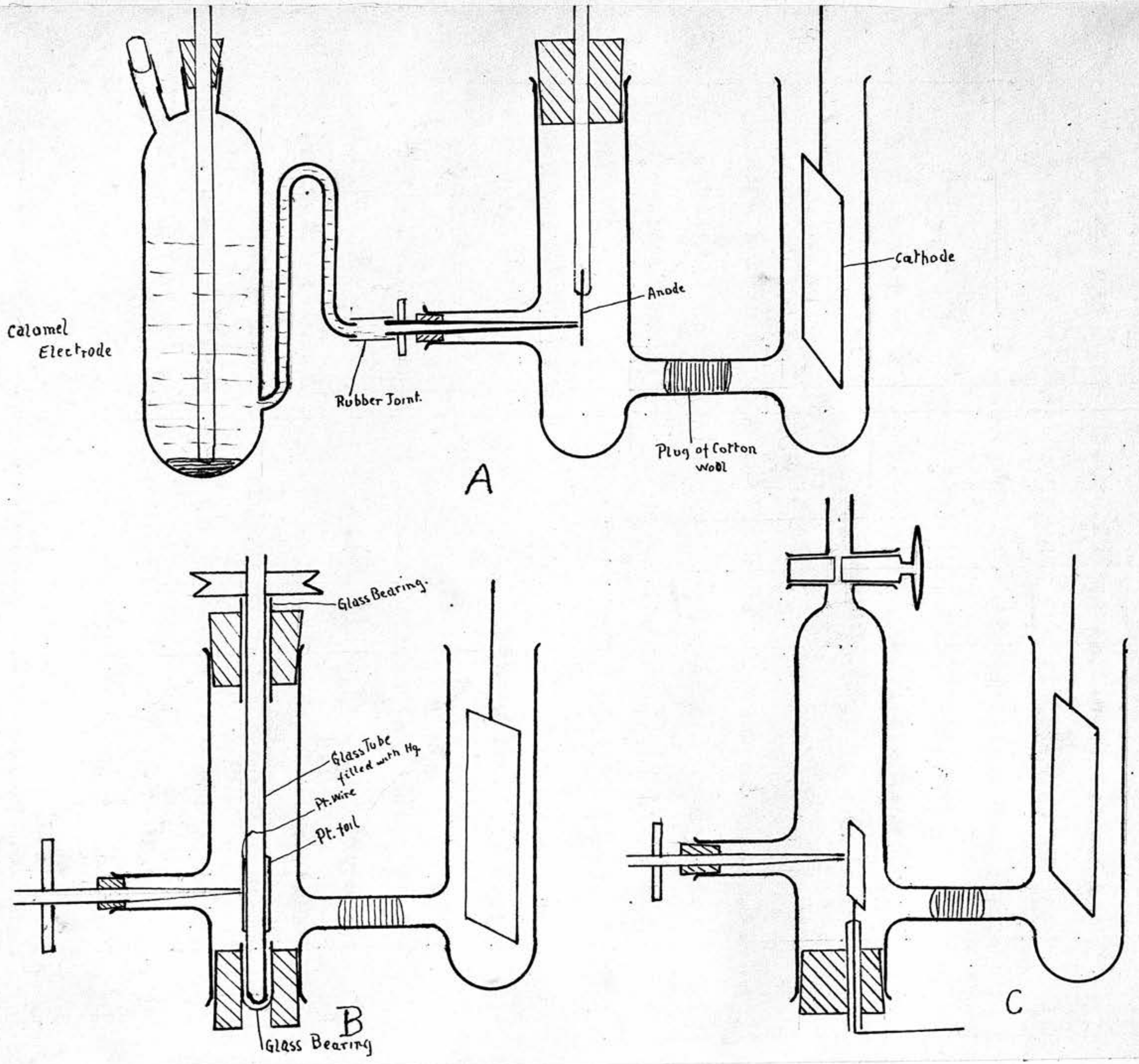
EXPERIMENTAL.

APPARATUS.

FIGURE I. shows the arrangement of the apparatus used for determining the relation between current and anode potential. The variable applied E.M.F., measured by the voltmeter, V, was taken from the moveable points X and Y on the potentiometer, A. The polarising current thus produced passed along the path XpqGY, and was measured by the system of galvanometers G_1, G_2, G_3. As the variation in the strength of the polarising current was much beyond the range of any one instrument, three of varying degrees of sensitivity were used, arrangements being made for short-circuiting each when the current became too strong for it. This system was found to be superior to a series of shunts. By means of the potentiometer, D the difference in potential between the anode, p, and the standard normal calomel electrode C, was measured. The standard of potential was a Weston Cadmium Cell, E.M.F. 1.02 volts. A Lippmann Capillary Electrometer(L) was used to locate the point at which the bridge was in equilibrium. The apparatus was capable of giving results with an accuracy of 4 millivolts.

The/

FIGURE II.


Calomel Electrode
Rubber Joint.
Anode
Cathode
Plug of Cotton wool
A
Glass Bearing.
Glass Tube filled with Hg.
Pt. wire
Pt. foil
Glass Bearing
B
C

The electrolysis cells used in these experiments are illustrated in FIGURE II. Sketch (a) shows the normal type. As trichloracetic acid was reduced at the cathode, it was considered advisable to separate the electrodes as is shown. The nozzle, G. of the calomel electrode was brought close against the anode when stationary, but with rotating anodes a clearance of 0.5.mm. was allowed.

In all cases, except where mention to the contrary is made, the electrolyte consisted of a normal solution of trichloracetic acid. Strictly speaking, the chief reaction during the electrolysis of trichloracetic acid is not a synthetic one, as no carbon to carbon union is made, but ester formation is so closely bound up with KOLBE'S Electrosynthesis that it was considered justifiable to apply deductions made from these experiments to the cases of true electrosynthesis. The suggestion made by FICHTER, FRITSCH and MULLER(1) that the action is one in which trichlormethyl alcohol is an intermediate product appears extremely improbable when it is considered how unstable this compound is, and how comparatively slow the processes of esterification are.

ARRANGEMENT/

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(1) Helv. Chimia Acta 6 502 (1923)

ARRANGEMENT of RESULTS.

From direct potentiometer readings the potential difference between the anode and a normal calomel electrode was calculated. In order to obtain the potential of the electrode on the hydrogen standard it was necessary to add 0.27 volts to this figure. Of this 0.27 volts, +0.29 represented the difference in potential between a calomel electrode and a normal hydrogen electrode, and -0.02 volts was the boundary potential at the surface, $\frac{N}{1}$ KCl | $\frac{N}{1}$ CCl_3COOH, calculated (1) by the formula of LEWIS and SARGEANT.

The results of current and anode potential readings were plotted on graphs with current (i) as ordinate and anode potential (V_H) as abscissa. It has been shown (2) that there is some theoretical justification for assuming that within limits the anode potential is a linear function of the logarithm of the current as long as no changes take place in the processes occurring at the anode, and also that curves shewing the relation between the logarithm of the current and the potential of the anode have the additional practical advantage that any 'knickpunkts', or sharp increases in the gradient, are/

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(1) J.Am.Chem.Soc. <u>31</u> 363 (1909)

(2) Preuner & Ludlam op.cit. Also -
Westhaver - Zeit.Phys.Chem. <u>51</u> 65 (1905)
Haber & Russ Ibid. <u>47</u> 251 (1904)

are much more pronounced than in the ordinary current-potential curves. In certain cases, therefore, the results were plotted with log $\dot{i}$ as ordinate and V_H as abscissa, when any departure from the straight line was taken as evidence of a new process making its appearance at the anode. The logarithmic curves are shown in red.

PRELIMINARY EXPERIMENTS.

Preliminary investigations showed that, for a polished platinum anode in a normal solution of trichloracetic acid, there existed a certain critical potential between 2.32 and 2.37 volts. Below this value gas left the anode as a steady stream of very fine bubbles which rose rapidly from the electrode surface. When, however, the anode potential reached this value, the character of gas evolution changed completely. At a comparatively small number of distinct points on the electrode bubbles appeared to grow, some rapidly and some slowly. Each bubble adhered very firmly to the electrode until, having reached a diameter of 0.5-1.5mm. it rolled slowly up to the top of the electrode and was dislodged. Meanwhile the stream of fine bubbles diminished rapidly and finally ceased. At the points/

points vacated by the large bubbles small crystals of trichlormethyl trichloracetate were seen, and the odour of carbonyl chloride was noticeable. This change in the character of gas evolution was intimately connected with the production of trichlormethyl trichloracetate, for, as long as the gas left the anode as a fine stream, no ester at all was found and no smell of phosgene observed, but as soon as the production of large bubbles began, the ester made its appearance. The conclusion drawn from a number of experiments was that this change in the appearance of the bubbles of gas evolved at the anode could be regarded as the criterion of ester formation.

