ELECTROCHEMICAL STUDIES IN MOLTEN PHOSPHATES

by

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ABSTRACT

Although metaphosphates have been used extensively as solvents in electrochemistry, work on the electrolysis of the phosphates has given variable results. It has been shown (2,11) that in the electroreduction of the phosphate ion, phosphorus is produced but Lucas (16) in his work on electrolysis of sodium metaphosphate in molten lithium chloride-potassium chloride concluded that the electrode reactions were extremely complex.

In the present work the overall electrode products were confirmed and it was established that sodium metaphosphate was a cationic conductor (23). The electro-reduction of phosphates was then examined by voltammetry and chronopotentiometry in the molten metaphosphate and as solutions in molten lithium chloride-potassium chloride and sodium chloride-potassium chloride over the temperature range 400°-800°C. Three electroactive species reduced at potentials more anodic than the solvent, were found by chronopotentiometry; these were identified as the orthophosphate, the pyrophosphate and tripolyphosphate ions. The reduction potentials were about -0.7V, -1.1V and -1.5V respectively, using a large graphite pot as a non-polarisable anode.

It is known that molten phosphates, as with silicates and borates form mixtures of polymeric oxyanions. The compositions of the phosphates have been determined by hydrolysis of quenched glasses followed by paper chromatography (32,33, 37). Electro-

analytical techniques indicate a larger amount of the lower polymers in the melt than was found in the glasses, and this has been explained by depolymerisation at high temperatures. At current densities below 0.2A.cm.$^{-2}$ complete dissociation to the orthophosphate can occur and it is this ion which is electro-reduced to phosphorus. The following reaction mechanism has been postulated:

(1) Depolymerisation giving PO_4^{3-}

(2) Electro-reduction $PO_4^{3-} + 2e = PO_2^{-} + 2O^{2-}$

(3) Redox reaction $5\ PO_2^{-} + 2O^{2-} = 2P + 3PO_4^{3-}$

Overall from (2) and (3)

(4) $$PO_4^{3-} + 5e = P + 4O^{2-}$$

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1. INTRODUCTION

1.1. Phosphates in Electrochemistry

Molten sodium metaphosphate was first electrolysed in 1931 by Centnerszwer and Szper (1). The overall products were quoted as phosphorus and trisodium orthophosphate at the cathode and oxygen at the anode. It was assumed that sodium as the primary cathodic product reacted to give the final products. Yocom (2) whilst using sodium metaphosphate to produce phosphides examined the cathodic process by radio-active tracer techniques and indicated that sodium metal was not produced.

Phosphate-halide-oxide mixtures have been used by Andrieux (3, 4) and Yocom (2) to produce phosphides of transition metals. With tungstic oxide it is possible to produce the metal (5, 6). Francis (7) found that phosphates were of limited use for metal production as the decomposition potential range was small.

The solvent properties of phosphates have been used in determining the decomposition potentials of metal oxides (8), in concentration cells (9) and in polarographic studies (10, 11).

The behaviour of phosphates in molten solvents has been examined. Shams El Din (12, 13) has carried out potentiometric titrations in nitrate and chloride melts; Mitchell (14) considered the ortho-pyrophosphate equilibrium in bromide solutions, whilst chronopotentiometry in lithium chloride-potassium chloride eutectic has been used by Senderoff (15) and Lucas (16).

1.2. Composition of Melts

The phosphates can be considered as condensation products of metal oxides and phosphorus pentoxide based on phosphorus with sp^3 bond structure. Van Wazer (17) specifies molten phosphates as the combination of certain structural units as follows:

PO_4^{3-}	ortho	$O^- - \underset{\displaystyle O^-}{\overset{\displaystyle O}{\overset{\displaystyle \vert}{\underset{\displaystyle \vert}{P}}}} - O^-$
$PO_{3.5}^{2-}$	end group	$- O - \underset{\displaystyle O^-}{\overset{\displaystyle O}{\overset{\displaystyle \vert}{\underset{\displaystyle \vert}{P}}}} - O^-$
PO_3^-	middle group	$- O - \underset{\displaystyle O^-}{\overset{\displaystyle O}{\overset{\displaystyle \vert}{\underset{\displaystyle \vert}{P}}}} - O -$
$PO_{2.5}$	branching group	$- O - \underset{\displaystyle O}{\overset{\displaystyle O}{\overset{\displaystyle \vert}{\underset{\displaystyle \vert}{P}}}} - O -$

Additional units to be considered are $P_2O_7^{4-}$ pyro - from 2 end groups.

O^{2-}	unreacted oxide

These structural groups can react with each other to reform according to the following equilibria:-

$$2\ PO_3^- = PO_{2.5} + PO_{3.5}^{2-} \quad (1.1)$$

$$2\ PO_{3.5}^{2-} = PO_3^- + PO_4^{3-} \quad (1.2)$$

$$2\ PO_4^{3-} = 2PO_{3.5}^{2-} + O^{2-} \quad (1.3)$$

Sodium phosphate melts can be considered as large polymeric oxyanions and mobile cations. This tends to produce the minimum number of structural units, to avoid variations in counter ion concentration (17). Hence the equilibrium in the above reactions is well over to the left.

Depending upon the ratio (R) of M_2O/P_2O_5, two main types of polymeric structure can be postulated; chain phosphates $M_{n+2}P_nO_{3n+1}$ made up of a number of middle groups and two end groups; ring phosphates $M_nP_nO_{3n}$ for R = 1, of which sodium tri-metaphosphate is an example $(NaPO_3)_3$. It can be seen that as n increases the chain and ring structures become similar and tri-metaphosphate melts are such an equilibrium. Phosphates with ratios below unity can be formulated; these ultraphosphates tend to have high phosphorus pentoxide vapour pressures and readily absorb water.

All the types of phosphates can be included in the general formula $M_{nR}P_nO_{\frac{n(5+R)}{2}}$ (for R between 0 and 3). The average chain length $\bar{n}$ for linear polymers can be estimated from the formula

$$\bar{n} = \frac{2}{R-1} \qquad (1.4)$$

1.3 Electrolysis of molten phosphates.

The overall products obtained from the electrolysis of both meta and pyro phosphates have been verified as phosphorus at the cathode and oxygen at the anode (2, 11).

Although the phosphate melts would be expected to act as cationic conductors in keeping with other polyoxyanionic melts e.g. silicates and borates (18), the high cathodic potential required for alkali metal ion reduction is not reached. The electrolytic reduction and oxidation of the appropriate "PO_4" group can thus be considered at both electrodes.

(a) Metaphosphates

Anode (1) $PO_3^- = \frac{1}{2}P_2O_5 + \frac{1}{2}O^{2-}$

(2) $\frac{1}{2}O^{2-} = \frac{1}{4}O_2(g) + e$

$$PO_3^- = \tfrac{1}{2}P_2O_5 + \tfrac{1}{4}O_2(g) + e \qquad (1.5)$$

This is equivalent of chain branching and oxidation of the oxide to give the oxygen gas.

Cathode $PO_3^- + 5e = P + 3O^{2-}$ (1.6)

(b) Pyrophosphates

Anode (1) $PO_{3.5}^{2-} = \frac{1}{2}P_2O_5 + O^{2-}$

(2) $O^{2-} = \frac{1}{2}O_2(g) + 2e$

$$PO_{3.5}^{2-} = \tfrac{1}{2}P_2O_5 + \tfrac{1}{2}O_2(g) + 2e \qquad (1.7)$$

$$\text{Cathode} \quad PO_{3.5}^{2-} + 5e = P + 3.5O^{2-} \qquad (1.8)$$

The phosphorus pentoxide and oxide formed at the electrodes would react with the molten phosphate in accordance with reactions (1.1) and (1.3) above. This would lead to the orthophosphate found as a cathode product (2, 16).

Work on the cathode reactions showed a major discrepancy. Yocom (2) and Caton and Freund (11) were not able to proceed beyond a decomposition potential of approximately -1V, whereas Andreeva (8) and Francis et alia (7) obtained two decomposition potentials; the first occurred with phosphorus evolution, whilst the second was assumed to be the production of sodium. The limiting current could be caused by a finite concentration of reducible ion in the main phosphate melt. It was therefore decided to investigate,

(1) the overall electrode reactions,

(2) the occurrence of a limiting current at the cathode,

(3) the species reacting at the cathode

(4) the electrode reactions at the cathode.

Initial experiments in the phosphate melts were to be implemented by work on dilute solutions of the phosphates in suitable solvents.

2. COULOMETRY UNDER ATMOSPHERIC CONDITIONS

The overall electrode reactions were examined using an open vertical furnace to facilitate observation of the products. Having confirmed that phosphorus was evolved at the cathode and oxygen at the anode, the concentration variations around the electrodes were used to determine the amount of current carried by the cation.

2.1. Apparatus

2.1.1. Furnace

A 12 in. long vertical tube furnace was constructed by winding nichrome wire on a 3 i.d. silica tube. It was wound in 3 zones and gave an overall resistance of ca 15 ohm. A load of 400 watt was sufficient to raise the temperature from cold to 700°C in four hours. The temperature was kept constant to within $\pm$ 5°C over the bottom 4 in.

2.1.2. Cell and Electrode Materials

Molten phosphates are extremely corrosive attacking many metals and refractories. However, at 700°C, pure alumina crucibles can be used for many hours without serious attack.

Platinum is a suitable electrode material as long as phosphorus is not produced. Rapid disintegration occurs if the decomposition potential of the phosphate is exceeded. This is probably due to the formation of a low melting eutectic between the platinum and the platinum phosphide (19). Tungsten rod of 1 mm. dia. is a suitable cathode, but the anodic oxidation

allows solution of tungsten oxide.

In the experiments carried out on transport measurements, the anolyte and catholyte were kept in separate alumina containers joined by a salt bridge, Fig. 1. It was found that a melt impregnated porous U-shaped alumino-silicate brick could be successfully employed for a number of runs, whilst asbestos string disintegrated in a few minutes. A platinum anode and tungsten cathode were used.

2.2. Procedure

Anhydrous sodium trimetaphosphate, supplied by Albright & Wilson (Oldbury) was used as the electrolyte. The alumina pots, each containing about 3 g. of the phosphate, were placed on a brick support in the furnace and the bridge lowered into position. The temperature in the furnace measured by a chromel-alumel thermocouple placed near the pots, was raised to 700°C and maintained for at least an hour before lowering the electrodes into the melt. Electrolysis was continued for approximately three hours; at an applied e.m.f. of 4V, taken from 2, 2V accumulators a current of about 35 mA was obtained. Milliammeter readings were taken every fifteen minutes during electrolysis and the total charge estimated graphically. The current remained constant within 2-3 mA during a run and an external coulometer was not used. After an electrolysis run, the bridge and electrodes were first removed. The alumina pots were then taken out of the furnace separately and the melts

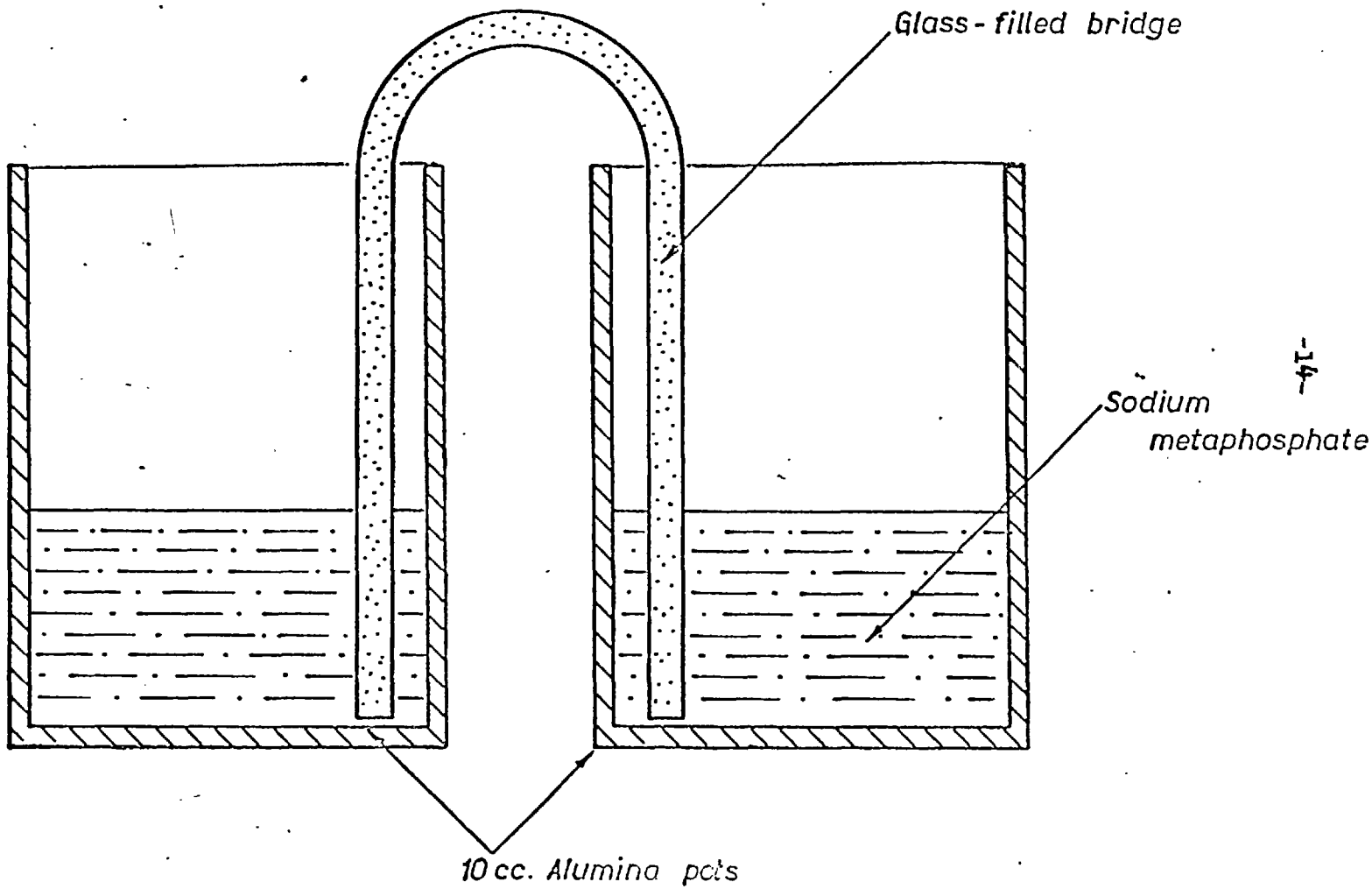


FIG. 1 ELECTROLYSIS CELL

poured on to aluminium sheets.

