#### ANODE PHENOMENA IN THE ELECTROLYSIS OF POTASSIUM ACETATE SOLUTIONS. PART II. DISCHARGE POTENTIAL OF THE ACETATE ION.

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In 1898 Bose<sup>1</sup> found that the decomposition potential of a 3.5 N aqueous solution of potassium acetate between smooth platinum electrodes was 2.05 volts. Preuner and Ludlam<sup>2</sup> measured the potential difference at a platinum anode during the electrolysis of a 0.5 N solution of potassium acetate (0.5 N also with respect to added acetic acid), and found a break in the current-potential curve not at 2.05 volts but at 2.54 volts. Thev also showed that at this potential ethane began to be evolved amongst the anodic gases, while the percentage of oxygen began to diminish. Fairweather and Walker<sup>3</sup> confirmed the existence of a definite potential for the formation of ethane in the electrolysis of a N solution of potassium acetate, but found the value to be about 2.15 volts. It has been generally assumed that Preuner and Ludlam's potential of 2.54 volts represents the "discharge potential" of the acetate ion at a smooth platinum electrode, though it has been pointed out by Gibson<sup>4</sup> that the evolution of ethane at this potential might also mean that at 2.54 volts the anode has acquired an oxidising potential high enough to allow the reaction to proceed. It is possible, however, to ascribe the evolution of oxygen below this potential to the primary discharge of acetanions followed by a secondary reaction of the discharged ions with water. For the present, therefore, we shall refer to this "discharge potential" as the "critical" potential for the formation of ethane, without making any assumptions as to its actual meaning.

Preuner and Ludlam's value, while it has been generally accepted as being correct, is much higher than that of other investigators, and makes the "discharge" potential of the acetate ion abnormally high in comparison with that of other anions. It was decided to make a more detailed study of the effect of concentration of acetate and of temperature on the value of the potential. Moreover, it was shown recently by the present authors<sup>5</sup> that at low-current densities methane is also evolved along with ethane at the anode, and in investigating the conditions most favourable for the formation of methane the effect of varying anode potential is also of interest. The objects of this investigation were therefore :---

(1) To determine the "critical" potential for the formation of ethane during the electrolysis of aqueous potassium acetate solutions of varying concentration and at different temperatures.

(2) To see whether this potential is also a critical potential for the formation of methane which takes place along with that of ethane.

The determination of the critical potential was carried out by two methods, following the procedure of Preuner and Ludlam. Firstly, measurements were made of the current strength and of the anode potential during the electrolysis, and the resulting values plotted on a

 <sup>&</sup>lt;sup>1</sup> Bose, Electrochem., 5, 153, 1898.
<sup>2</sup> Z. physikal. Chem., 59, 682
<sup>3</sup> J.C.S., 3111, 1926; see also Walker, J.C.S., 2040, 1928 (footnote).
<sup>4</sup> Proc. Roy. Soc., Edin., 44, 140, 1924; see also J.C.S., 127, 475, 1925.
<sup>5</sup> Trans. Far. Soc., 27, 35, 1931, referred to in text as Part I. <sup>2</sup> Z. physikal. Chem., 59, 682, 1907.

current density-anode potential graph. The critical potential is indicated by a break or point of inflexion on the curve. Secondly, samples of the anode gases were collected at different anode potentials and the particular potential found at which ethane is first evolved. In many cases the gas samples were obtained during electrolyses in which the anode potential was measured directly as in the first method, but it was found to be more convenient, when the relationship between current density and anode potential had been determined for a given concentration of electrolyte, simply to collect the gas at a definite current density, from which the anode potential could be obtained. The values of critical potential found by both of these ways coincided in nearly every case, and this can be taken therefore as a good example of a case where a break in the current potential curve does mark the commencement of a new reaction at the As will be seen from the current density-anode potential curves, anode. and more readily from the log C.D.-anode potential curves, the break in the curve does not consist of a sudden sharp rise in the current density at a given potential, but rather of a small region in which the rate of increase of anode potential with current density becomes more rapid.