With anodes of iridium the same phenomenon was noticed, and the critical point was found to be the same as for platinum, 2.32-2.37 volts.

When anodes of gold, and a film of platinum on glass were employed, no change in the character of gas evolution was observed, even when anode potentials as high as 3 volts were reached. The gas given off from a gold anode, working with a current density of 3 amps per sq.cm. and at a potential of 2.5 volts, was analysed and found to be 99 per cent. oxygen. No carbon dioxide was found.

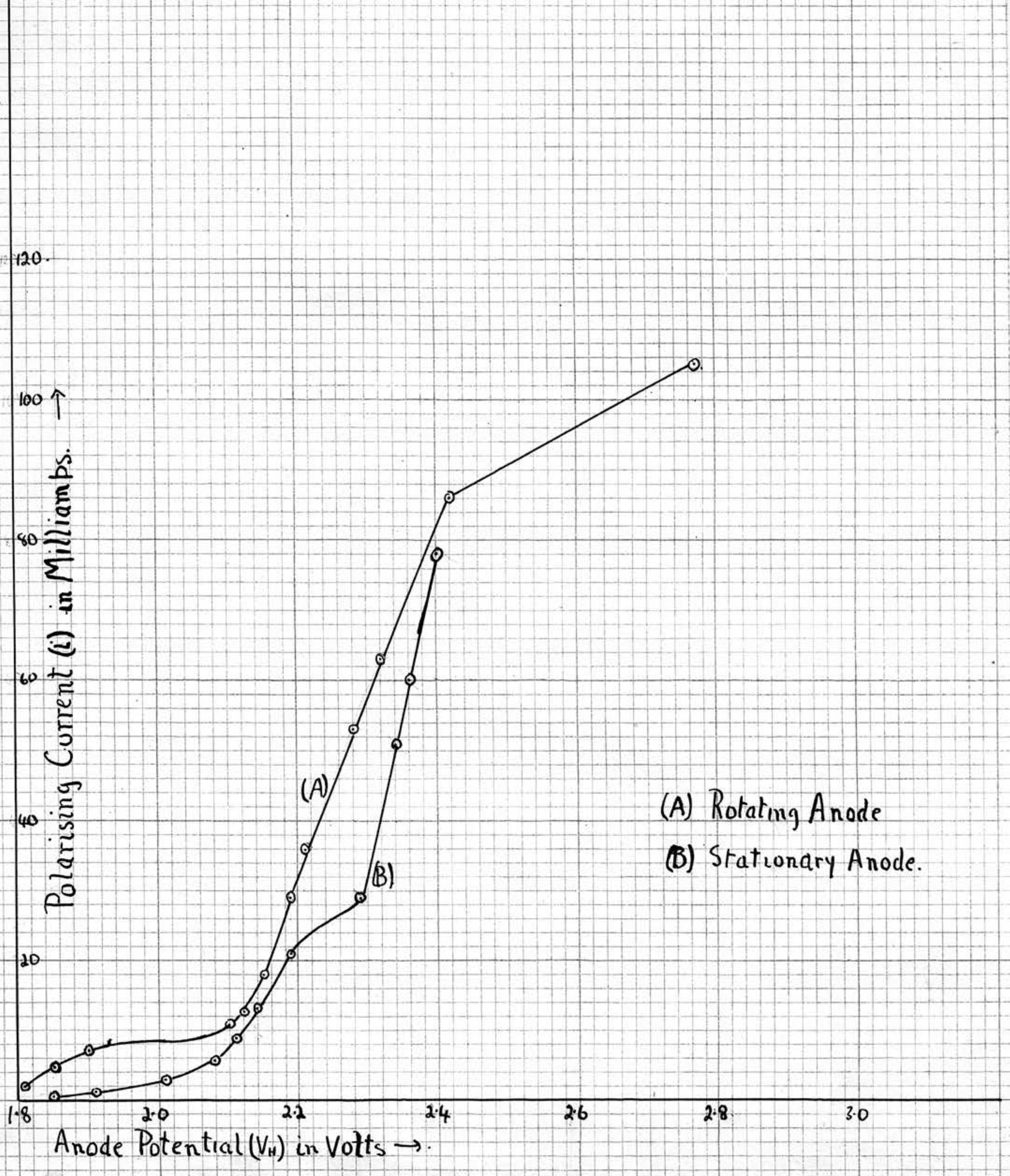
These/

These experiments showed, moreover, that a considerable interval of time was required for the anode to regain equilibrium after each rise in the applied E.M.F. In general, with a constant applied E.M.F. the current decreased and the anode potential increased slightly as time went on.

It was also noticed that in the neighbourhood of 2.28-2.38 volts the anode potential of polished platinum rose rapidly while the current reading either remained steady or decreased. This caused a flattening of the current-potential curve over a region from 2.28-2.6 volts. It was thought at first that this was due merely to the coating of the anode with a poorly conducting film of insoluble ester, but as will be shown later, this effect, if present at all, is small in comparison with changes which appear to take place in the anode itself.

DETERMINATION/

Figure III.


120
100 ↑
80
60
40
20
Polarising Current (i) in Milliamps.
(A)
(B)
(A) Rotating Anode
(B) Stationary Anode.
1·8
2·0
2·2
2·4
2·6
2·8
3·0
Anode Potential (V_H) in Volts →

DETERMINATION of the CURRENT-ANODE POTENTIAL CURVES for ANODES of POLISHED PLATINUM, GOLD, and PLATINUM on GLASS.

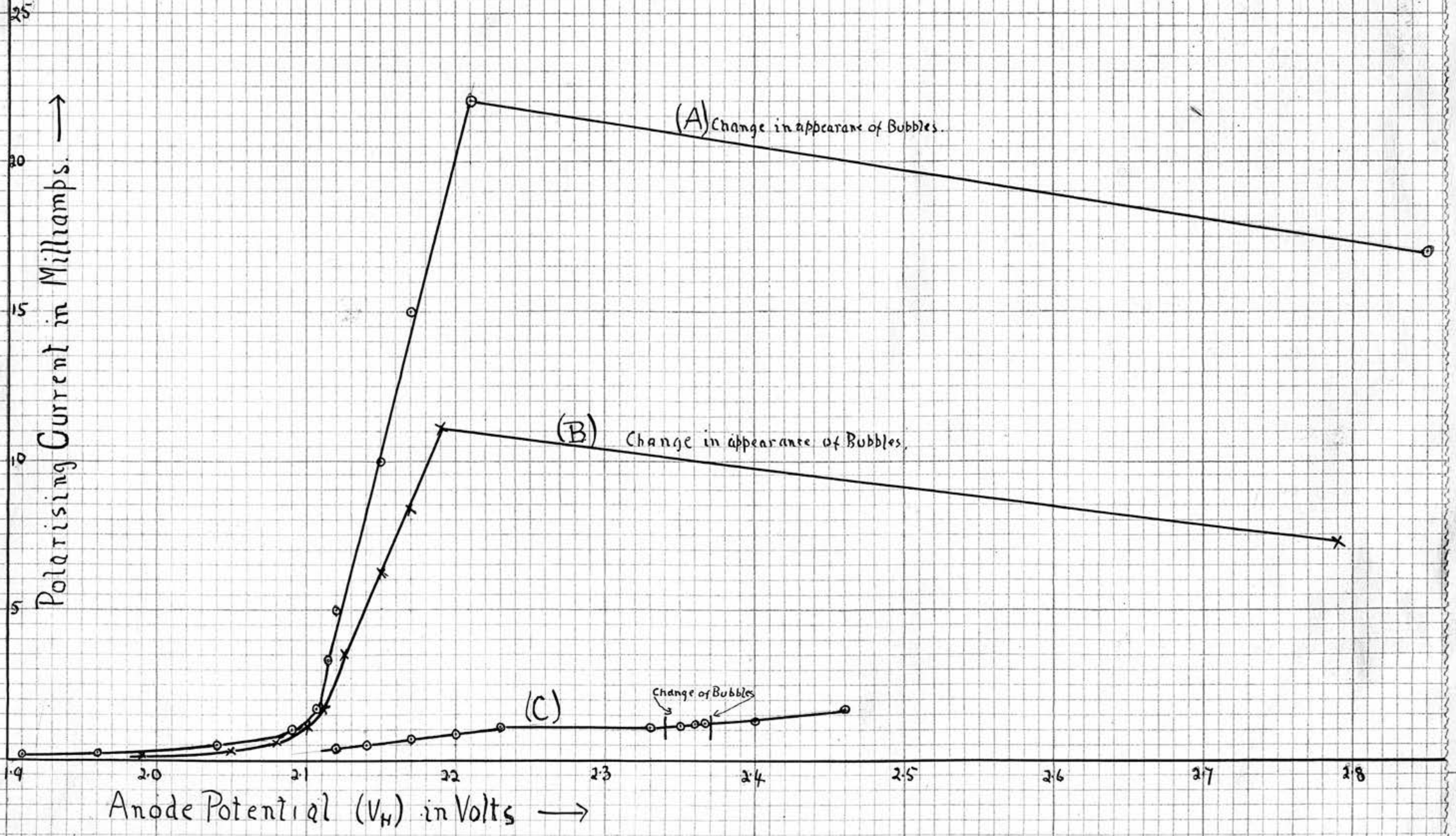
As the preliminary investigations showed that the point at which the production of trichlormethyl trichloracetate began was between 2.32 and 2.37 volts, the portions of the curves lying below 1.9 volts, being unnecessary for the present work, were disregarded after it had been seen that there was no unexpected discontinuity in the curve in the region from 1.0-2.0 volts.