2.2.1. Electrode reactions

For a passage of one Faraday, the electrode reactions in terms of sodium metaphosphate are:-

$$\text{Anode } NaPO_3 = Na^+ + \tfrac{1}{2}P_2O_5 + \tfrac{1}{4}O_2(g) + e \qquad (2.1)$$

$$\text{Cathode } {}^1/_5\ NaPO_3 + e = {}^1/_5 P + {}^3/_5 O^{2-} + \tfrac{1}{5}Na^+ \qquad (2.2)$$

If the phosphate is considered as a completely cationic conductor the overall reaction will be

$${}^6/_5\ NaPO_3 = (\tfrac{1}{2}\ P_2O_5 + \tfrac{1}{4}O_2(g)) + ({}^3/_5\ Na_2O + {}^1/_5\ P) \qquad (2.3)$$

Anolyte Catholyte

The changes in the Na/P ratios (R) of the anolyte and catholyte glasses on electrolysis can therefore be related to the movement of sodium ions from the anolyte to the catholyte and the volatilisation of the phosphorus produced at the cathode.

2.2.2. Analysis of phosphate glasses

The Na/P ratio of phosphate glasses can be accurately determined by hydrolysis of small samples using 0.1N sulphuric acid. This method used by Holmes, Jeffes et alia (20) was modified by a pH titration rather than use of indicators.

100 mg. of the electrolyte glasses were taken together with 10 cc. of 0.1N sulphuric acid, and placed in a small flask fitted with a reflux condenser.

Duplicate samples were heated on a water bath for 16 hours. The resultant orthophosphoric acid was titrated using 0.1N caustic soda.

The total number of "PO_4" units can be obtained from the alkali required between pH4 and pH9 i.e. NaH_2PO_4 to Na_2HPO_4.

If alkali equivalent to pH4 = T_1

alkali equivalent to pH9 = T_2

$$R = Na/P = \frac{10 - T_1 + T_2}{T_2} \qquad (2.4)$$

A typical titration curve is shown in Fig. 2. The differential curve was used to determine the end points T_1 and T_2.

2.3. Results.

Based on the above electrode reactions if a and c are moles of metaphosphate in anolyte and catholyte respectively before electrolysis and n the number of Faradays of electricity passed during the run, then R values should become $\frac{a - n}{a}$ and $\frac{c + n}{c - 0.2n}$ respectively. In a typical electrolysis, 144 mA.hr. of electricity were passed through a cell which initially contained 2.50 g. of anolyte and 2.57 g. of catholyte. The resultant R values were 1.1 and 1.8 for the anode and cathode glasses respectively compared with the calculated values of 0.8 and 1.3 respectively. Since this indicated loss of phosphorus from the electrolyte the possibility of phosphorus pentoxide loss at the anode was examined. Gases from the cathode had shown the presence of this gas, which was taken as confirmation of phosphorus production followed by oxidation. No phosphorus

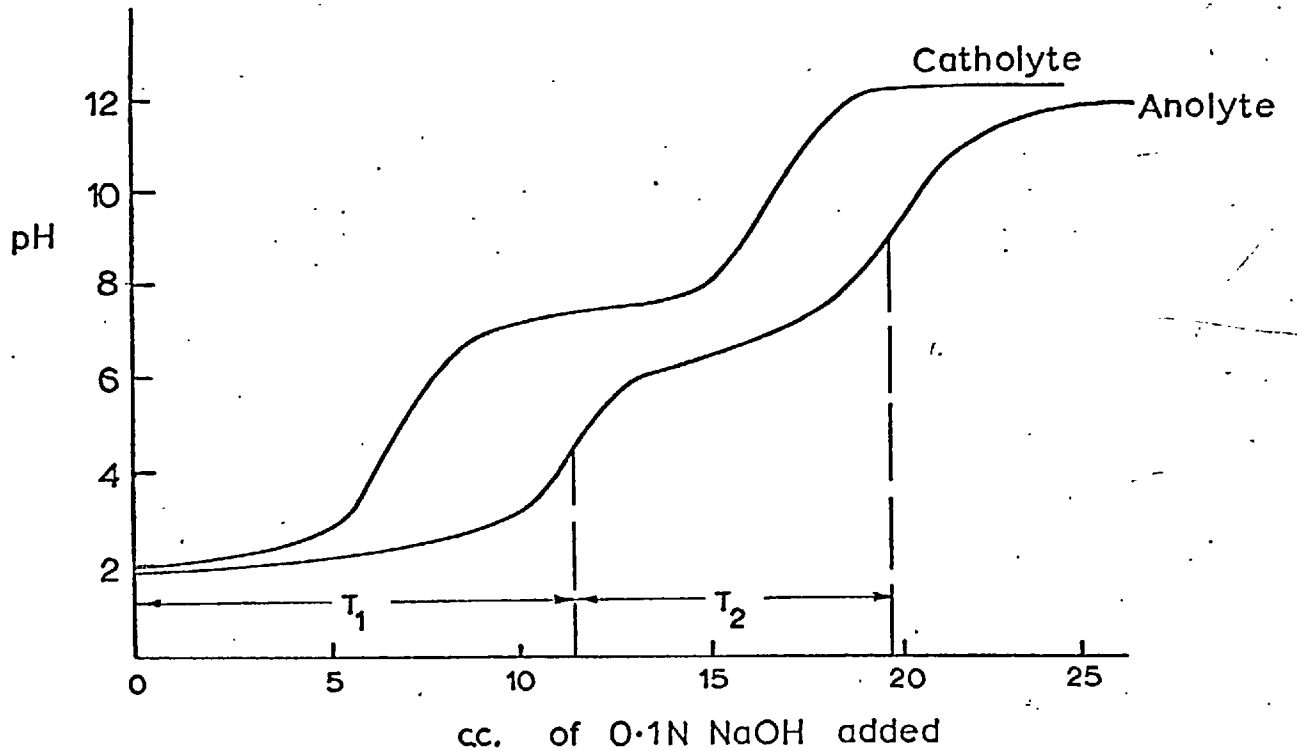


FIG. 2 TYPICAL TITRATION CURVE FOR HYDROLYSED GLASS

pentoxide could be detected in the anode gases.

2.3.1. Reaction between sodium metaphosphate and alumina

In the hydrolysis of the electrolysed glasses it had been noted that some precipitation occurred. The titration results were unaffected by the presence of this precipitate, which disappeared under markedly alkaline conditions. Examination of the precipitate indicated the presence of aluminium and phosphate only. Some attack on the alumina crucibles at the three-phase boundary had already been noted and the weight of alumina removed was then determined.

Mellor (21) mentions the existence of a number of aluminium phosphates and the following reaction between alumina and sodium trimetaphosphate can be postulated:

$$Al_2O_3 + Na_3P_3O_9 = Al_2O_3.xP_2O_5 + xNa_3PO_4$$

This is the equivalent to the removal of 2x g atoms of phosphorus per mole of alumina.

If m_a moles of alumina are lost from the anode pot and m_c moles from the cathode pot, then the R values should be amended to

$$\frac{a - n}{a - 2m_a x} \quad \text{for the anolyte}$$

$$\text{and } \frac{c + n}{c - 0.2n - 2m_c x} \quad \text{for the catholyte}$$

The aluminium phosphates are equivalent to the x values shown.

aluminium orthophosphate $AlPO_4 = Al_2O_3 \cdot P_2O_5$

aluminium pyrophosphate $Al_4(P_2O_7)_3 = Al_2O_3 \cdot 1\frac{1}{2}P_2O_5$

aluminium metaphosphate $Al(PO_3)_3 = Al_2O_3 \cdot 3P_2O_5$

A 2g sample of electrolysed glass was hydrolysed and the precipitate was analysed quantitatively for aluminium by the 8-hydroxyquinoline method (22). The result (12.wt. per cent aluminium) gave an x-value of 2.4. The technique of precipitation is difficult and very dependent on pH; it was assumed that $Al_2O_3 \cdot 2P_2O_5$ was formed, which would correspond to 14 wt. per cent of aluminium.

Possible reactions between alumina and the glass in presence of the electrodes and bridge materials were examined by heating the glasses under various conditions without electrolysis for three hours at 750°C.

The results are shown in Table 1.

TABLE I

Composition of Phosphate Glasses Heated in Alumina Pots without Electrolysis

Addition to pot	Weight of glass (g)	Alumina loss (g)	R by analysis	Calculated x
Nil	2.047	0.200	1.25	1.02
Platinum electrode	2.036	0.195	1.26	1.08
Tungsten electrode	2.079	0.167	1.47	1.96
Aluminosilicate	2.033	0.173	1.25	1.18

It would seem that the normal reaction between alumina and metaphosphate melts is the formation of the orthophosphate. The electrolysis and the presence of tungsten tends to promote the formation of $Al_2O_3.2P_2O_5$. These aluminium phosphates are soluble in the glass but precipitate on hydrolysis.

2.3.2. Transport measurements in molten sodium metaphosphate (23)

Assuming the formation of $Al_2O_3.2P_2O_5$ during the electrolysis, the phosphorus loss gives R values of $\frac{a - n}{a - 4m_a}$ for the anolyte and $\frac{c + n}{c - 0.2n - 4m_c}$ for the catholyte as shown above. From these values, a calculated "n" value can be determined from the analysis of the electrolysed glasses and determination of R. This calculated "n" can be considered as nt^+, where n Faradays are passed and t^+ is the transport number of the sodium ion. Table 2 gives the results of a number of electrolysis runs.

For one run a platinum crucible was used as the anolyte container, shown by (Pt). The low value of t^+ may have resulted from the electrochemical oxidation of the platinum and subsequent reaction with the melt which is equivalent to some phosphorus removal. During the run 54 mg. of platinum were lost.

TABLE 2

Analysis of anode and cathode glasses after electrolysis

Faradays passed $n.10^3$	Moles of glass $a.10^3$	Moles of alumina lost $m_a.10^3$	R	$nt^+.10^3$	t^+
Anolyte					
3.60	29.4	1.37	1.09	3.4	0.95
5.39	39.7	1.96	1.14	5.1	0.95
6.25	29.0	1.55	1.00	6.2	0.99
5.38	25.5	1.76	1.10	5.2	0.97
2.84(Pt)	31.7	-	0.92	2.5	0.90
Catholyte					
$n.10^3$	$c.10^3$	$m_c.10^3$			
3.60	30.7	1.86	1.52	3.5	0.97
5.39	31.3	2.33	1.74	5.0	0.93
6.25	31.6	2.05	1.72	6.3	1.01
5.38	25.2	1.86	1.83	5.4	1.00
2.84	25.9	0.74	1.28	2.1	0.96

These results confirm the cationic conduction in sodium metaphosphate melts and indicate that the above electrode reactions can be considered as 100 per cent efficient.