## Experimental.

**Apparatus.**—The electrolyses were carried out in an H-shaped glass vessel, similar to that described by Gibson, in which the anode and cathode gases were collected in different compartments separated from one another by a thick plug of glass-wool. The anode consisted of a smooth platinum wire, 4'4 cm. long and o'1 cm. in diameter, and the cathode was a thin foil of platinum of 2 sq. cm. surface area. A glass tube containing the same solution as the electrolysis vessel was pressed close up to the wire anode and connected through a solution of normal KCl to a normal calomel electrode, so that measurements were made of the *P.D.* of the cell

# + Pt. | $CH_3COOK$ sol. | N KCl | $HgCl_2$ , N KCl | Hg –

of which the mercury is the negative electrode. By adding 0.283 volts, the potential difference between the anode and the solution (the anode potential, A.P.) on the hydrogen scale is obtained. All the values in the tables refer to this scale. No correction was made for liquid junction potentials, which are of the order of 0.01 volts when calculated by the formula of Lewis and Sargent.

A variable E.M.F. was applied across the terminals of the electrolysis vessel and successive readings of the polarising current and anode potential taken, time being allowed for these to become constant after every increase of the applied E.M.F. In the preliminary experiments the solution was stirred during the anode potential measurements, but it was found that sufficiently reproducible results could be obtained with the stirring produced by the gases evolved-additional stirring simply has the effect of slightly lowering the anode potential for a given current density. The first measurements were carried out at room temperature, which varied throughout the course of the whole work between 10° and 20° C., but was fairly constant during any single experiment. However, in order to obtain more uniform curves and in order to study the effect of temperature variation, measurements were also made in which the electrolysis vessel was placed in a thermostat at temperatures of  $5^{\circ} \pm 1^{\circ}$ ;  $20^{\circ} \pm 0.1^{\circ}$ ;  $35^{\circ} \pm 0.1^{\circ}$  and  $50 \pm 0.1^{\circ}$ respectively. Except where otherwise stated the solutions of potassium acetate contained an equivalent amount of added acetic acid to prevent the solution becoming alkaline during the course of the electrolysis.

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## Relation between Current Density and Anode Potential.

The values of current density and anode potential for solutions of potassium acetate of various concentrations at room temperature are plotted in Fig. 1. From these it will be seen that the current begins to rise rapidly at potentials between  $2 \cdot 0$  and  $2 \cdot 3$  volts and that on the whole the steepness of the curves decreases with increasing concentration of the electrolyte. In the case of the N/5 solution there is a noticeable break or point of inflexion in the curve at about  $2 \cdot 2$  volts, which is not very apparent on the other curves. If, however, the log of current density is plotted against the A.P. as has been done in Fig. 1a, the existence of a change in the slope of the straight line at about  $2 \cdot 15$  volts is noticeable in almost every case. These



experiments were performed at room temperature and not at a definite constant temperature. In the curves obtained from the experiments carried out in the thermostat, the existence of a break at  $2\cdot 1-2\cdot 2$  volts is very marked, as will be seen from Fig. 2 and particularly from Fig. 2a, in which the values for N potassium acetate at various constant temperatures are plotted. They contain also the curves for the 2N solution at  $5^{\circ}$ . The breaks in the logarithmic curves consist of a decrease in the slope of the straight line within a small range of anode potential, the slope then resuming its original value. Within this small potential range the anode potential increases much more rapidly with increasing current density. Up to the

critical potential, *i.e.*, the potential at which the slope of the logarithmic curve changes, the relationship between the current density I and anode potential P is of the form,

$$P = a + b \log (I + c),$$

where a, b, and c are constants. Logarithmic relationships of this type have been found to hold for the evolution of hydrogen at certain cathodes and of oxygen at platinum anodes.<sup>6</sup> For two cases in which a large series of