(a) POLISHED PLATINUM ANODES.

Several experiments were made with a large platinum anode of surface area 16 sq.cms, (illustrated in FIGURE IIb.) which could be rotated at a high speed. The results, however, were somewhat erratic. The time required for the anode to come into equilibrium after each change in the applied E.M.F. was excessively long, being sometimes three hours. Furthermore, over certain regions the anode potential rose rapidly, while the current and applied E.M.F. remained constant. Two curves obtained in this way are shown in FIGURE III. The erratic behaviour is obvious but it will be noted that there is no semblance of a 'knickpunkt' about 2.35 volts.

Figure IV.

Shewing current - potential curve for same anode polarised under different conditions in $\frac{1N}{1}$ CCl_3COOH.



In order to examine the phenomenon more closely, a small anode of platinum wire 1 cm. long was used. Prior to the experiment it was scrubbed with fine emery paper, polished and washed with water. It was then fitted into the cell and an E.M.F. of 2.0 volts was applied across the terminals. A small current of 0.5-1 milliamp. flowed through the cell and the anode acquired a potential of 1.8-1.9 volts. It was allowed to become completely polarised under these conditions for 18-20 hours. Thereafter the applied E.M.F. was raised and a series of readings of current and anode potential were taken. After each alteration in the applied potential, time was allowed for the anode to regain equilibrium. During this interval the current and anode potential were read every five minutes, and from the table so obtained, the values at infinite time were found by rough extrapolation. The results of these experiments differed markedly from all previous ones but they were easily reproducible. The curves from four reliable experiments resembled each other in every respect.

FIGURE IV.A, shows a typical result. At 2.10 volts a sharp 'knickpunkt' occurred, whereafter the current rose rapidly till a potential of 2.21 volts was reached, when a sudden rise of the anode potential to 2.8-2.9 volts took place and the current decreased./

decreased. During this increase of potential the critical value was passed and ester formation began.

The applied E.M.F. was now lowered to a very small value, the current stopped momentarily, and the anode shaken to remove any adhering ester. A second series of current and anode potential readings was then taken. The anode potential rose rapidly while the current increased slowly. No 'knickpunkt' at 2.10 and no sudden rise of potential were observed, and it was possible to make an accurate determination of the point at which the bubbles of gas changed in appearance and ester was first formed. The curve obtained was identical with that shown in IV C. Table I gives the observations taken in the vicinity of the critical point and it will be seen that ester formation began about 2.34-2.37 volts.

TABLE/

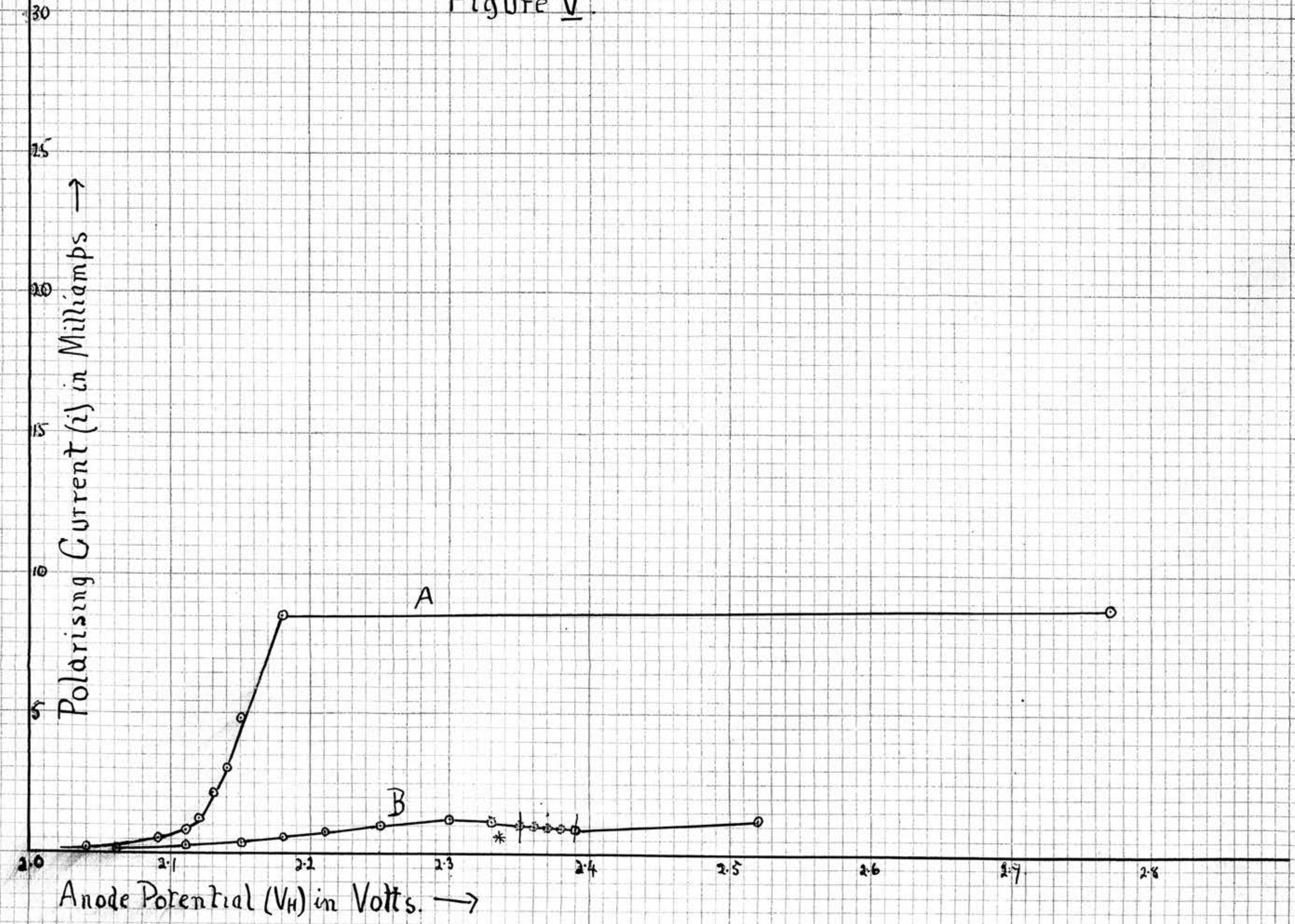
TABLE I.

TIME	APPLIED E.M.F.	CURRENT	ANODE POTENTIAL	REMARKS.
5.20	2.7 volts	1.78	2.27	Fine stream of bubbles.
5.25	2.7 "	1.70	2.29	leave anode.
5.30	2.7 "	1.65	2.30	
5.35	2.7 "	1.60	2.31	
5.40	2.7 "	1.56	2.32	No change
5.45	2.7 "	1.52	2.33	" "
5.50	2.7 "	1.50	2.335	Signs of change of Bubbles.
5.55	2.7 "	1.49	2.336	Further signs of change.
6.0	2.7 "	1.49	2.34	Still further signs of change.
6.10	2.8 "	1.70	2.37	Change complete.

Several experiments were performed in which the anode was first polarised at a potential of 1.9-2.0 volts for 18-20 hours, and then its potential was raised to, and kept at, 2.6-2.9 volts for five minutes. The applied E.M.F. was then lowered and a series of readings taken as in the previous experiments. The results are illustrated by curves B. and C., FIGURE IV.