3. VOLTAMMETRY IN MOLTEN PHOSPHATES

3.1. Apparatus

The melt was contained in a dense graphite pot manufactured from Morganite Carbon EY9; this was also used as a non-polarisable electrode. The working electrode was either a 3mm. dia. dense graphite rod enclosed in boron nitride or 1 mm. dia. tungsten rod insulated with alumina. The assembly was placed inside a 55 mm. i.d. silica tube closed by a silicone rubber bung and through which argon was passed (Fig. 3).

A Fanell 350V stabilised voltage supply in series with a Cambridge variable resistance box of 10,000 ohm maximum was used to charge the electrode and the charging current read on a milliammeter. The voltage between the micro-electrode and pot was determined on a Radiometer pH Meter; it was also displayed on a Tetronix 545B Oscilloscope.

3.2. Decomposition potentials

Decomposition potentials were determined for sodium metaphosphate under dry argon to avoid the effects of air and moisture. The working electrode was the 3 mm. dia. graphite and the voltage determined against a reference electrode of Ag/Ag(I) shown in Fig. 4. The 0.01 M solution of $AgPO_3$ was produced by anodic dissolution of silver in sodium metaphosphate. When the graphite pot was used as a reference, values approximately 0.3V more cathodic were obtained. A typical curve is shown in Fig. 5.

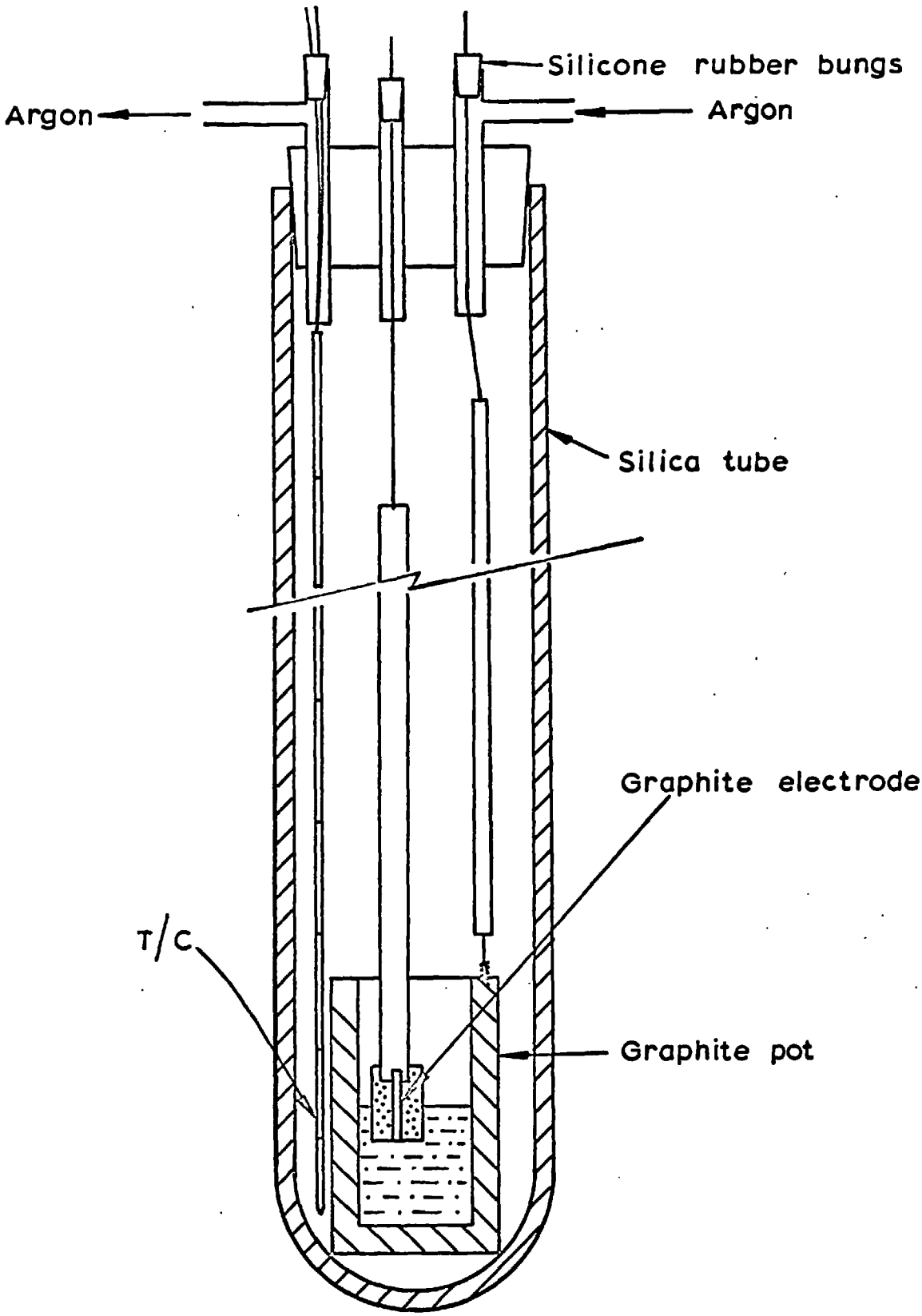


Fig. 3 ELECTROLYSIS CELL

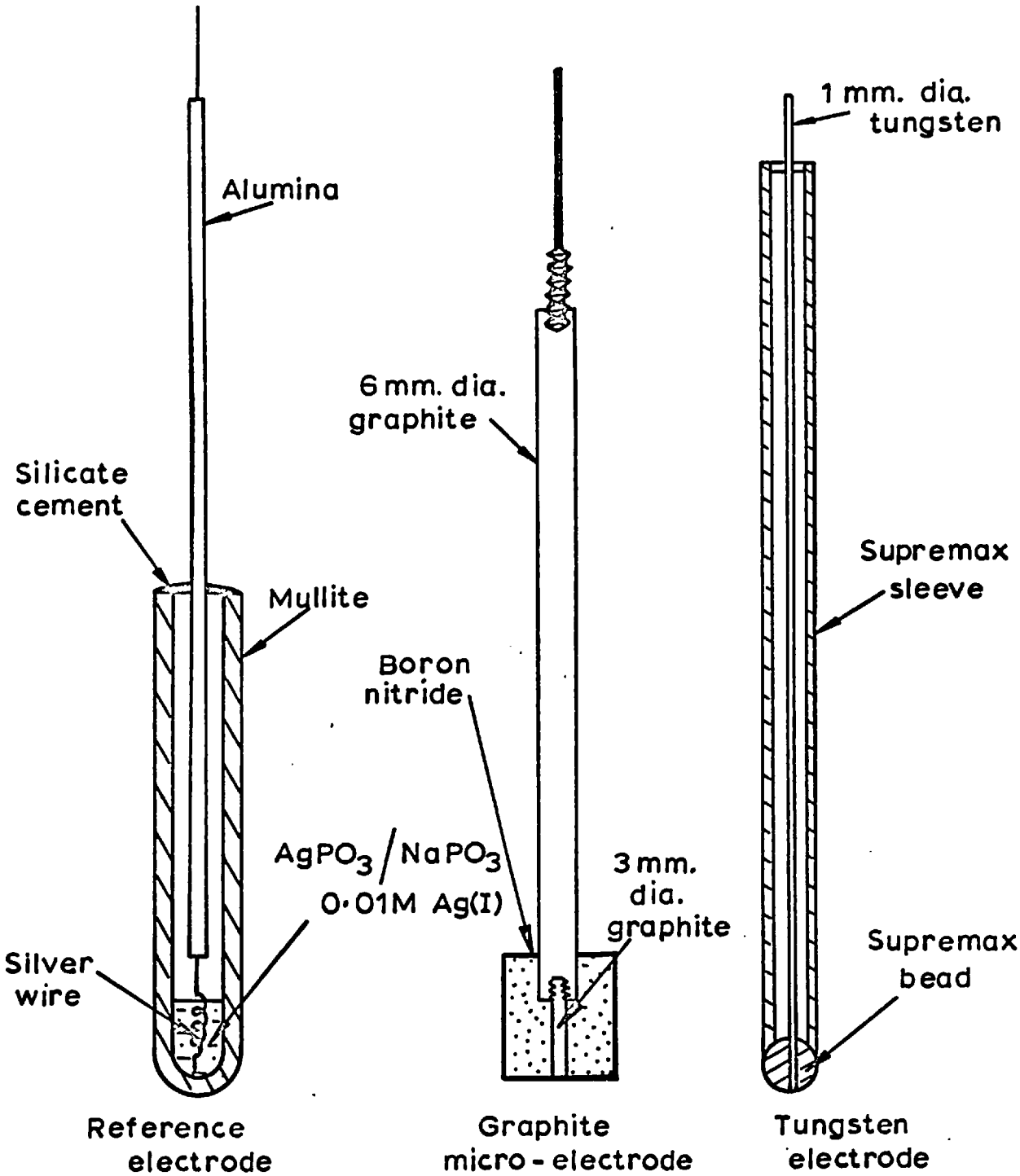


Fig. 4. ELECTRODE ASSEMBLIES

The effect of temperature changes was determined and results are shown in Table 3.

TABLE 3

Variation of Cathodic Decomposition Potential with Temperature - Ag/Ag(I) reference

Temp °C	Decomposition Potential Volts
810	- 0.43
775	- 0.45
750	- 0.46
710	- 0.47
690	- 0.48

This result of 50 mV per 120°C or 0.4mV/°C compares with the 50mV obtained between 820° and 930°C by Francis (7) and $\frac{dE}{dT}$ of 4×10^{-4} V/°C quoted by Andreeva (8) for sodium pyrophosphate.

The potential span between the anode and cathode electrode processes was about 1.1V which is the same as that obtained by Yocom (2).

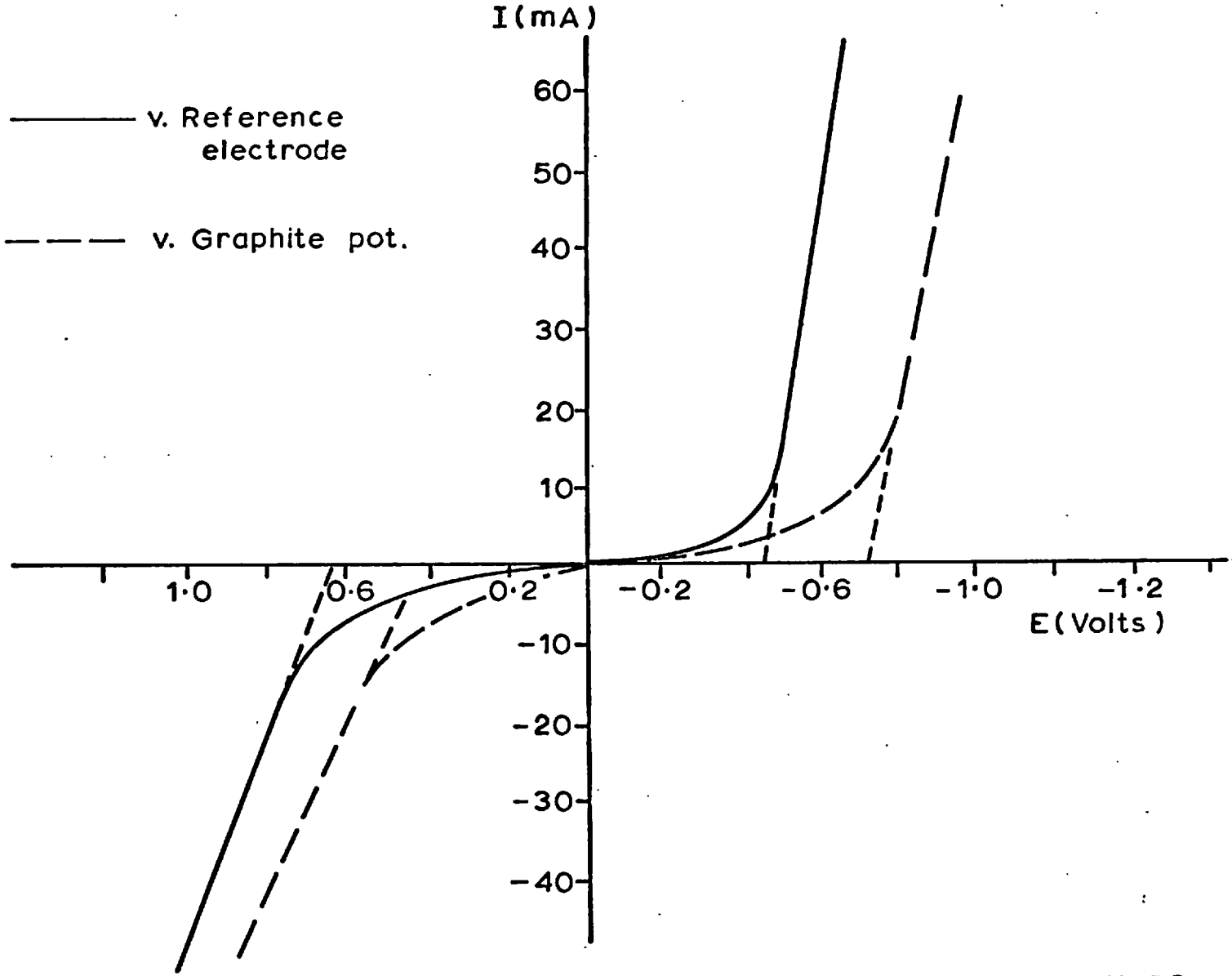


Fig.5. DECOMPOSITION POTENTIALS FOR MOLTEN $NaPO_3$ AT 750°C

3.3. Limiting Current Determinations

In their experiments on sodium production in metaphosphate melts Yocom (2) had used current densities of 0.26 amp/cm.^{2} at 850°C and Caten and Freund (11) 0.25 amp/cm.^{2} without any second decomposition. However, Francis (7) had employed increasing current densities up to a value of 3 amp./cm.^{2} at 820°C. The cathodic reaction was initially examined at 700°C, using the 3 mm. dia. graphite electrode against the graphite pot. The rising part of the curve occurred from about 3mA i.e. 0.07 amp./cm.^{2} and this corresponded to the current density at which burning of the phosphorus was seen to occur under atmospheric conditions. On increasing the current to 20mA cyclic variations of 0.2 - 0.3V occurred and a mean value was taken. These cyclic variations of equilibrium potential values continued over the current range 20 mA - 30mA; corresponding to a potential range of approximately -1.2V to -1.8V. At 35 mA the electrode potential rose to above -2V and remained steady. Further increases of current gave a steady increase in steady-state potential, as shown on the oscilloscope. When this was repeated for a new melt at about 730°C the value of current for the second process was 65mA.