Conc.	Temp.	Current Density Millamp.	Anode Potential	Percentage of				Ratio CH₄
of Electrolyte.	°C.	(per sq. cm.).	(volts).	CO <sub>2</sub> .	O <sub>2</sub> .	СН4.	C <sub>2</sub> H <sub>6</sub> .	$\overline{C_2H_6}$
{   0°2 N	10-20	3.61 4.33 5.05 5.78 7.22	2.09 2.11 2.12 2.13 2.15	2·5 2·8 33·7 50·5 49·2	93°5 92°4 41°0 12°5 4°3	0 2.6 3.0 3.3	0 0 15•9 27•8 36•8	0.00 0.11 0.10
{	5	0.25 0.30 1.50 1.81 3.61	2·19 2·24 2·26 2·30 2·33	16·3 47·5 56·9 58·5 55·8	72'4 4'2 1'3 1'4 1'2	0 11•5 6•4 6•4 3•5	0 31·1 31·3 30·0 34·9	0'37 0'21 0'21 0'10
$\left\{  \textbf{r} \cdot \textbf{o} \ N \right.$	20	1•44 1•81 3•б1	2·13 2·19 2·25	20•0 53•6 53•3	70'0 5'8 1'7	0 14.2 5.2	0 19·3 35·7	0.75 0.15
{ I'O N	35	1.81 3.61 5.05	2*04 2*11 2*20	13.8 40.5 57.9	80.7 53.1 7.4	0 0 8•3	0 0 17•6	  0'47
$\left\{  \text{i`o } N \right.$	50	10·82 11·55 18·05	2.12 2.16 2.23	32•7 73·8 75·4	55 <sup>.8</sup> 2 <sup>.1</sup> 1.5	0 6·2 3·7	0 13.6 14.1	0°45 0°26
2.0 N	50	1·44 3·61 5·05 7·22	1'94 2'03 2'11 2'15	27°9 57°0 74°0 74°1	65°4 37°2 2°1 1°4	0 0 8·3 8·4	0 0 11.8 12.6	
{ 3.5 N	20	0°18 0°36 1°44	1·98 2·04 2·22	40°5 46°1 61°8	42.6 1.5 1.1	0 32·8 23·5	0 9*3 8*6	
{ 3.5 N	50	0.72 1.44 1.81	1·89 1·95 1·98	62·9 68·9 80·2	32·3 23·3 1·3	0 0 0	0 0 5'7	 1.77

TABLE I.

measurements are available in the region of C.D., during which oxygen is evolved, *viz.* (1) for the N/10 solution at room temperature and (2) for the N solution at 50° the relationship holds almost exactly. The actual values of *a*, *b*, and *c* in these two cases are: (1) 1.922, 0.217, and 0.460, and (2) 1.870, 0.223, and 0.121, respectively. The maximum difference between observed and calculated values of the anode potential is 0.01 volt, but the difference is in general very much less, about 0.002-0.005 volt.

Glasstone, "The Electrochemistry of Solutions," page 381, 1931.

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The values of the critical potential to the nearest o or volt determined as the potential in the log C.D./A.P. curve at which the slope of the line changes, have been tabulated in Table II. These potentials are indicated

	Current Density	Anode	Percer	Ratio	
Conc. of Electrolyte.	Milliamp. (per sq. cm.).	(Volts).	СН4.	C <sub>2</sub> H <sub>6</sub> .	$CH_4/C_2H_6.$
$\begin{cases} 0.5 N \\ \text{(room temp.)} \end{cases}$	2·88 3·61 4·33 5·05	2·15 2·19 2·23 2·27	0 0 9*0 7*7	0 0 34*2 35*9	 0'26 0'22
$\begin{cases} 1 \cdot 0 \ N \\ \text{(room temp.)} \end{cases}$	0'72 1'44 2'17 3'61	2.07 2.15 2.23 2.26	0 0 17.7 7.7	0 0 23•6 32·9	0.75 0.23

TABLE IA.

on the curves by an arrow. In the case of the 3.5 N solution at  $20^{\circ}$  and  $50^{\circ}$  there was no definite critical potential on the curve. Before comparing these results with those obtained by the gas analysis method, the details of the latter method will be described.