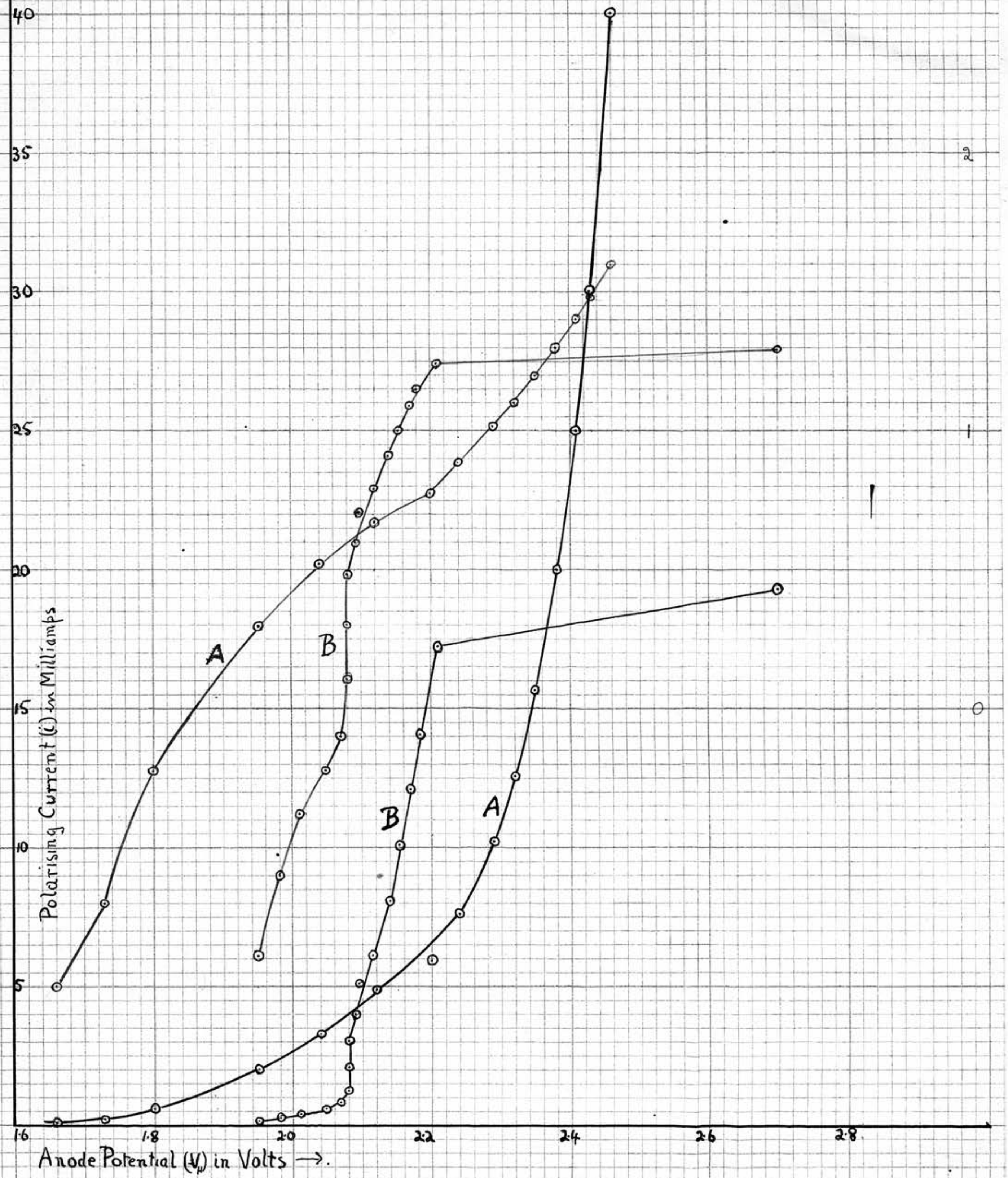
Curve B shows the anode in a state intermediate between those represented by A. and C. It should/

Figure V.



*The points with dotted circles represent readings taken before the Anode attained equilibrium.

Figure VI.

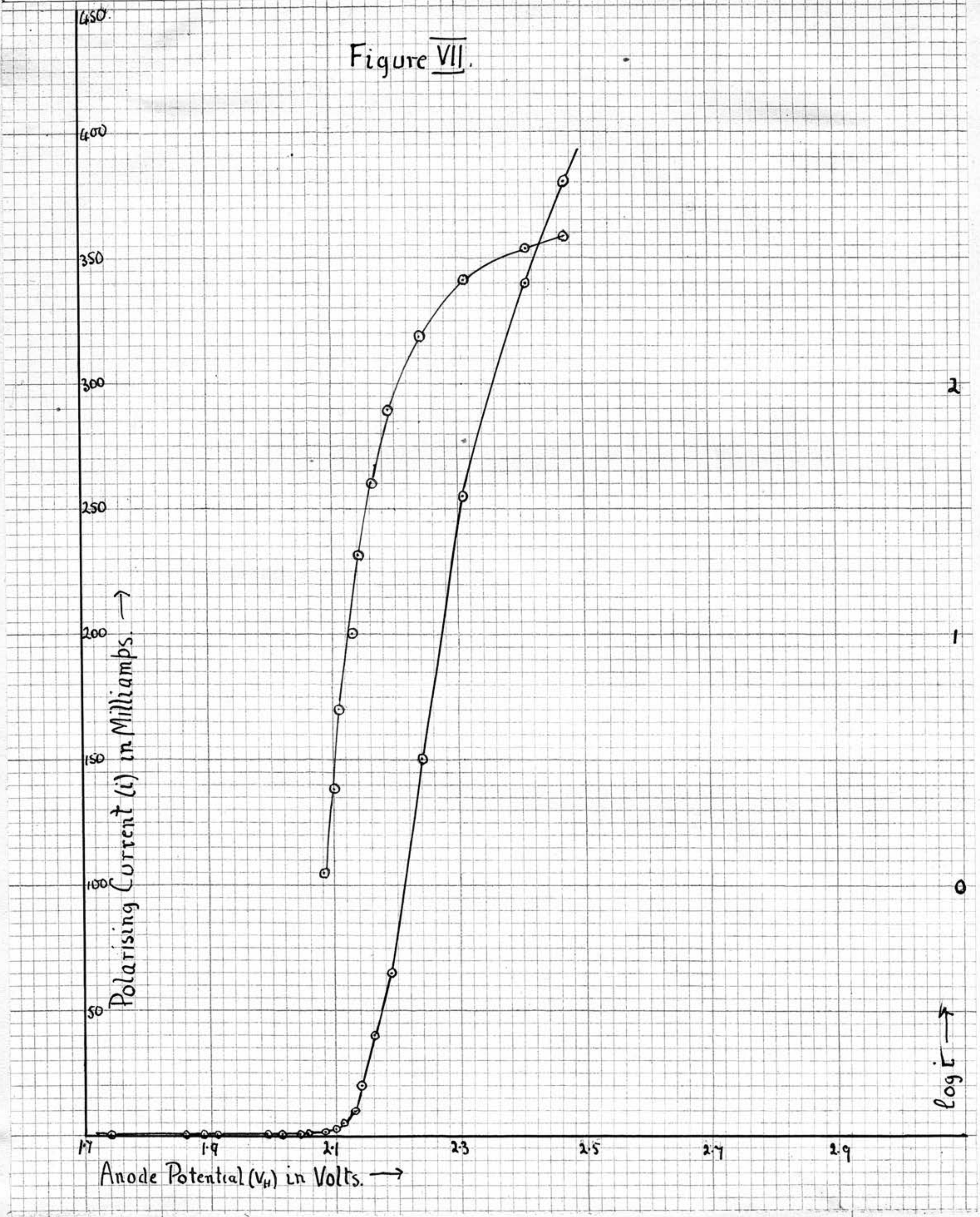

40
35
30
25
20
15
10
5
Polarising Current (i) in Milliamps
1·6
1·8
2·0
2·2
2·4
2·6
2·8
Anode Potential (V_A) in Volts →.
A
B
B
A
2
1
0

should be noted that in the case of B, and to some extent in the case of C, the anode potential below 2.15 volts showed a tendency to fall although the applied E.M.F. was kept constant.

Curve C represents the results of three reliable experiments in which the anode potential was not allowed to fall below 2.1 volts after the preliminary polarisation at high potential. The points at which the change in the appearance of the bubbles of gas was first noticed and at which the change was complete are shown on this curve (2.34-2.37).

The curves in FIGURE V give the results of experiments performed under similar conditions with the same anode in a twice normal solution of trichloracetic acid. It will be seen that the results resemble in all respects those of the previous experiments. FIGURE VI shows curves for the same platinum anode in decinormal trichloracetic acid. In case A the anode was not polarised prior to the experiment, while in case B it was treated in the manner described above. Little or no change took place in the appearance of the bubbles and no ester was observed even after prolonged passage of a heavy current, yet the form of curve B is exactly the same as that of IV A, which /

Figure VII.