To avoid the high current, the 3 mm. dia. graphite electrode was replaced by a 1 mm. dia. tungsten rod which was just allowed to touch the melt surface. Again it was possible to

obtain a second decomposition and polarograms for temperatures of 660-810°C are shown in Fig. 6. From the E-I curves it was possible to estimate the diffusion current i_d at varying temperatures. Results are given in Table 4.

TABLE 4

Diffusion currents in Molten sodium metaphosphate

Temperature °C	Diffusion current - i_d amp. cm^{-2}
660	0.20
690	0.35
710	0.45
750	0.70
810	1.20

3.4 Decay curves

The potential reached by the electrode for any charging current I is made up of the reversible electrode potential E_o and overpotentials caused by the ohmic resistance of the melt together with the activation and diffusion potentials for the electrode process. In this system the ohmic potential or IR drop is the largest. Hickling (24) showed that if a measurement of potential could be made very shortly after the switching off the polarising current, a value for E_o could be obtained.

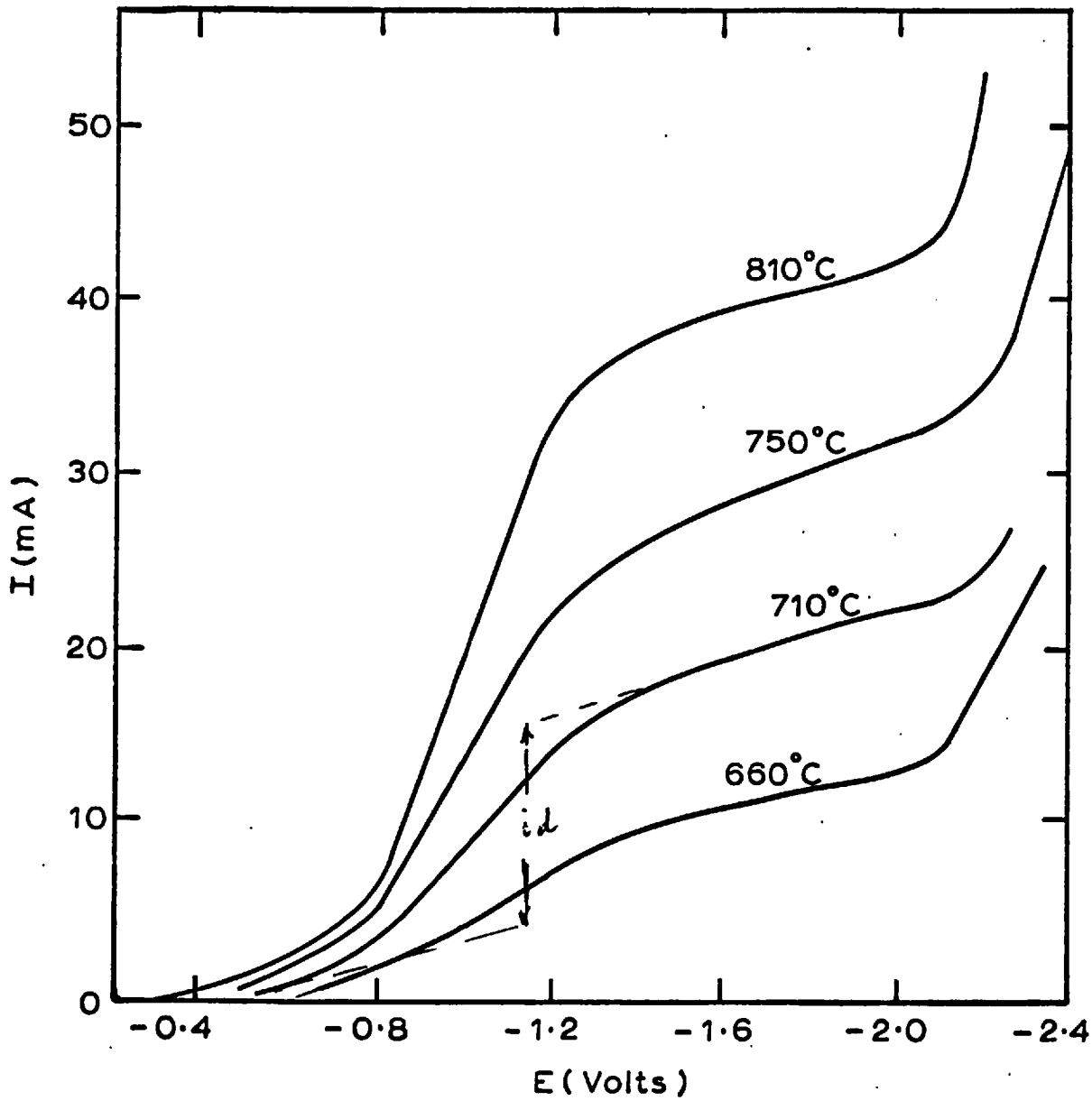


Fig. 6. E-I CURVES FOR MOLTEN $NaPO_3$ - TUNGSTEN CATHODE v. GRAPHITE POT.

Francis (7) used this method to determine decomposition potentials in molten phosphates.

Using the oscilloscope as a voltmeter, it was possible to examine the decay of electrode potential, at different charging currents, when the current was switched off. Typical open circuit cuves are shown in Fig. 7 for currents above and below the i_d values. When values of larger than i_d were used two processes could be detected at about 0.8V apart. The lower one corresponded to the first decomposition potential, but the more cathodic did not correspond to the -2V for the second decomposition potential. However, as was shown in Section 3.3., the steady state potentials between -1.2V to -1.8V were subject to cyclic variations. It would seem that the process occurring at -1.6V had been obscured by these variations in voltage.

3.5 Electrode Products

The cathode products at-0.7V to the graphite pot had been examined during the coulometry experiments (Section 2). Decay curves had indicated that electrode products diffuse into the bulk melt, since the electrode potential reaches initial values after leaving for some minutes. In examining products at -2V the current was increased until a steady potential of -2 to -3V was seen on the oscilloscope and the charging current maintained for periods up to 60 min. The open circuit conditions were then obtained by withdrawing the tungsten electrode rapidly well above the melt and allowing the assembly to cool under argon. It was

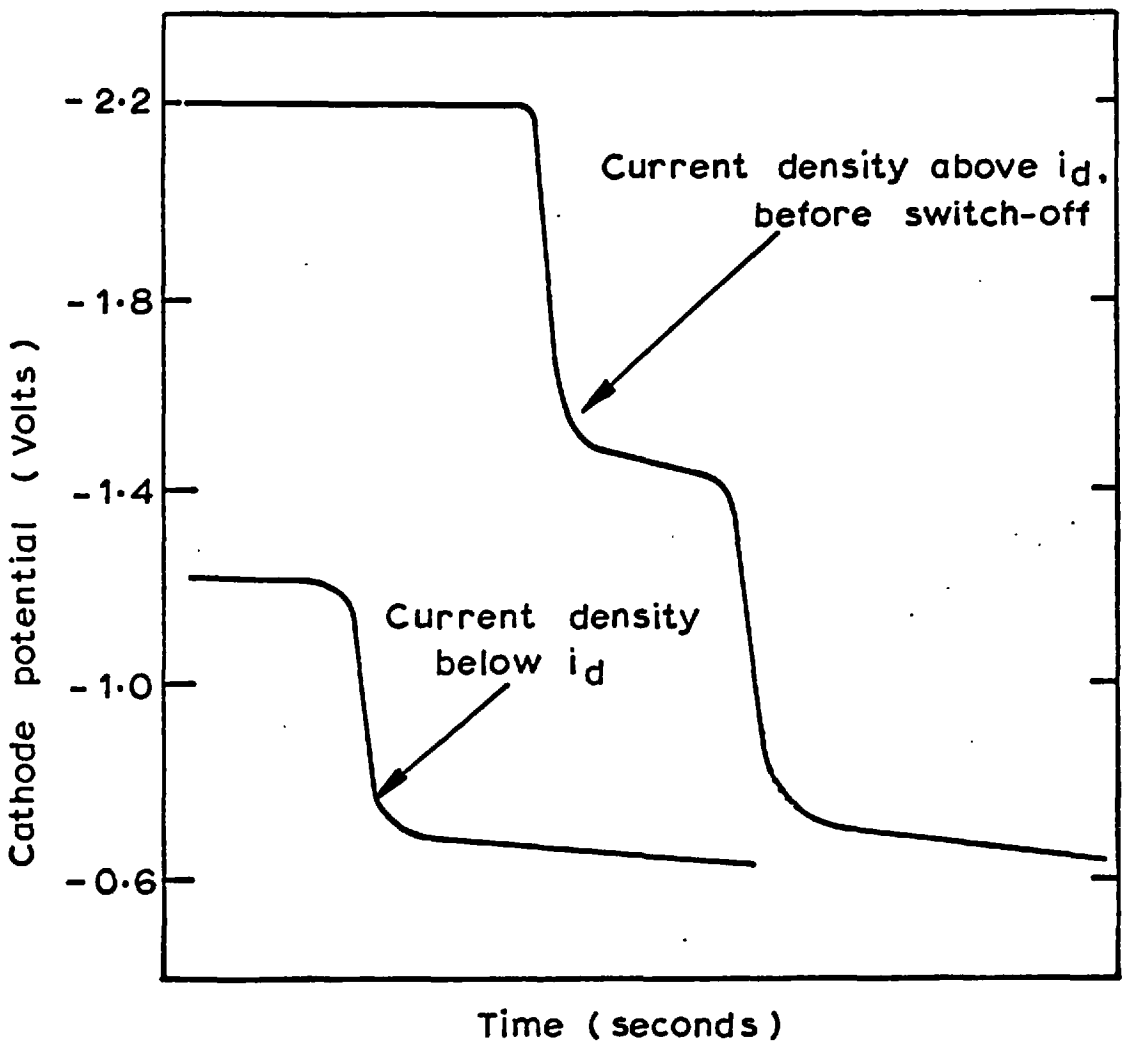


Fig.7. DECAY CURVES IN MOLTEN $NaPO_3$ AT 730°C.

found that a deposit had formed around the electrode and the amount depended upon the number of coulombs passed e.g. about 50 mg. of deposit formed at 50mA for one hour at 730°C. On breaking the glassy envelope around the deposit, a brown granular powder was found smelling very strongly of phosphine. This was placed in a desiccator for analysis. The deposit did not adhere to the electrcde surface and could be easily removed. No deposit was formed at electrode potentials between -1 to -1.5V.

If it is assumed that electro-reduction of the sodium ion occurs at the cathodic potential above -2V a possible product is sodium phosphide. Brauer and Zintl (25) have shown that a sodium phosphide Na_3P can be produced by heating the stochiometric quantities of sodium with molten phosphorus. The bonds from the phosphorus are considered mainly covalent with some ionic character, whereas the sodium bonds are partly metallic and partly covalent.

X-ray data is available for the phosphide and attempts were made to pack a powdered sample of the deposit into a capillary tube for X-ray examination; this was difficult due to caking of the sample. It was found possible to produce a fibre-like sample using polystyrene cement as a bond and an X-ray diffraction pattern was obtained. This seemed to correspond to the X-ray pattern for sodium orthophosphate and a comparison sample was made. Results are shown in Fig. 8. These

(1)

Anydrous

Na_3PO_4





(2)

Deposit

from

Cathode.