## Relation between Anode Potential and Composition of Anode Gases.

Samples of the gas evolved at the anode while the anode potential was kept constant at various values on either side of the critical potential were analysed for the following constituents: carbon dioxide, oxygen, carbon

		Critical Potentials.			
Concentration of Electrolyte.	Temperature °C.	Graphical Method.	Gas Analysis Method.		
0'2 N	About 20	2.10	2.11		
0*5 N	,,	2.10	2'21		
1.0 N	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	2.12	2.10		
3.5 N	,,	2.00	-		
1.0 N	5	2.12	2.31		
,,	20	2.13	2.10		
**	35	2.10	2.10		
,,	50	2'12	2'14		
2•0 N	50	2.07	2.07		
3.5 N	20		2'01		
**	50		1.96		
	Average	2'12	2°16 (neglecting last two values)		

TABLE II.

monoxide, methane and ethane. The analyses were carried out by means of a Bone and Wheeler apparatus with mercury as the confining liquid, and the separation of methane from ethane was effected by means of liquid

air as already described by us.<sup>7</sup> The results of various experiments are shown in Table I., in which, to save space, only the percentages of carbon dioxide, oxygen, ethane and methane are given, since they illustrate the course of the main anodic reactions. The residue consisted of small amounts of carbon monoxide and of nitrogen from dissolved air. Table IA. contains some of the results of the previous paper (Part I.), for which anode potential measurements are now available, and therefore only the percentages of ethane and methane are reproduced.

From the results of Tables I. and IA. the critical potential, *i.e.*, the potential at which evolution of ethane commences, has been calculated and the values are tabulated, along with the values obtained by the graphical method, in Table II. The critical potential has been taken as the mean of the last measured potential at which no ethane is evolved and the first measured potential at which ethane is formed, *e.g.*, in the case of the N solution at 20° no ethane is evolved at 2°13 volts, and 19°3 per cent. of ethane was found at 2°19 volts. The evolution of ethane must commence somewhere between these two potentials and therefore the mean of the two values, *viz.* 2°16 volts may be taken as the most accurate value of the critical potential.

## Critical Potential for the Formation of Ethane.

In Table II. the values of the critical potential determined by the two methods are compared. It will be seen that the values obtained by both methods agree very well and that for very widely differing conditions of temperature and concentration of acetate there is very little variation in the potential at which ethane commences to be formed. The average value is 2.14 volts and is therefore considerably lower than Preuner and Ludlam's value of 2.54 volts. The variation from the mean value is seldom as large as o'r volt. Preuner and Ludlam, using the Nernst logarithmic expression, calculated the potential for a solution normal with respect to acetate ions, from their value of 2.54 volts obtained with a solution half normal with respect to both acetate and acetic acid, and obtained a value of 2.26 volts. From our results it is seen that in the concentration range 0.2 to 2.0 Nthere is very little variation in the critical potential. If this potential be assumed to be the discharge potential of the acetanions and to follow the Nernst concentration expression, no appreciable variation within this range is to be expected since a tenfold increase in the concentration, even assuming complete dissociation of the acetate, will decrease the discharge potential by about 0.06 volt only. With concentrations from  $2 \circ N$ upwards, however, there does appear to be a definite decrease of the potential, in agreement with the results of Fairweather and Walker,<sup>3</sup> who found that for 3, 4 and 5 normal solutions ethane formation takes place at lower anode potentials the more concentrated the solution. It is also seen that variation of the temperature does not greatly influence the potential at which evolution of ethane commences. As the temperature is increased, there is a small lowering of the critical potential, which is more marked in the more concentrated solutions.