450
400
350
300
250
200
150
100
50
1·7
1·9
2·1
2·3
2·5
2·7
2·9
2
1
0
log i →
Polarising Current (i) in Milliamps →
Anode Potential (V_H) in Volts →

which would indicate that the actual formation of ester does not cause the great rise in anode potential referred to on page 18.

(b) EXPERIMENTS with ANODES of GOLD, and a FILM of PLATINUM on GLASS.

A gold anode, 0.5cm. long and 1 mm. in diameter, was treated in exactly the same way as described on page 20 . The results are recorded in FIGURE VII. It will be seen that extremely high currents were necessary to produce the anode potentials observed with platinum anodes, and so the evolution of gas was very brisk. In this and the following experiment the electrodes came into equilibrium very rapidly after each rise in the applied E.M.F. at potentials above 2.2 volts.

A piece of glass tube, closed at one end, was coated with a layer of "Glanz Platin" and ignited whereby it was covered with a continuous film of platinum. The electrode so formed was polarised as described on page 20 . The results are plotted in FIGURE VIII.

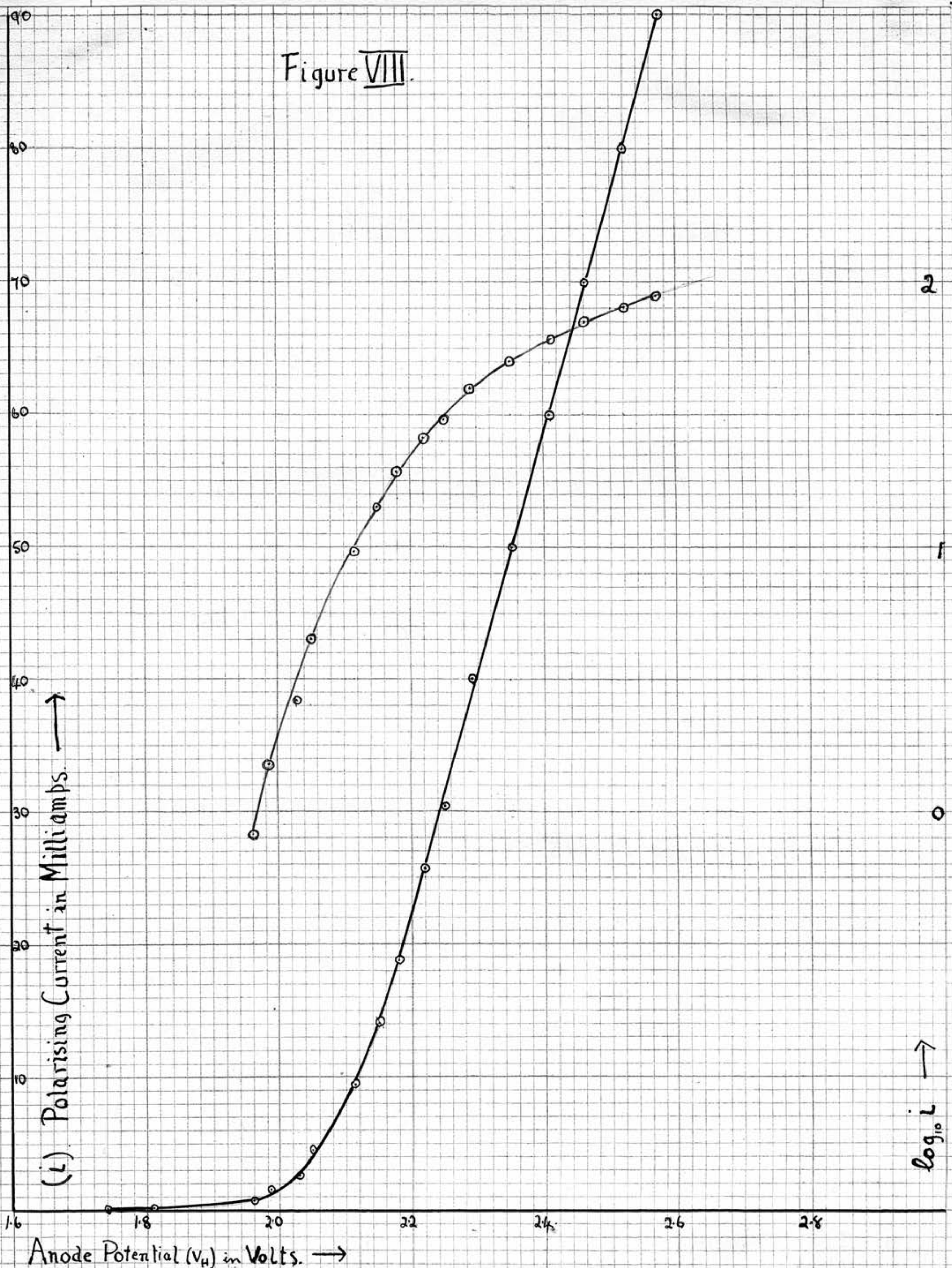
DISCUSSION/

DISCUSSION OF RESULTS.

The first important feature of these results from the point of view of determining the mechanism of KOLBE'S Electrosynthesis, is the fact that this reaction is independent of the density of the current at the anode. This is clearly illustrated by FIGURE IV which shows that the potential and state of the anode are the factors which determine whether the reaction will or will not take place.

Now the influence of anode current density on the reaction is one of the main supports of the Discharged Ion Theory which supposes that, until the concentration of the discharged anions becomes large enough for them to react with each other, they react with the surrounding water, and the concentration of the discharged anions is obviously directly proportional to the density of the current at the anode. This theory is now only tenable if we accept the hypothesis advanced by NERNST and LE BLANC that each ion possesses a definite Discharging Potential. That is to say, in the experiments under consideration no trichloracetate ions are discharged until the anode acquires a certain definite potential.

Figure VIII.


90
80
70
60
50
40
30
20
10
(i) Polarising Current in Milliamps →
1·6
1·8
2·0
2·2
2·4
2·6
2·8
Anode Potential (V_H) in Volts →
2
1
0
log₁₀ i →

It may be remarked that if this theory be not accepted, the truth of the Oxidation Hypothesis is established, for then the only possible explanation of the non-formation of ester below 2.34 volts is that the oxidising power of the anode is not sufficient to bring about the reaction,- $2CCl_3COOH + O = CCl_3COOCCl_3 + CO_2 + H_2O$, at potentials below this value.

The problem, therefore, resolves itself into ascertaining whether there is any reason to believe that the discharging potential of the trichloracetate ion is in the neighbourhood of 2.35 volts. The only evidence of the discharging potentials of anions which is at present available for chemists is that furnished by "knickpunkts" in the curves showing the relation between current (or logarithm of current) and anode potential for indifferent anodes in a solution containing the ion in question. An examination of the curves obtained in these experiments, in particular the curves showing the relation between the logarithm of the current and the anode potential, reveals no evidence of a "knickpunkt" about 2.35 volts. This is especially well shown in the cases of anodes of gold and platinum on glass at which no disturbing processes, such as ester formation, took place. It is, therefore, concluded that the Discharging/

Discharging Potential of the trichloracetate ion does not lie near the point at which the formation of trichlormethyl trichloracetate begins.

Another interesting result of these experiments is the singular behaviour of platinum anodes evolving oxygen in a solution of trichloracetic acid. This phenomenon may readily be explained as follows.

Several authors(1) have attributed the polarisation E.M.F. of an anode to the accumulation therein of atomic oxygen. The anode overvoltages of the various metals may then be attributed to their powers of accelerating or retarding the reaction $O+O \rightarrow O_2$. In a metal of high overvoltage, this reaction is retarded and a large accumulation of active or atomic oxygen is produced. As molecular oxygen (O_2) is useless as far as oxidation is concerned, this hypothesis shows why anodes with high overvoltages possess great oxidising powers.

We therefore assume that platinum under the conditions/

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(1) BENNETT and THOMPSON, J.phys.chem. 20 300 (1916)
BANCROFT, Ibid. 376.
OSTWALD, Zeit.Elektrochem. 6 40 (1899).
LEWIS and JACKSON, Zeit.phys.chem. 56 207.

conditions of these experiments is capable of existing in at least two different states characterised as follows:-

STATE (α) A state of low oxidising power in which the metal accelerates the reaction $O + O \rightarrow O_2$.

STATE (β) A state of high oxidising power in which the metal retards the action $O + O \rightarrow O_2$.