FIG. 8

X-Ray Patterns - Cu/Kx

indicate that the major portion of the deposit is the orthophosphate. A possible mechanism for the formation of the deposit around the cathode is as follows:-

$$Na^+ + e = Na \quad (3.1)$$

$$8Na + 4NaPO_3 = Na_3P + 3Na_3PO_4 \quad (3.2)$$

The reaction between sodium and sodium metaphosphate was examined by placing a small piece of sodium in an alumina tube and holding this below the surface of molten metaphosphate contained in an alumina crucible. The glass was then allowed to cool and removed from the crucible. A brown colouration was noticed and the "phosphine" smell was evident.

The sodium content of the deposit was determined by placing 25 mg. of the deposit in 5 ml. of concentrated nitric acid in which it dissolved, and then made up to 25 ml. Assuming the solution was sodium orthophosphate in nitric acid,10 ml. were taken, and the phosphate was precipitated with ammonia and barium chloride. The filtrate was evaporated to almost dryness and 10 ml. of zinc uranyl acetate reagent added (22). A bulky precipitate was obtained which was collected in a sintered glass crucible and allowed to dry in air. The weight was equivalent to about 5 mg. of sodium in the 10 mg. of deposit; from equation 3.2 the sodium content would be 47 per cent.

4. CHRONOPOTENTIOMETRY IN MOLTEN PHOSPHATES

Chronopotentiometry uses the change of concentration potential at the electrode with time under constant current conditions as a basis for measurement. The results are more amenable to quantitative interpretation than polarography when solid electrodes are used. Sand (26) showed that the transition time τ seconds is given by the relationship

$$\tau^{\frac{1}{2}} = \frac{\pi^{\frac{1}{2}} nF A D^{\frac{1}{2}} C}{2i} \qquad (4.1)$$

for a linear diffusion of electro-active species under a constant electrolysis current i amp.cm.$^{-2}$

where C = conc. of reducible species - mole.cm.^{3}

D = diffusion coefficient for species - cm.^{2}sec.$^{-1}$

F = Faraday = 96,500 coulombs

n = number of faradays per molar unit of reactants.

Delahay (27) has considered potential-time variations and Paunovic (28) has reviewed the theoretical and practical aspects of chronopotentiometry.

4.1. Apparatus

The apparatus was similar to that used in Section 3.1 for voltammetry. Again, a 1 mm. W electrode was used as a micro-electrode but to avoid variation in exposed area, an enclosed electrode was employed. A high-alumina glass (Supremax) was used as an insulating sleeve and this was sealed on to a glass bead formed by wiping the heated tungsten with the glass. The end of the electrode was then ground flat and polished on a

diamond pad. Since the molten phosphate adhered to the glass, the electrode was removed from the melt at the end of each run. Adherent phosphate glass tended tc crack the end bead due to differences in thermal expansion. When visible cracking was apparent, or when the chronopotentiogram indicated area variations, the glass sleeve was cut off, the bead removed, remade and the sleeve resealed on to it.

A Tetronix Storage Oscilloscope Type 564 was used to display the charging curve at varying current densities.

4.2. Experimental

Using the graphite pot as a non-polarisable anode, sodium metaphosphate was electrolysed in the temperature range 660-800°C. For low current densities the voltage built up to a steady-state value. When this exceeded about IV a first transition appeared, and, when the current density charged the electrode to 2V, a second transition was noticed. This second transition occurred with cyclic variations of voltage, which had been previously noticed during limiting current determinations (Section 3.3).

The voltage difference between the two processes corresponds to that obtained on the decay curves (Section 3.4). An oscilloscope trace showing two transitions and variations in voltage is shown in Fig.9.

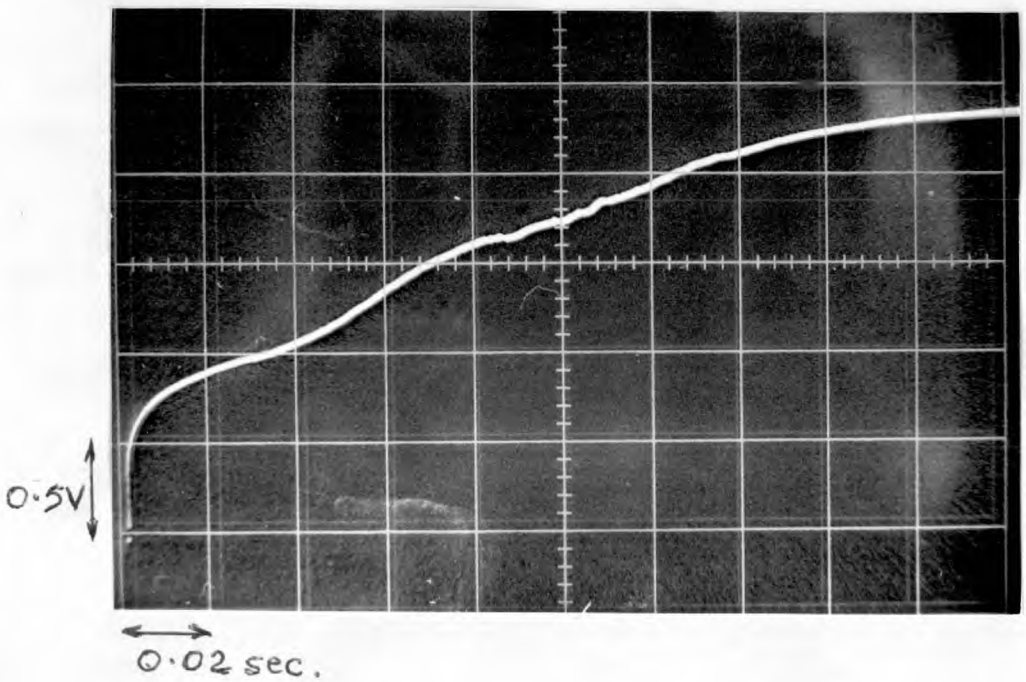


FIG. 9. TRANSITIONS IN MOLTEN SODIUM METAPHOSPHATE AT 720°C.

The first transition is unaffected by subsequent processes and typical results are shown in Table 5.

TABLE 5

Transition times in molten sodium metaphosphate at 710°C

i amp.cm.$^{-2}$	τ secs	$i\tau^{\frac{1}{2}}$
0.64	1.4	0.77
0.72	0.8	0.68
0.84	0.38	0.42
0.96	0.19	0.42
1.20	0.09	0.36
1.80	0.038	0.34
2.40	0.024	0.36

This pattern of decreasing values of $i\tau^{\frac{1}{2}}$ as current increases was shown at other temperatures. The variation from Sand's behaviour i.e. constancy of $i\tau^{\frac{1}{2}}$, is shown in Fig.10. This decrease in the product $i\tau^{\frac{1}{2}}$ with current density has been considered by Delahay and Berzins (29) and is a diagnostic criterion for the occurrence of a chemical reaction prior to reduction.

4.3. Transition times for prior chemical reaction

The simplest system is represented by a substance Y transformed to an electro-active form O (28)

(1) $Y \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O$ and (2) $O + ne = R$

where the applied potential is insufficient to reduce Y. For

this system the transition time is dependent upon current densities. At low current densities the Y form will have time to change to O form, whereas at high current densities the conversion is negligible during the pulse time and the initial equilibrium value of O controls the electrode potential and transition time.

If the diffusion coefficients are taken as equal and for $\left[(k_f + k_b)^{\frac{1}{2}}\tau^{\frac{1}{2}}\right] > 2$, the transition time is given by

$$i\tau^{\frac{1}{2}} = \tfrac{1}{2}\pi^{\frac{1}{2}}nFC^{o}D^{\frac{1}{2}} - \frac{\tfrac{1}{2}\pi^{\frac{1}{2}}i}{K(k_f + k_b)^{\frac{1}{2}}} \qquad (4.2)$$

Where K is the equilibrium constant for reaction (1)

The final constant value of $i\tau^{\frac{1}{2}}$ is given by

$$(i\tau^{\frac{1}{2}})_{i\to\infty} = \frac{\tfrac{1}{2}\pi^{\frac{1}{2}}nFC^{o}D^{\frac{1}{2}}}{1 + \frac{1}{K}} \qquad (4.3)$$

Since the metaphosphate is a highly polymeric melt containing oxyanions of the form $(P_nO_{3n+1})^{-n-2}$ it is possible that the lower polymers will be the reducible ions. The reaction preceding electro-reduction may then be a depolymerisation.

Meadowcroft & Richardson (30) studied the distribution of phosphate chains in phosphate glasses. The depolymerisation reaction is

$$2(P_nO_{3n+1})^{-n-2} = (P_{n-1}O_{3n-2})^{-n-1} + (P_{n+1}O_{3n+4})^{-n-3} \qquad (4.4)$$

giving the production of the monomer via reaction

$$2P_2O_7^{-4} = PO_4^{3-} + P_3O_{10}^{5-} \qquad (4.5)$$

This could account for the existence of a prior chemical reaction and also the appearance of two transition times.

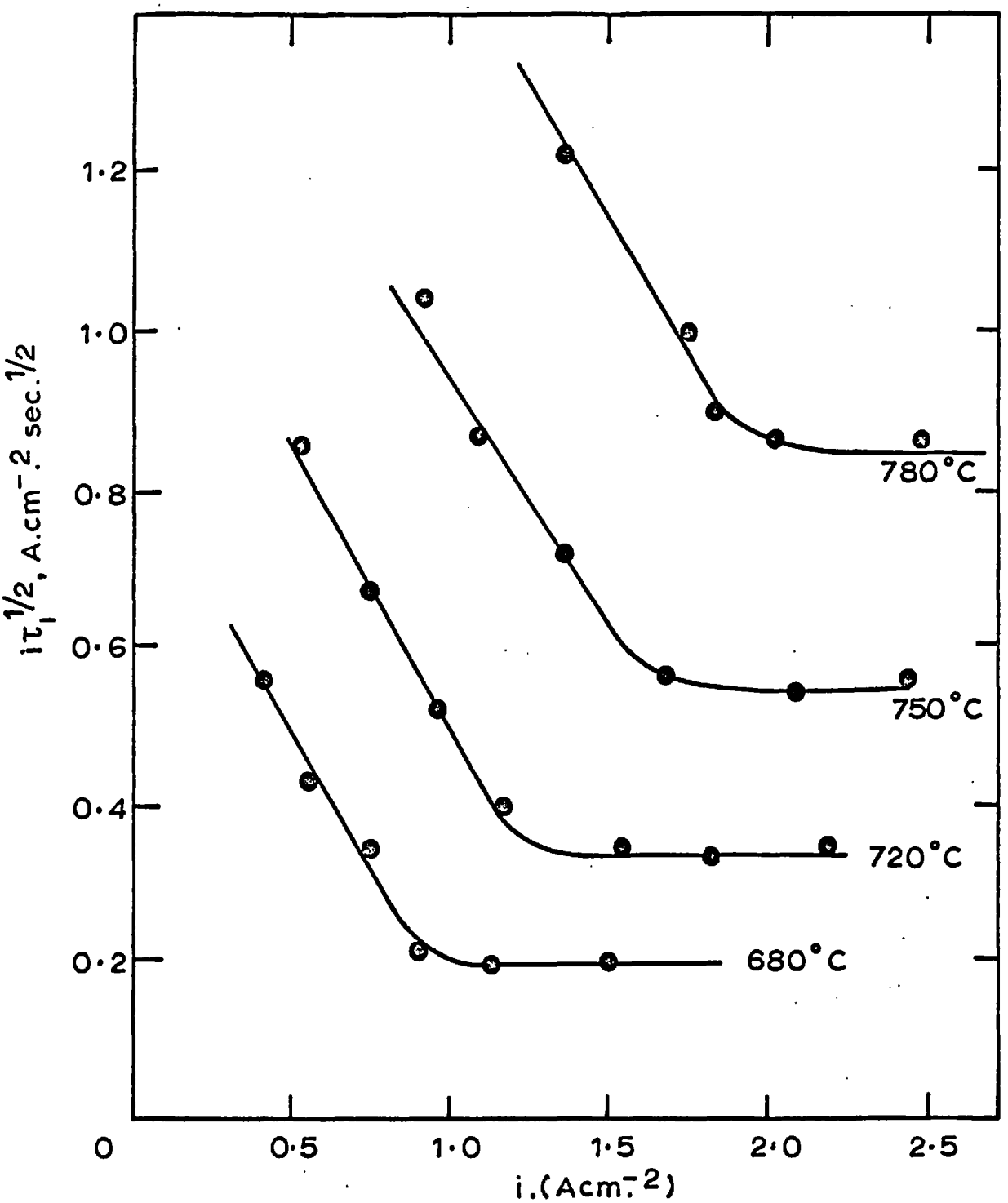


Fig.10. VARIATIONS OF TRANSITION TIMES WITH CURRENT DENSITY

4.4. Multiple transition times

Two steps in the potential time curve can be obtained from (a) a single electro-active ion reducing in two stages or (b) two ions being reduced at different cathodic potentials.