## Interpretation of the Critical Potential.

It has thus been established that at a smooth platinum anode a break in the current potential curve and the commencement of ethane evolution both occur at a potential of 2.14 volts, and that this potential is only

<sup>7</sup> Walker and Shukla, J.C.S., 368, 1931; see also Fart I.

slightly influenced by the temperature and by the concentration of acetate in the solution. At this anode potential a new reaction evidently begins to take place and the potential may be explained in three ways:

(1) Potential at which the reaction,

2

$$_{2}CH_{3}COOH + O = C_{2}H_{6} + _{2}CO_{2} + H_{2}O$$
 . . (1)

commences.

(2) Discharge potential of the acetanions.

(3) Potential at which discharged acetate ions cease to react with water and commence to react with one another.

The first interpretation has generally been favoured by the supporters of the oxidation theory of Kolbe's reaction, but this view is in our opinion open to certain objections (see Part I.). Preuner and Ludlam adopted the second view and considered it to be evidence for the discharged anion theory that evolution of ethane does not commence till a definite potential is reached. Their value of 2.54 volts has been generally given in the literature and text-books as the discharge or decomposition potential of the acetate ion. If this view is correct the evolution of oxygen below the critical potential must be ascribed to the discharge of hydroxyl or oxygen ions. There is, however, no conclusive evidence for this assumption, which is also open to criticism (see Part I.), and it seems just as probable that below the critical potential acetate ions are being discharged, and that the change in the anode reaction consists merely in the change from

to

$$CH_{3}COO + H_{2}O = 2CH_{3}COOH + O . . (2)$$
  
$$2CH_{3}COO = C_{3}H_{6} + 2CO_{3} . . . (3)$$

In fact the nature of the break in the current-potential curve might be taken to support this view, since it does not consist of a sudden rise in the current such as occurs in the discharge of a new ion species at a definite potential, e.g. in the cathodic discharge of metallic ions. A definite decision as to the meaning of the critical potential is not possible, however, and all one can say is that at that potential, whether it is a true discharge potential or not, a new reaction occurs. The results described do show, however, that the primary factor in determining the commencement of the anodic process is the anode potential, and not the particular value of the current density which is only of secondary importance. For example in the concentration range 0.2 to 2.0 N between 5° and 50° ethane evolution may commence at current densities between 0.9 and 11.6 milliamperes per sq. cm., depending on the particular conditions, whereas the anode potential at which the ethane reaction begins is constant at about 2.14 volts. It is possible that the anode potential corresponds to a definite concentration of discharged ions at the anode surface, and that not until this concentration of discharged ions is reached can they react together to form ethane. A large concentration of acetate in the solution, and low temperature both favour the formation of ethane, and that is because both these factors have the effect of increasing the anode potential for a given current density. Increase in current density after the critical potential has been reached will still further increase the anode potential and therefore increase the yield of ethane (cf. Fairweather and Walker, loc. cit.3, page 3114).

#### Formation of Methane.

So far only the formation of ethane has been considered, but the experiments described in this paper also provide further information re-

garding the production of methane. The most convenient method of comparing the various experiments is to examine the ratio of methane to ethane. The results of Table I. confirm the observations previously made that the first appearance of methane in the anode gases occurs along with that of ethane, and it may now be said that both these hydrocarbons commence to be formed at the same critical potential of 2.14 volts, at which the amount of oxygen evolved drops to a small percentage. Whereas, however, the amount of ethane formed above this anode potential increases with increasing current density until it reaches a maximum value of about 90 per cent. of that theoretically possible,<sup>3</sup> the amount of methane appears to be at a maximum at the point where it is first formed and rapidly decreases with increasing current density, as is clearly seen from Tables I. In the results given in Part I.,5 the highest value of the and IA. methane/ethane ratio was 1.89. In the further experiments of Table I. values as high as 3.5 have been obtained. The following series of electrolyses at low current densities of a 3.5 N solution at about 10° illustrate even more clearly the decrease of the  $CH_4/C_2H_6$  ratio with increasing current density (Table III.).