When the platinum anode is polarised for many hours at a low potential, the metal is brought into State (α), so that when the applied E.M.F. is raised, the reaction, $O + O \rightarrow O_2$, is accelerated and comparatively low anode potential, high current, and brisk evolution of oxygen results. This is represented by the region 2.0-2.2 volts, see FIGURE IV. A. & B. When a potential slightly exceeding 2.2 volts is reached, state (α) becomes unstable and the platinum passes to state (β). The amount of oxygen being formed at the anode becomes too great for the reaction, $O + O \rightarrow O_2$, now retarded, to dispose of, and so the potential of the anode rises to a high value before equilibrium is reached. By being polarised for a short time at a high potential, the anode is brought into state (β) which remains metastable below 2.2 volts and so it is possible to obtain such a /

a curve as IVC. That the state (β) is only metastable at low potentials is shown by what may be termed the transition curve, IVB, and by the observation, already made, that the anode potential tends to fall and the current to rise while the applied E.M.F. is constant at potentials below 2.2 volts.

In the case of an anode of a film of platinum on glass, it appears that state (α) is extremely stable, and that anode potentials as high as 3 volts may be reached without transition to state (β) taking place at any appreciable rate. With platinised platinum also, the state (α) seems to be very stable, but PREUNER and LUDLAM (1) have drawn attention to the fact that when anodes of this material are used with heavy currents over a prolonged period, their potential rises and they pass to the polished or white variety, acquiring at the same time the power of oxidising acetic acid toethane. This would indicate that a slow transition from state (α) to state (β) takes place.

The erratic behaviour of the large anode is now to some extent explained; at 2.1 volts (III) a "knickpunkt" is observed; from 2.2-2. transition takes place, but the large size of the anode prevents too/

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(1) op. cit.

too great a rise of potential so that when the platinum has passed into a stable condition the current rises according to OHM'S Law.

To sum up, the foregoing experiments show that the reaction by which trichlormethyl trichloracetate is produced from trichloracetic acid is one of oxidation, and may be represented by the equation,

$$2\ CCl_3\ COOH + O\ =\ CCl_3COOCCl_3 + CO_2 + H_2O.$$

While the platinum anode is in the state(α)(low oxidising power) no ester is formed, no matter what may be the strength of current or anode potential. (Curves IVA and VIII), but as soon as the platinum anode passes to the state of high oxidising power and acquires a potential of 2.34-2.38 volts, sufficient energy is at hand to bring about the reaction formulated above.

DETERMINATION/

DETERMINATION of the AMOUNT of OXYGEN EVOLVED in UNIT TIME BEFORE and AFTER the POINT at which ESTER FORMATION BEGINS.

The conception of Discharging Potentials of ions advanced by NERNST, Le BLANC and their schools involves the following statement, "All of the ions in the solution take part in the conduction of the electric current but only those ions, the separation of which requires least expenditure of work or energy, are deposited or separated at the electrodes"(1). Let us assume, for the moment, that in spite of the evidence already given, the point at which ester formation begins, namely 2.34-2.38 volts, represents the discharging potential of the trichloracetate ion. Clearly, all oxygen evolved at the anode at lower potentials during the electrolysis of a solution of trichloracetic acid must result from the discharge of hydroxyl or oxygen ions. This is, therefore, a process requiring less expenditure of energy than the discharge of trichloracetate ions. At a potential just below the critical value the electrical energy is/

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(1) LE BLANC - Textbook of Electrochemistry - Trans. by Whitney and Brown - New York 1907. Page 303.

is sufficient to liberate a certain volume of oxygen per hour. When the critical potential is passed, trichloracetate ions are discharged but, as this is a process requiring more energy than the separation of oxygen, it will cause no diminution in the intensity of the discharge of OH or O ions but will merely be superimposed on this reaction, with the result that as much or more oxygen should be evolved per unit time above 2.35 volts as below it.

If, on the other hand, the point 2.35 volts marks the commencement of an oxidising action, it will be expected that less oxygen will be evolved in unit time after the critical point than before it, and, in fact, if the oxidation is complete, the gas evolved at potentials above 2.35 volts should be solely carbon dioxide.

EXPERIMENTAL.

The cell illustrated in FIGURE II (C) was used. A small current of 0.5 milliamps was passed through the electrolyte for 18 hours prior to the experiments so that the electrode might be completely polarised, and the electrolyte saturated with oxygen. The current was then adjusted so that the anode potential was just below 2.35 volts. The gas evolved was/

was collected and analysed. The anode potential and current were read every 5 minutes. Thereafter, the applied E.M.F. was raised until complete change in the appearance of the bubbles at the anode took place. The current was passed for some time in order to saturate the solution with carbon dioxide and to expel any oxygen therefrom. The current was read every five minutes while the sample of gas was being collected.

TABLE II. gives the average results from several experiments with normal and twice normal solutions of trichloracetic acid, and shows quite definitely that oxygen was used up in the process.

The conclusions previously made as to the mechanism of this reaction were therefore confirmed.

TABLE II.

	TIME of SAMPLE	AVERAGE CURRENT amps.	ANODE POTENTIAL.	OXYGEN.	CARBON DIOXIDE	AMP. HRS.	OXYGEN per amp. hr.	OXYGEN per HR.
$\frac{N}{1}$ CCl_3COOH	120mins.	0.014	2.13-2.17	5.7cc	0.2	0.028	203cc	2.8cc
	105 "	0.013	2.17-2.24	4.9cc	0.2	0.023	213cc.	2.8cc
	65 "	0.026	2.46-2.8	0.4cc	11.2	0.028	14cc.	0.4cc
	30 "	0.030	2.46-2.8	0.2cc	9.2	0.015	13cc.	0.4cc
2N CCl_3COOH	175 "	0.010	1.98	2.1cc	2.5	0.029	72cc.	0.8cc*
	40 "	0.018	2.5-2.8	0.2cc	6.8	0.012	17cc	0.3cc.

* Anode not previously polarised.

THE/

THE ELECTROLYSIS of a MIXTURE of GLACIAL ACETIC and SULPHURIC ACIDS.

MURRAY, as we have already mentioned, found that when a mixture of 10 per cent. acetic acid and 10 per cent. sulphuric acid was electrolysed no oxidation of the former acid took place. It was thought possible that the solutions employed by him might have been too dilute, so it was decided to electrolyse a mixture of glacial acetic acid with concentrated sulphuric acid and just sufficient water to render the mixture a fairly good conductor of electricity in order to ascertain:-

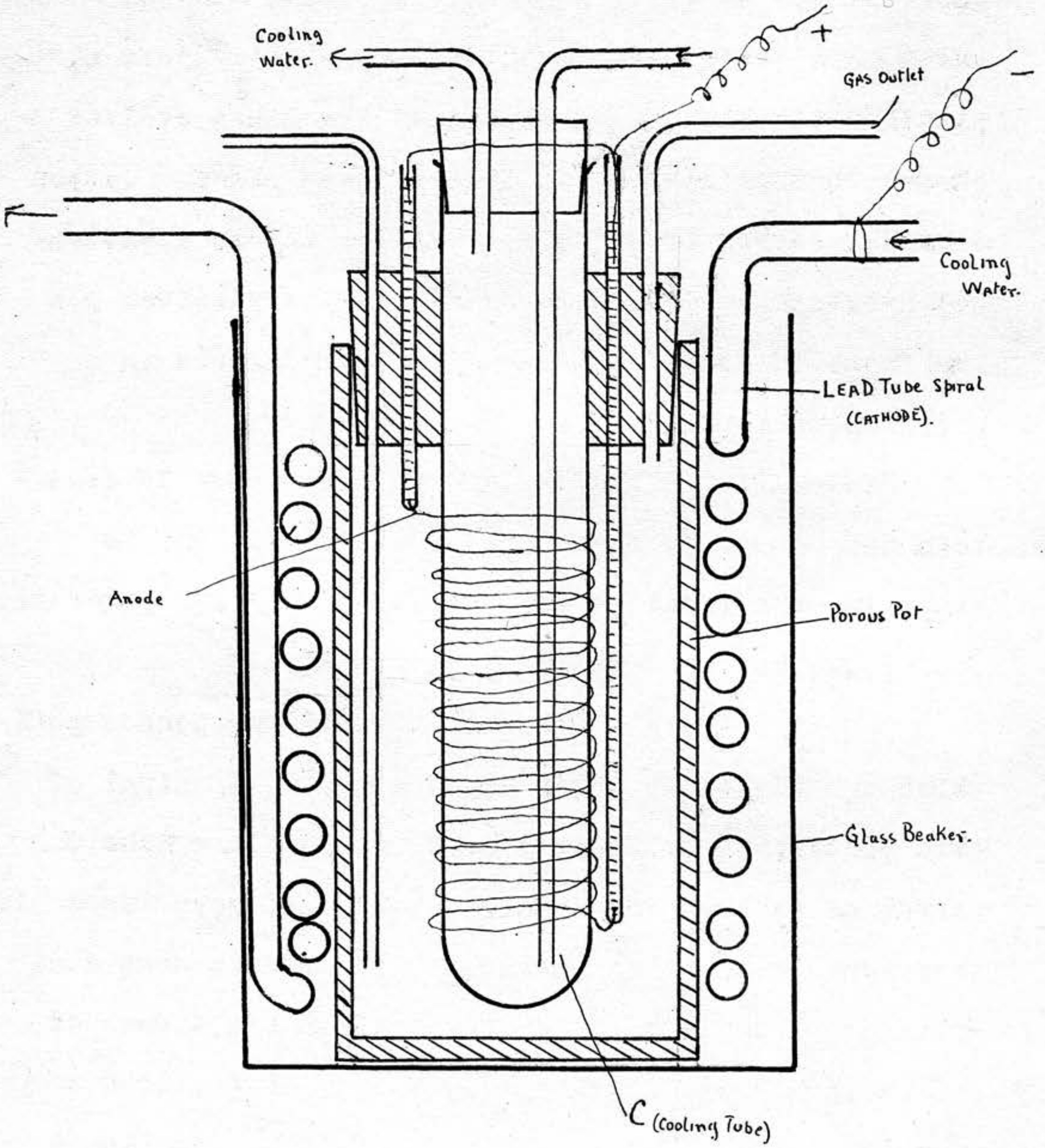
(1) Whether or not un-ionised acetic acid could be oxidised electrolytically,