(a) Single ion

The kinetic scheme is,

$$(1) O_1 + n_1 e = R_1$$

$$(2) R_1 + n_2 e = R_2$$

It can be shown that the two transition times τ_1 and τ_2 are given by

$$\tau_1 = \pi F^2 C^2 D n_1^2 / 4i^2 \quad (4.6)$$

and $$\tau_2 = \pi F^2 C^2 D (2 n_i n_2 + n_2^2) / 4i^2 \quad (4.7)$$

or $$\frac{\tau_2}{\tau_1} = 2\left(\frac{n2}{n_1}\right) + \left(\frac{n2}{n_1}\right)^2 \quad (4.8)$$

This would give a constant ratio of τ_2 / τ_1, independent of concentration.

Two species

For the scheme	Moles/cc. electroactive ion
(1) $O_1 + n_1 e = R_1$	C_1
(2) $O_2 + n_2 e = R_2$	C_2

the first transition is due to depletion of O_1, but if the current is increased O_2 is reduced. Thus after τ_1 the current corresponds to the simultaneous reduction of O_1 and O_2.

If τ_2 is the time from the first transition time τ_1, $\tau_1 + \tau_2$ represents the total time from the switching on of the charging current. The transition times are then given by

$$\tau_1 = \pi F^2 C_1^2 D_1 n_1^2 / 4i^2 \tag{4.9}$$

$$\tau_2 = \pi F^2 (2 n_1 n_2 D_1^{\frac{1}{2}} D_2^{\frac{1}{2}} C_1 C_2 + n_2^2 D_2 C_2^2) / 4i^2 \tag{4.10}$$

Assuming $D_1 = D_2$

$$\frac{\tau_2}{\tau_1} = 2\left(\frac{n_2}{n_1}\right)\left(\frac{C_2}{C_1}\right) + \frac{(n_2 C_2)^2}{(n_1 C_1)^2} \tag{4.11}$$

Even if n_1 and n_2 are constant the ratio varies with C_2/C_1 variation and hence τ_2/τ_1 might be expected to vary with temperature. This was noted in the above experiments and indicates the presence of two species. For this system the Sand equation can be stated as

$$i\tau_1^{\frac{1}{2}} = \tfrac{1}{2}\pi^{\frac{1}{2}} F C_1 D_1^{\frac{1}{2}} n_1 \tag{4.12}$$

and $i\left[(\tau_1 + \tau_2)^{\frac{1}{2}} - \tau_1^{\frac{1}{2}}\right] = \tfrac{1}{2}\pi^{\frac{1}{2}} F C_2 D_2^{\frac{1}{2}} n_2 = i(\tau_2')^{\frac{1}{2}}$ (4.13)

putting $(\tau_2')^{\frac{1}{2}} = (\tau_1 + \tau_2)^{\frac{1}{2}} - \tau_1^{\frac{1}{2}}$

Using these relationships it was found that both $i\tau_1^{\frac{1}{2}}$ and $i(\tau_2')^{\frac{1}{2}}$ decreased with increasing current density and finally reached a constant value. This was taken to correspond to the initial equilibrium concentration values for O_1 and O_2 and results are given in Table 6.

TABLE 6

$i\tau_{i\to\infty}^{\frac{1}{2}}$ in sodium metaphosphate

Temp °C	$i\tau_1^{\frac{1}{2}}$ A cm.$^{-2}$ sec.$^{\frac{1}{2}}$	$i(\tau_2')^{\frac{1}{2}}$
680	0.20	0.40
720	0.35	0.52
750	0.55	0.65
780	0.85	0.99

The ratios of $i\tau_1^{\frac{1}{2}}$ and $i(\tau_2')^{\frac{1}{2}}$ are related by the following equation:-

$$\frac{i\tau_1^{\frac{1}{2}}}{i(\tau_2')^{\frac{1}{2}}} = \frac{n_1 C_1 D_1^{\frac{1}{2}}}{n_2 C_2 D_2^{\frac{1}{2}}} \qquad (4.14)$$

In this equation both C and D can vary with temperature. To consider the variation of diffusion coefficient with temperature the Stoke-Einstein relationship was used. This does not normally apply to ionic melts but D. M. Wrench (39) has shown that for cadmium ions in molten borates the diffusion coefficient varies directly with $\frac{T}{\eta}$ and phosphates are a similar polymeric melt.

Using the Stokes-Einstein relationship for diffusion coefficient

$$D = \frac{kT}{6\pi r\eta} \qquad (4.15)$$

when η = viscosity of melt at temperature T°K

k = Boltzmann constant

r = radius of diffusing species

it would be expected that the variation of D_1 and D_2 with temperature are similar. Hence the variations of $i\tau^{\frac{1}{2}}$ ratios with temperature are a measure of the variation of C with temperature. This indicates a marked increase in C_1 between 680° and 780° compared with C_2 in this temperature range. The viscosity of phosphate melts has been determined by Callis et alia (31) and values of 8.0 and 3.0 poise for sodium metaphosphate are obtained at 680° and 780° respectively. This would give T/η ratios of 11.9 at 680°C and 35.1 at 780°C. The diffusion coefficient would be expected to increase three times over this temperature range and $D^{\frac{1}{2}}$ ratios are 1:1.7.

It can be seen that $i\tau^{\frac{1}{2}}$ has increased more than four times whilst the $i(\tau_2')^{\frac{1}{2}}$ increase is about half this and is only a little above that expected from the increase in diffusion coefficient. This increase in the species O_1 would be expected from a depolymerisation reaction if O_1 was the lower polymer. Since the metaphosphate melt would be expected to give a large average chain length ($\bar{n} > 50$) the concentration of the lower polymers could well be low enough for depletion at high current densities. Westman and co-workers (32, 33) as well as

Meadowcroft (30) have examined the phosphate glasses by hydrolysis and chromatography. They indicate that the monomer is not present but that 3 per cent of the total phosphorus is pyrophosphate or dimer for sodium phosphate glasses of average chain length equal to five. However, using the Flory (34) distribution for bi-functional polymers, the amounts of monomer are significant.

4.5 Flory distribution applied to phosphates

Let W_n = weight per cent of n-mer

p = extent of polymerisation

$\bar{n}$ = average chain length of polymer

i.e. phosphorus atoms per chain

Then $$\bar{n} = \frac{1}{1 - p} \qquad (4.16)$$

and $$W_n = 100n\, p^{n-1}(1 - p)^2 \qquad (4.17)$$

Results for ortho, pyro and tripolyphosphates are shown in Table 7.

TABLE 7

Distribution of lower polymers in sodium phosphates

Na_2O/P_2O_5 (R)	$\bar{n}$	Per cent of Total Phosphorus by weight		
		ortho	pyro	tri
1.67	3	11.2	14.9	14.9
1.50	4	6.3	9.4	10.6
1.20	10	1.0	1.8	2.4
1.10	20	0.25	0.47	0.69

The amounts of the lower polymers present for R approaching 1.0 could give the results seen for the metaphosphate melts. In order to identify the species present and to minimise polymeric equilibria reactions it was decided to use crystalline ortho and pyro-phosphates dissolved in halide melts, as these are more simple systems and would be expected to exhibit lower $\bar{n}$ values.

5. CHRONOPOTENTIOMETRY IN MOLTEN HALIDES

Lucas (16) electrolysed sodium metaphosphate in lithium chloride-potassium chloride eutectic over the temperature range 450° - 700°C. At least two transition times were noted, but the relationship between the transitions was not fully established. Voltammetry in the same solvent had given reduction waves with half-wave potentials of -0.8V and -1.55V, which compare with τ_1 and τ_2 potentials as found in Section 4.2.

5.1. Experiments in Lithium Chloride - potassium chloride eutectic

Initial experiments were carried cut in lithium chloride-potassium chloride eutectic purified by pre-electrolysis under vacuum followed by filtration. The solute was added to the ground eutectic and placed in a graphite crucible, which acted as the non-polarisable anode. The experimental arrangement and procedure was similar to that used for molten sodium metaphosphate (section 4.1).

5.11. Solutes

Analytical reagent grade anhydrous sodium pyrophosphate was used. As the pure orthophosphate could not be obtained, an equi-molar mixture of Analar sodium peroxide and the sodium pyro-phosphate was employed. The sodium peroxide had been used by Shams El Din (35) instead of sodium oxide to avoid excessive absorption of moisture. The mixture was ground and dried for 12 hours at 120°C.

The phosphates were stored over magnesium perchlorate.

5.1.2. Transition times for sodium orthophosphate

It was found that only one transition time occurred for the sodium orthophosphate. The $E_{\tau/4}$ value was approximately -0.7V and a constant $i\tau^{\frac{1}{2}}$ value was obtained. Results are shown in Table 8.

TABLE 8

Chronopotentiometric measurements for sodium orthophosphate in LiCl. - KCl at 450°C

$C = 9.8 \times 10^{-5}$ mole. cm.$^{-3}$

i amp.cm.$^{-2}$	τ sec.	$\tau^{\frac{1}{2}}$ sec.$^{\frac{1}{2}}$	$i\tau^{\frac{1}{2}}$ A.cm.$^{-2}$ sec.$^{\frac{1}{2}}$
4.7×10^{-2}	1.2	1.10	5.2×10^{-2}
7.0	0.5	.71	5.0
8.7	0.3	.55	4.8
9.3	0.25	.50	4.7
9.7	0.22	.47	4.6
11.7	0.20	.45	5.2
13.2	0.14	.37	4.9

5.1.3. Transition times for sodium pyrophosphate

When the electrolysis of sodium pyrophosphate was carried out at 450°C two transitions were obtained; the second transition occurred at a potential approximately 0.4V more cathodic than the first. The experiments were repeated at temperatures of 500°C and 600°C and results are shown in Table 9.

TABLE 9

Transitions for sodium pyrophosphate in LiCl - KCl

Concentration = 5.8×10^{-5} mole. cm.$^{-3}$

$$(\tau_2')^{\frac{1}{2}} = (\tau_1 + \tau_2)^{\frac{1}{2}} - \tau_1^{\frac{1}{2}}$$

	i A.cm.$^{-2}$	τ_1 sec.	$\tau_1 + \tau_2$ sec.	$i\tau_1^{\frac{1}{2}}$ A.cm.$^{-2}$sec.$^{\frac{1}{2}}$	$i(\tau_2')^{\frac{1}{2}}$ A.cm.$^{-2}$sec.$^{\frac{1}{2}}$
450°C	0.78×10^{-2}	3.5	-	1.47×10^{-2}	-
	1.19	1.3	-	1.36	-
	1.55	0.8	7.5	1.39	2.87×10^{-2}
	1.82	0.6	5.5	1.41	3.04
	2.28	0.4	3.6	1.43	2.90
	2.73	0.3	2.6	1.49	2.88
500°C	2.28×10^{-2}	2.0	6.0	3.2×10^{-2}	2.4×10^{-2}
	2.91	1.0	3.2	2.9	2.3
	4.00	0.8	2.4	3.9	2.6
	5.10	0.4	1.5	3.2	2.1
	6.46	0.3	0.8	3.5	2.2
600°C	2.64×10^{-2}	5.0		5.9×10^{-2}	No second transition
	3.60	3.0		6.2	
	4.55	2.0		6.5	
	5.83	1.3		6.6	
	6.64	0.9		6.2	

Since the first transition occurred at the potential corresponding to the reduction of the orthophosphate ion, one can surmise that the second transition represents the reduction of the pyrophosphate ion. The results indicate loss of the pyrophosphate ion at the higher temperatures and would suggest that the pyrophosphate is completely converted to orthophosphate at 600°C.

Owing to the hygroscopic nature of the lithium chloride, difficulties in handling arose. The graphite crucibles were not readily cleaned and there was evidence of penetration by the melt. It was therefore decided to use a sodium chloride-potassium chloride mixture for further experiements.

5.2. Chronopotentiograms in sodium chloride - potassium chloride melts.

Equimolar sodium chloride-potassium chloride was prepared by mixing the required amounts of Analar grade reagents and heating for 12 hours at 120°C under vacuum. This was stored over magnesium perchlorate.

5.2.1. Sodium orthophosphate additions

Varying concentrations of the sodium peroxide - sodium pyrophosphate mixture were added to the chloride. To ensure complete reaction to give the orthophosphate, the initial experiments were carried out at 780°C. However, no second transition for this phosphate was found even when the melt temperature was 670°C. The concentrations were calculated as orthophosphate and results are given in Table 10.