TABLE III.

	Conc. of	Current Density in		Ratio			
Electrolyte.		(Milliamp. per sq. cm.).	CO <sub>2</sub> .	O <sub>2</sub> .	СН4.	C <sub>2</sub> H <sub>6</sub> .	CH <sub>4</sub> /C <sub>2</sub> H <sub>6</sub> .
<u> </u>	3'5 <i>N</i> (about 10° C)	0'18 0'29 0'72 1'44 2'17 3'6 7'22 10'82	35.6 33.8 55.0 53.0 73.0 66.9 70.0 64.7	1'2 2'6 0'5 0'8 0'2 0'9 0'7 1'8	41.5 46.1 32.2 29.8 15.8 16.8 4.1 2.2	9'8 9'4 7'9 9'9 8'6 11'5 21'1 27'6	4'3 4'9 4'1 3'0 1'84 1'45 0'19 0'08
{	9.9 N (about 10° C)	0'72 1'81	0 0'3	1.2 0	65*8 12*3	22'0 79'2	2 <b>.</b> 99 0.16

In order to see whether the ratio methane/ethane could be still further increased by increasing the acetate concentration a 9.9 N solution of potassium acetate (without added acetic acid) was electrolysed using a large platinum foil anode (14 sq. cm. surface area, waxed on one side) so that even smaller current densities might be used. The results are given in Table III. At a current density of 0.07 milliamps. per sq. cm. only three times as much methane as ethane was obtained, but the solution was appreciably alkaline through hydrolysis in this case, as is seen from the absence of carbon dioxide. It appears, therefore, from all the experiments made that the ratio methane/ethane has a maximum value at the critical potential, the maximum being greater the higher the concentration of the The effect of acetate concentration is best seen by comparing solution. values of the ratio taken from Table I. at the lowest current density in each case at which hydrocarbons are formed, *i.e.*, at a potential just slightly higher than the critical potential:

Conc. of sol.		•		$0^{\cdot}2 N$	0.5 N	$1 \cdot 0 N$	3.5 N
A.P				2.110	2.10-2.53	2.23	2.04
CH₄/C₂H <sub>6</sub>	٠	•	•	<b>0</b> .10	0'41-0'26	0.72	3*5-4*9

## THE EFFECT OF PHOSPHORUS VAPOUR

#### Conclusion and Summary.

The conditions for the formation of ethane and methane at a smooth platinum anode during the electrolysis of aqueous potassium acetate solutions have been more closely defined as a result of the experiments described in this paper. The results may be summarised as follows :---

(1) Below an anode potential of  $2 \cdot 14$  volts oxygen and carbon dioxide are the main gaseous products, and no hydrocarbons are evolved.

(2) At the critical potential of 2.14 volts methane and ethane commence to be formed along with a larger amount of carbon dioxide, and the proportion of oxygen begins to decrease rapidly. There is not sufficient evidence to show whether this critical potential represents a true discharge potential of the acetanion.

(3) For concentrations of acetate below 2° N the critical potential is independent of concentration, but with more concentrated solutions the value decreases. The critical potential decreases slightly with increase of temperature.

(4) At the critical potential the ratio methane to ethane is at a maximum, and then decreases rapidly with increasing current density, so that methane is formed only within a limited range of current density. The maximum value of methane/ethane increases with the concentration of acetate. With a 3.5 N solution under the most favourable conditions a value of nearly 5:t was obtained.

Of particular interest is the question of how the methane is formed. Certain possibilities were indicated in Part I., but a more detailed discussion of the problem will be held over until the conclusion of some further experiments now in progress on the influence of dissolved substances and of the solvent on the formation of methane.

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