(2) Whether such substances as ethane or methyl-alcohol might be produced by such an oxidation.

The possibility of reaction between discharged acetate ions was negligible in the experiments described in the following, as it was estimated that in the electrolyte the concentration of acetate ion was not more than 3×10^{-5} gram ions per litre.

PRELIMINARY/

Figure IX


Cooling Water.
+
Gas Outlet
-
Cooling Water.
LEAD Tube Spiral (CATHODE).
Anode
Porous Pot
Glass Beaker.
C (Cooling Tube)

PRELIMINARY EXPERIMENTS.

90cc. of glacial acetic acid were mixed with 10cc. of concentrated sulphuric acid and 8cc. of water, and the mixture submitted to electrolysis at platinum electrodes. Analysis of the gases evolved showed that oxidation had indeed taken place. Carbon dioxide, carbon monoxide and oxygen, but no unsaturated hydrocarbons, were detected and the residual gas was found to contain inflammable hydrocarbons in addition to hydrogen.

SYSTEMATIC EXPERIMENTS were performed to ascertain the nature of the hydrocarbons formed and to determine the relative amounts of the various products. The apparatus is illustrated in FIGURE IX.

The analyte was contained in the porous pot which was closed by a gas tight stopper, a spiral of thin platinum wire wrapped round the cooling tube C. served as anode. The ends of the spiral were fused into tubes containing mercury. The cathode consisted of a spiral of lead tubing through which a stream of cold water flowed and the cathode liquid was dilute sulphuric acid. The composition of the anode liquid was as follows:-

Glacial/

Glacial Acetic Acid - 106 grams.
Concentrated Sulphuric Acid - 27 "
Water 10 "

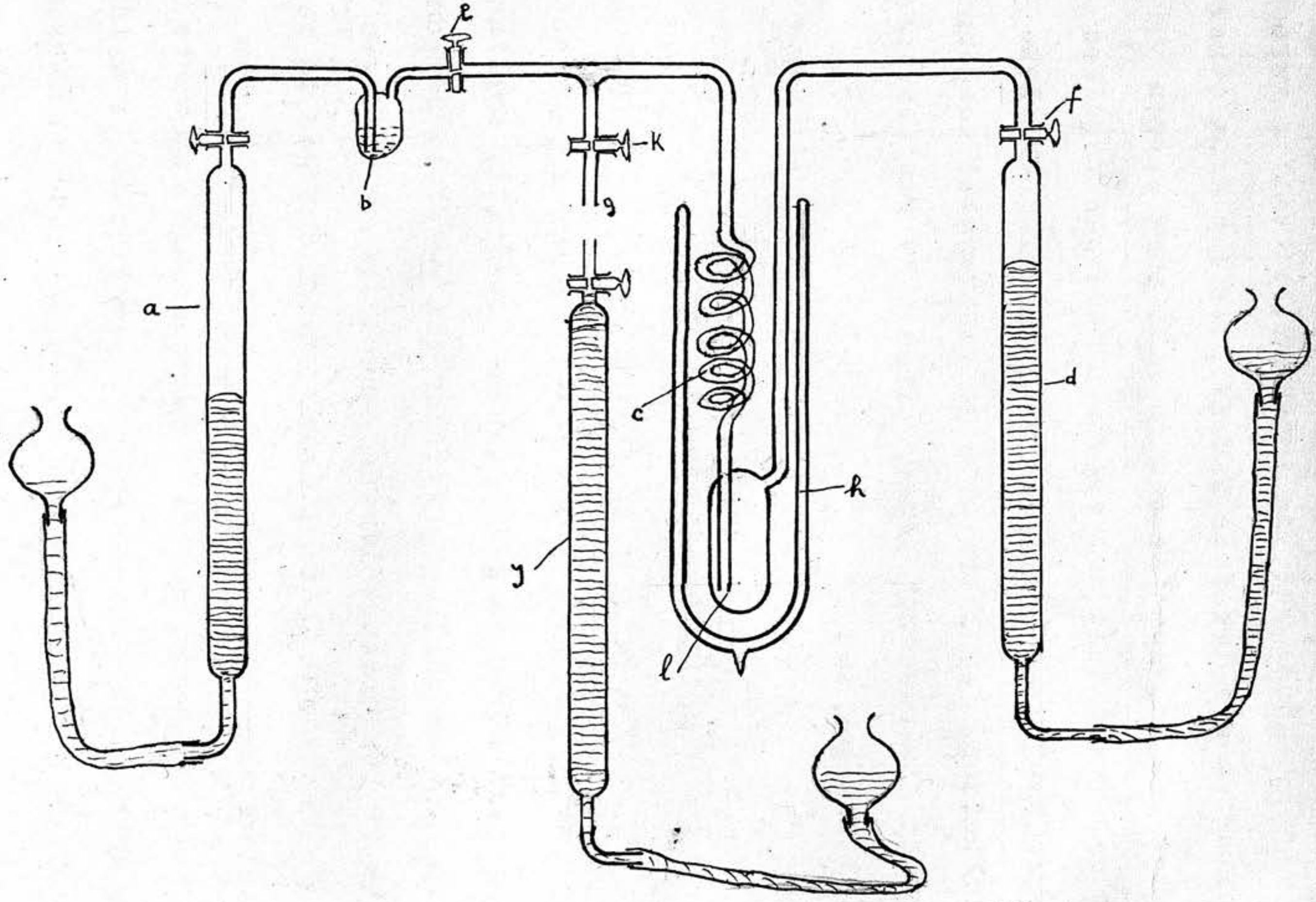
An anode current density of 2-3 amps. per sq. cm. was employed. Before each experiment all air was swept out of the anode compartment, either by allowing the electrolysis to proceed for some time prior to the collection of samples of gas, or, as in the cases where only the gases not carbon dioxide were wanted, by means of a stream of carbon dioxide. The anode gas was collected in a Hempel burette and analysed immediately. The volume of hydrogen evolved at the anode was calculated from the amount of electricity passed through the cell. The average results were:-

Volume of gas evolved at cathode = 170cc.

Total Volume of anode gas = 100cc. composed as follows:- Carbon Dioxide - 86cc; Carbon Monoxide - 8cc; Oxygen - 4cc; Inflammable Residue - 2cc.

EXAMINATION/

Figure X



EXAMINATION of the INFLAMMABLE RESIDUE.

120cc. of the inflammable residue were collected and freed as far as possible from other gases. A portion was burned with pure oxygen and it was found that one volume of the gas required approximately two volumes of oxygen for complete combustion. As there were no unsaturated compounds, carbon dioxide, nor oxygen present it was concluded that the gas was,

(a) Methane, or

(b) A mixture of ethane and hydrogen or ethane, methane and hydrogen.

The form of apparatus shown in FIGURE X was used to ascertain the gases present by a fractional distillation method which was specially applicable here, as the boiling points of the possible components of the mixture lay far apart, being Hydrogen --253°, Methane --150°, Ethane --90°. The gas to be examined was first contained over mercury in the vessel, (a), then passed slowly through (b) where it was dried with concentrated sulphuric acid, and into the spiral (C), where it was cooled; the condensed portion was retained in the reservoir (1), while the unliquefied part passed on and was collected in the burette/

burette (d). The difference between the volumes in (a) and (d) gave the volume of gas liquefied.