TABLE 10

Transition times for orthophosphate in sodium chloride-potassium chloride at 780°C

(a) $C = 5.8 \times 10^{-5}$ mole.cm.$^{-3}$

imA.cm.$^{-2}$	τ secs.	$i\tau^{\frac{1}{2}}$ mA.cm.$^{-2}$sec.$^{\frac{1}{2}}$
20.7	2.1	30.0
27.1	1.4	31.8
32.5	0.8	29.1 = 30.0 $\pm$ 1.2
43.0	0.45	28.8
53.6	0.32	30.8
65.0	0.21	29.8
71.3	0.16	28.6
94.5	0.11	31.2

(b)

C mole.cm.$^{-3}$	$i\tau^{\frac{1}{2}}$ mA.cm.$^{-2}$sec.$^{\frac{1}{2}}$
2.1×10^{-5}	11.2
4.7	25.4
7.2	35.4
9.8	50.3
13.8	66.8

These results are shown in Fig. 11 and indicate that Sand's behaviour is obeyed over the concentration range used.

The electrode process was further examined by considering the electrode potential variation with time. Plots of potential against $\log_{10}(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})$ and $\log_{10}(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})/t^{\frac{1}{2}}$ are shown in Fig. 12. The straight line plot of E v $\log_{10}(\tau^{\frac{1}{2}} - t^{\frac{1}{2}})/t^{\frac{1}{2}}$ suggests a reversible reaction with soluble reactants and products (28). From the slope of the curve the number of electrons transferred is two. This corresponds to the value determined by Lucas (16) for sodium metaphosphate in lithium chloride-potassium chloride eutectic when carrying out controlled potential coulometery at -1.00V with regard to a Pt(II)/Pt reference electrode.

If the orthophosphate is reduced and two electrons are transferred, this is equivalent to reducing pentavalent phosphorus to trivalent phosphorus. However, it is known that phosphorus is the overall product; consequently a further chemical reduction must occur in order to produce the phosphorus.

The following mechanism is suggested:-

$$(1)\quad PO_4^{3-} + 2e = PO_2^{-} + 2O^{2-} \qquad (5.1)$$

$$(2)\quad 5PO_2^{-} + 2O^{2-} = 3PO_4^{3-} + 2P \qquad (5.2)$$

eliminating the "hypo-phosphite" ion, the overall reaction becomes

$$(3)\quad 2PO_4^{3-} + 10e = 2P + 8O^{2-} \qquad (5.3)$$

$$\text{or}\quad PO_4^{3-} + 5e = P + 4O^{2-} \qquad (5.4)$$

This corresponds to the overall reduction process as suggested in Section 1.3 and which was used for the basis of the coulometry.

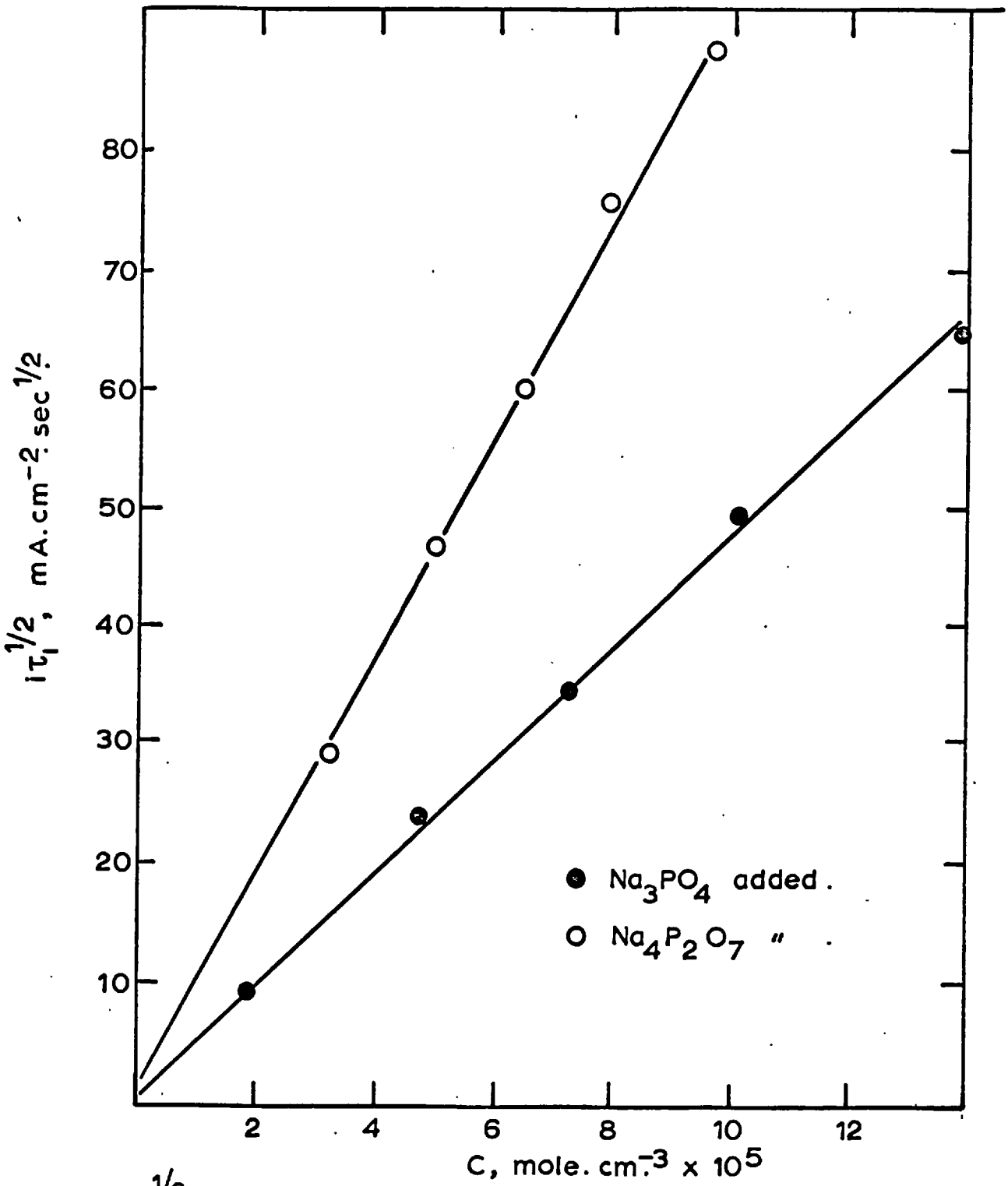


Fig.11. $i\tau^{1/2}$ vs. C FOR PHOSPHATES IN NaCl-KCl AT 780°C

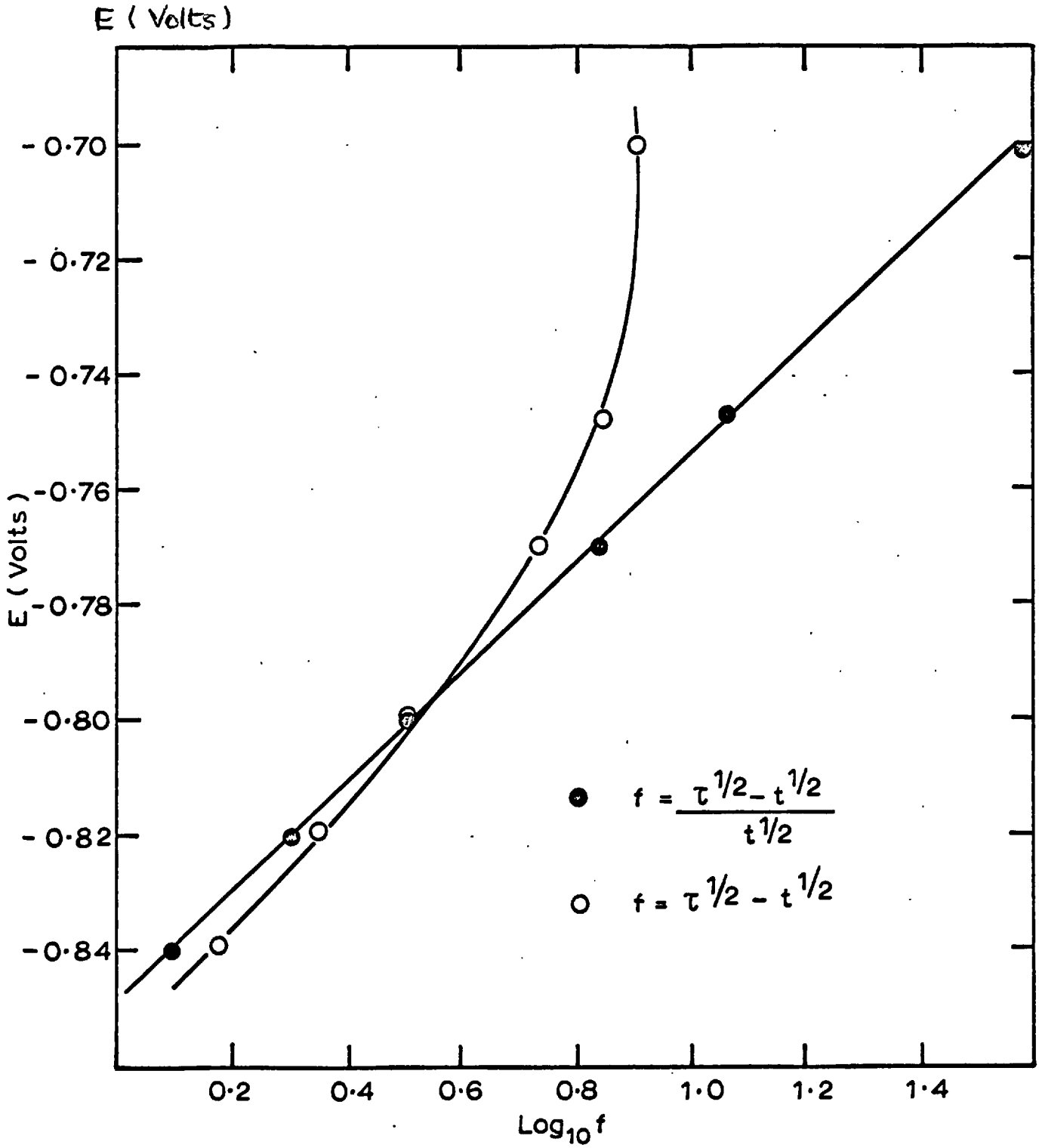


Fig.12. $E(V)$ v $\frac{2.303RT}{nF} \log_{10} f$ FOR Na_3PO_4 IN NaCl - KCl AT 780°C

5.2.2. Pyrophosphate additions

Sodium pyrophosphate was added to the sodium chloride-potassium mix and the electrolysis was examined at varying temperatures. Results at temperatures of 670°C and 710°C, both giving two transitions, are shown in Table 11. A typical charging curve for sodium pyrophosphate in molten sodium chloride-potassium chloride is given in Fig. 13(a).

TABLE 11

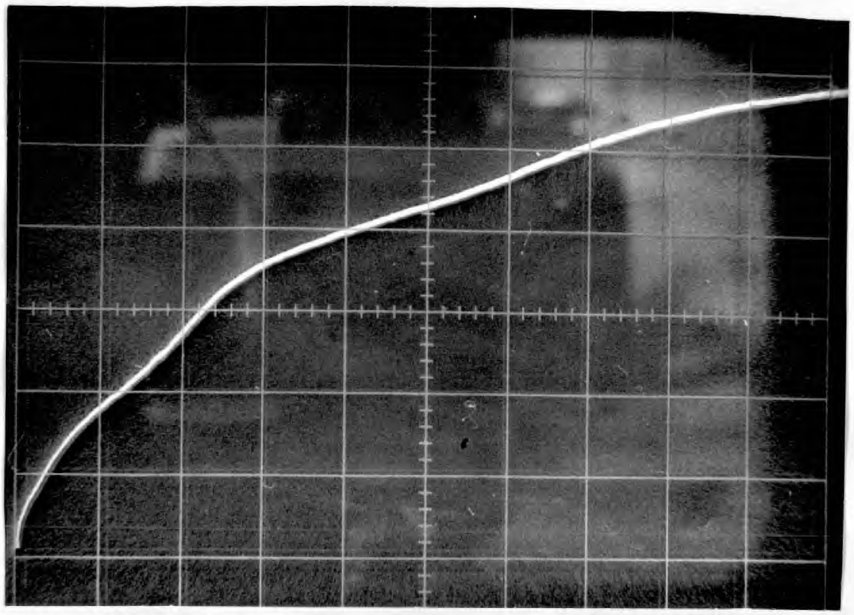
Transition times for sodium pyrophosphate in NaCl-KCl melt