After all the gas had been cooled, the stopcocks (e) and (f), were closed, a burette filled with mercury was attached to (g) and the stopcock (K) opened. The temperature of the bath (h) was then raised to the required value and the gas distilling over was collected in the burette (y). All movements of the gas were made under pressure, that is, during the process of liquefaction the pressure in (d) was greater than one atmosphere, and that in (a) greater than that in (d). Similarly, the gas distilled under pressure into (y).

Of 91cc. of the gas, 87cc condensed in (l) at the temperature of liquid air and of this 83cc. distilled over into (y) under a pressure of 36 ins. of mercury at a temperature of -146°C. The remaining 4cc. were accounted for by the contraction of the gas in the apparatus according to Charles' Law. This showed conclusively that no appreciable amounts of hydrogen or ethane were present and that the gas was probably methane, which hypothesis was confirmed by the results of the combustion of the gas boiling below -146° given in Table III.

TABLE/

TABLE III.

SAMPLE.	1	2	3
Volume of gas burned.	11.1cc.	9.6cc.	10.8cc
Contraction after combustion and absorption of CO_2.	32.9cc.	28.2cc.	31.8cc
Volume of O_2 required.	21.8cc.	18.6cc	21.0cc
Therefore Volume of O_2 required for 100cc. gas	196 cc.	194 cc.	195 cc.
Volume of O_2 required for 100cc. methane.	200 cc.	200 cc.	200 cc.
Therefore Discrepancy per cent.	2	3	2.5

In order to determine whether any traces of ethane were present in the original inflammable residue, a portion which had not been treated in the cryogenic manner described above was burned with pure oxygen. The results indicated that no ethane was present.

Volume of oxygen reqd. for combustion of 100cc. gas = 194cc. Methane requires 200cc. The error of 3 per cent is the same as in the previous experiments.

EXAMINATION /

EXAMINATION of the RESIDUAL ELECTROLYTE.

The electrolyte, after electrolysis, was neutralised with a concentrated solution of caustic potash and distilled. The distillate was redistilled under a fractionating column, and the portion passing over below 100° was collected. This was tested for formaldehyde, with negative results, but it was found that considerable amounts of methyl alcohol were present. The whole of the last distillate was saturated with potassium carbonate when methyl alcohol separated as a layer on the surface of the aqueous solution. The upper layer of alcohol was introduced into a dry fractionation flask and distilled. The liquid boiled between 65° and 70°C confirming the supposition that it was methyl alcohol. About 0.5-1.0c.c. was obtained.

A further confirmation was obtained by the preparation of the methyl ester of m-nitrobenzoic acid from this alcohol by leaving it in contact with m-nitrobenzoic anhydride at 60° for several hours. A white crystalline solid melting at 75° was formed, methyl m-nitrobenzoate melts at 78°.

DISCUSSION of RESULTS.

These results show that acetic acid in the un-ionised state can be oxidised by oxygen developed electrolytically at a platinum anode and that by this oxidation at least one of the products regarded as characteristic of the electrolysis of potassium acetate, namely methyl alcohol, is formed. The very small amount of oxygen evolved at the anode shows that the oxidising action is very vigorous, and the small value of the ratio,

$$\frac{\text{Vol. Carbon Dioxide Evolved}}{\text{Vol. Hydrogen - 2 vol. Oxygen}}$$

which is 0.53, shows that most of the current is expended in destructive oxidising processes such as,

$$CH_3\ COOH+2O_2 \longrightarrow 2CO_2+2H_2O,$$

in which the value for this ratio is 0.5.

The fact that no ethane is produced in this electrolysis, while not affecting the general oxidation theory, renders rather improbable the hypothesis of FICHTER and KRUMMENACHER and others that ethane formation is due to the oxidation of acetic anhydride to acetyl peroxide, since, under the conditions existing in this experiment, the production of acetic anhydride is much more to be expected than in those experiments where large yields of ethane are obtained.

The/

The presence of methane among the reaction products recalls certain experiments performed by M.A. GORDON (1) on the action of sodium persulphate on acetic acid or acetates which led him to the conclusion that persulphates effect the catalytic decomposition of acetic acid according to the equation,

$$CH_3\,COOH = CO_2 + CH_4.$$

In the electrolysis under investigation the active part of the electrolyte was sulphuric acid in fairly concentrated solution and it is possible that a certain amount of persulphuric acid was produced at the anode. This acid would no doubt act on acetic acid in the same way as did sodium persulphate in the case already quoted.

THE/

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(1) loc. cit.

THE ELECTROLYSIS of a MIXTURE of SULPHURIC ACID and ACETIC ANHYDRIDE.

With a view to testing the truth of the statement of FICHTER and KRUMMENACHER that ethane is formed as the result of the oxidation of acetic anhydride by electrolytic oxygen, a mixture of sulphuric acid and acetic anhydride was submitted to electrolysis in the manner described in the previous experiment. The composition of the analyte was:-

Acetic Anhydride	100cc.
Sulphuric Acid	20 cc.
Water	5 cc.

The composition of the anode gas was found to be, Carbon dioxide - 87 per cent; Carbon monoxide - 3 per cent; Oxygen - 8per cent, Inflammable residue - 1.4 per cent. A quantity of the inflammable residue was collected, purified from the other gases, and burned, with the following results:-

100cc. gas required for complete combustion (a) 208, (b) 200cc. Oxygen, CH_4 requires 200cc.

It was therefore concluded that the gas was methane and that no trace of ethane was present. This experiment, therefore, would tend to show that ethane is not produced by the electrolytic oxidation of acetic anhydride.

CONCLUSION/

CONCLUSION and SUMMARY.

It has been shown in this paper that the work of previous investigators in the field of Electrosynthesis gives no evidence which directly contradicts the idea that it is an oxidation process as KOLBE himself imagined.

From experiments on the behaviour of current and anode potential, and the composition of the anode gases in the vicinity of the point at which electrosynthesis or the allied reaction, ester formation begins, direct evidence in favour of the Oxidation Theory and antagonistic to the Discharged Ion Theory has been obtained. Furthermore, it has been shown that non-ionised acetic acid may be oxidised electrolytically and that methyl alcohol occurs among the reaction products. Lastly, it has been found that, although acetic anhydride is vigorously oxidised at a platinum anode, no ethane is produced and this is taken as direct evidence against the theory, that Electrosynthesis involves the oxidation of acid anhydrides.

We are therefore justified in formulating the Electrosynthetic reactions after the manner first proposed by KOLBE as follows.

(1)/

(1) $2R.COOH+O = R.R+2CO_2+H_2O$

(2) $2R.COOH+O = R.COOR+CO_2+H_2O$

(3) $R.COOH+O = R.OH+CO_2$

(4) $CH_3CH_2COOH+O = CH_2:CH_2+CO_2+H_2O$.

It must be admitted that the foregoing equations are still somewhat vague, but they represent completely our present knowledge of the subject. There is, in our opinion, no reliable foundation for the assumptions that anhydrides, peroxides, per-acids, or other intermediate compounds are produced. In fact there is much evidence to the contrary. Before such theories can be accepted, entirely new experimental evidence as to the organic chemistry of these reactions must be supplied.

The formation of ethane by the electrolysis of potassium acetate is in reality a very special case of oxidation for it involves an oxidising agent possessed of the following properties.

(a) It is capable of developing very high oxidising powers,

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

(c) It is capable of creating and maintaining round itself a large concentration of the appropriate oxidisable material. (This is done by the attraction and discharge by the anode of acetate ions which thereafter react with water regenerating the acid).

It/

It has been shown that ordinary electrolytic oxidation of un-ionised acetic acid leads to the formation of methyl alcohol. This might well be regarded as the normal process while the production of ethane should be looked upon as the abnormal oxidation reaction. In this respect it is somewhat unfortunate that KOLBE'S discovery preceded that of HOFER and MOEST. We have shown, moreover, that any alteration in the external conditions, calculated to diminish the actual concentration of acet~~ate~~ic ~~ions~~ acid at the anode, tends to reduce the yield of ethane and promote the normal oxidising actions involving one molecule of acid and one atom of oxygen. The very limited zone of oxidation of a platinum anode explains why easily oxidisable, non-ionised, substances such as alcohols or aldehydes appear among the end products. They are in a sense crowded out of the oxidising zone as soon as formed and there is no force which tends to attract them back again.

These considerations show that the Oxidation Theory is capable of offering a simple and complete explanation of the various processes occurring during the electrolysis of the salts of organic acids and presents a key to the solution of what have in the past been regarded as mysterious anode phenomena.