Concentration = 5.9×10^{-5} mole.cm.$^{-3}$

$$(\tau_2')^{\frac{1}{2}} = (\tau_1 + \tau_2)^{\frac{1}{2}} - \tau_1^{\frac{1}{2}}$$

	imA.cm.$^{-2}$	τ_1 sec.	$\tau_1+\tau_2$ sec.	mA.cm.$^{-2}$sec.$^{\frac{1}{2}}$ $i\tau_1^{\frac{1}{2}}$	$i(\tau_2')^{\frac{1}{2}}$
670°C	9.3	2.5	-	14.7	-
	11.7	1.5	8.5	14.4	18.7
	18.8	0.7	3.5	15.7	19.4
	21.0	0.5	2.5	14.8	18.4
	27.5	0.3	1.5	14.9	18.9
710°C	11.7	4.0	-	23.4	-
	16.5	1.5	4.0	20.7	12.8
	19.8	1.2	3.2	21.7	13.7
	25.0	0.8	2.0	22.4	13.1
	26.7	0.6	1.6	20.7	12.9

(a) $Na_4P_2O_7$



(b) $Na_4P_2O_7$ + Na_3PO_4

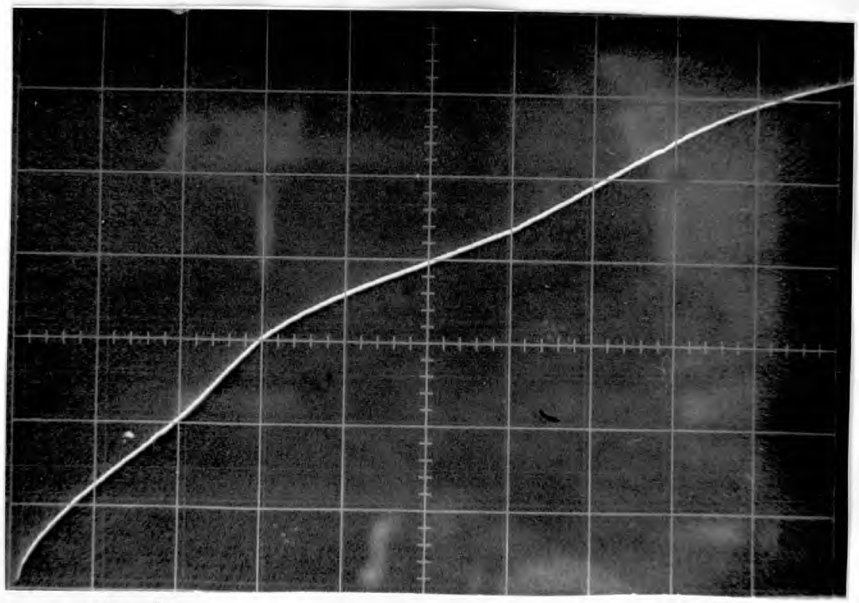


FIG. 13 Transition times in molten NaCl-KCl at 670°C.

These results show the same trend as the experiments in which pyrophosphate was dissolved in lithium chloride-potassium chloride eutectic. (See Table 9).

It was found that at temperatures of 750°C and above the second transition did not occur. In order to determine the effect of pyrophosphate additions under conditions which gave only the orthophosphate transition, the experiments were carried out at 780°C. Results could then be compared with the orthophosphate additions at this temperature and these are given in Table 12. Charging curves for the orthophosphate and pyrophosphate are compared in Fig. 14

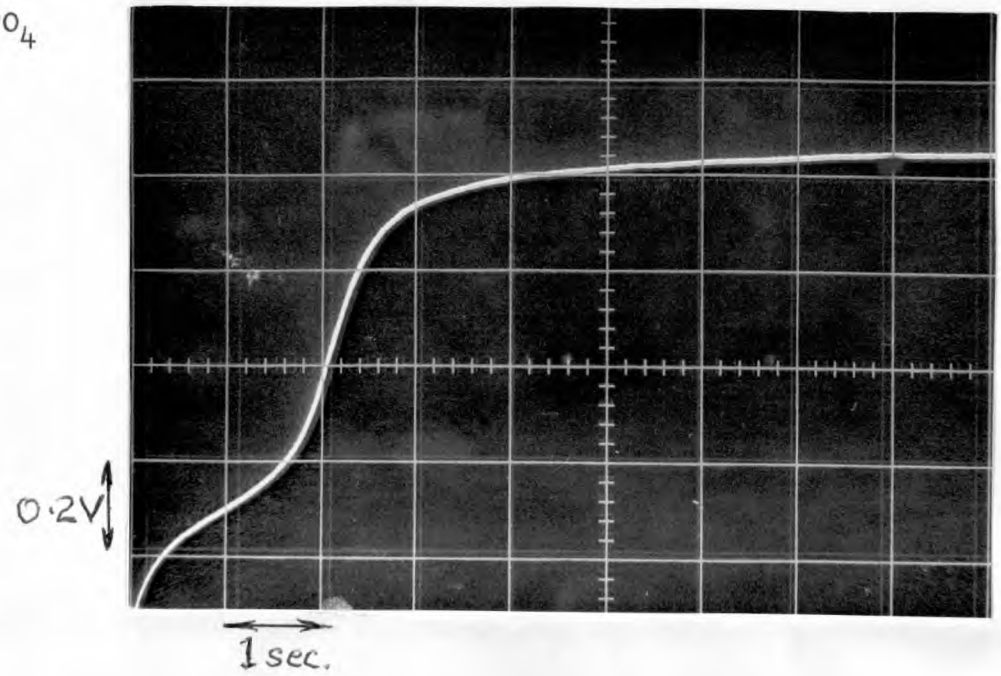
TABLE 12

$i\tau_1^{\frac{1}{2}}$ versus concentration of pyrophosphate at 780°C

Conc. mole.cm.$^{-3}$	$i\tau_1^{\frac{1}{2}}$ mA.cm.$^{-2}$ sec.$^{\frac{1}{2}}$
2.9×10^{-5}	30.0
4.8	47.8
6.1	60.5
7.5	76.5
9.3	89.5

These values are compared with the orthophosphate in Fig. 11. It can be seen that each mole. of pyrophosphate is equivalent to two moles. of orthophosphate.

(1) Na_3PO_4



(2) $Na_4P_2O_7$

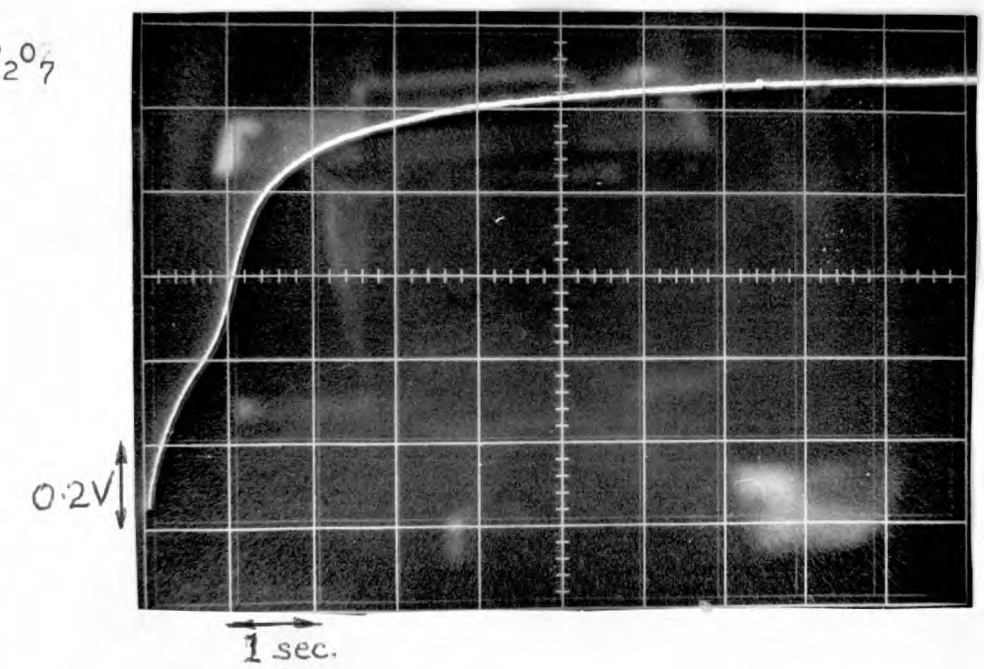


FIG. 14. Transition times in molten NaCl-KCl at 780°C.

If one extends the Flory distribution shown in Section 4.3.3. for $\bar{n} = 2$

R	$\bar{n}$	Per cent of Total Phosphorus		
		ortho	pyro	tripoly
2.0	2	25.0	25.0	18.7

This would be equivalent to molar concentrations of 25%:12.5%:6.2% and in the limit 1 mole of dimer would give 2 moles of the monomer.

It is possible that the reaction $P_2O_7^{4-} + O^{2-} = 2PO_4^{3-}$ also occurs. It has been shown by Shams El Din (36) that the equilibrium is displaced well over to the orthophosphate in chloride melts. Mitchell (14) compares his value of $K = 81 \pm 3$ for the equilibrium in molten potassium-bromide with calculated value of approx. 100 at 1000°K obtained from data of Meadowcroft (37) and Holmes et alia (20). Some oxide occurs in the Analar reagents used; the oxide content of the chlorides was equivalent to 0.1×10^{-5} mole.cm.$^{-3}$.

5.2.3. Orthophosphate-pyrophosphate equilibria

It has been shown that pyrophosphate dissociates into the orthophosphate even at the lowest temperature that can be used for sodium chloride-potassium chloride melts. The effect of increasing the pyrophosphate concentration cannot, therefore, be obtained directly. To minimise the dissociation of the pyrophosphate, the temperature was kept as low as possible and orthophosphate-pyrophosphate mixtures were added instead of pyrophosphate alone.

For each composition the electrolysis cell was placed in the hot furnace and the transition time determined as soon as the temperature reached 670°C.

Assuming that for the orthophosphate

$$i\tau_1^{\frac{1}{2}} = \tfrac{1}{2}\pi^{\frac{1}{2}} F D_1^{\frac{1}{2}} n_1 C_1 \qquad (5.5)$$

and for the pyrophosphate

$$i(\tau_2')^{\frac{1}{2}} = \tfrac{1}{2}\pi^{\frac{1}{2}} F D_2^{\frac{1}{2}} n_2 C_2 \quad \text{and} \quad D_1 = D_2 \qquad (5.6)$$

$$r = \frac{i\tau_1^{\frac{1}{2}}}{i(\tau_2')^{\frac{1}{2}}} = \frac{n_1 C_1}{n_2 C_2} \qquad (5.7)$$

In this relationship n_1 has been determined as two (Section 5.2.1). Assuming the added ortho-pyrophosphate ratio (C_1/C_2) remains unchanged, the value of n_2 can be calculated. Results are shown in Table 13

TABLE 13

Orthophosphate-pyrophosphate mixtures in NaCl - KCl at 670°C

$n_1 = 2$

C_1/C_2	r	Calculated n_2
5.9	2.0	5.9
3.4	1.5	4.6
2.4	1.3	3.7
1.8	0.9	4.0

These results indicate that the equilibrium mixture of orthopyrophosphate at 670°C is for C_1/C_2 approximately equal to two and that the n_2 value is four. The C_1/C_2 value of 5.9 represents an excess of orthophosphate, some of which would form pyrophosphate. Assuming that the reaction between orthophosphate and pyrophosphate is dimerisation as shown in Section 5.2.2.

$$2 \text{ orthophosphate} \rightleftharpoons \text{pyrophosphate} \qquad (5.8)$$

From equation (5.7) a value of r = 2.0 should be given by $C_1/C_2 = 4.0$ for $n_1 = 2$ and $n_2 = 4$. The amount of orthophosphate dissociation to give this equilibrium concentration can be determined

Let x = degree of dissociation of orthophosphate

C_1^o = original concentration of orthophosphate

C_2^o = original concentation of pyrophosphate

For equilibrium conditions

$$C_1 = C_1^o(1 - x)$$

$$C_2 = C_2^o + \tfrac{1}{2} C_1^o x$$

i.e.
$$\frac{C_1}{C_2} = \frac{C_1^o}{C_2^o} \quad \frac{(1 - x)}{1 + \frac{1}{2} C_1^o/C_2^o . x.} \qquad (5.9)$$

Putting the above values

$$4.0 = \frac{5.9\ (1 - x)}{1 + \frac{1}{2}(5.9x)}$$

$$x = \frac{1.9}{3 \times 5.9} = 0.11$$

Thus a dissociation of 11 per cent of the orthophosphate is sufficient to change the calculated n_2 value to four. Assuming the electro-reduction of the pyrophosphate ion occurs with the transfer of four electrons

$$(P_2^{5+} + 4e = 2P^{3+} \qquad (5.10)$$

This corresponds to the valency reduction found for the orthophosphate. Charging curves of the ortho-pyrophosphate mixture are compared with the pyrophosphate alone in Fig. 13.

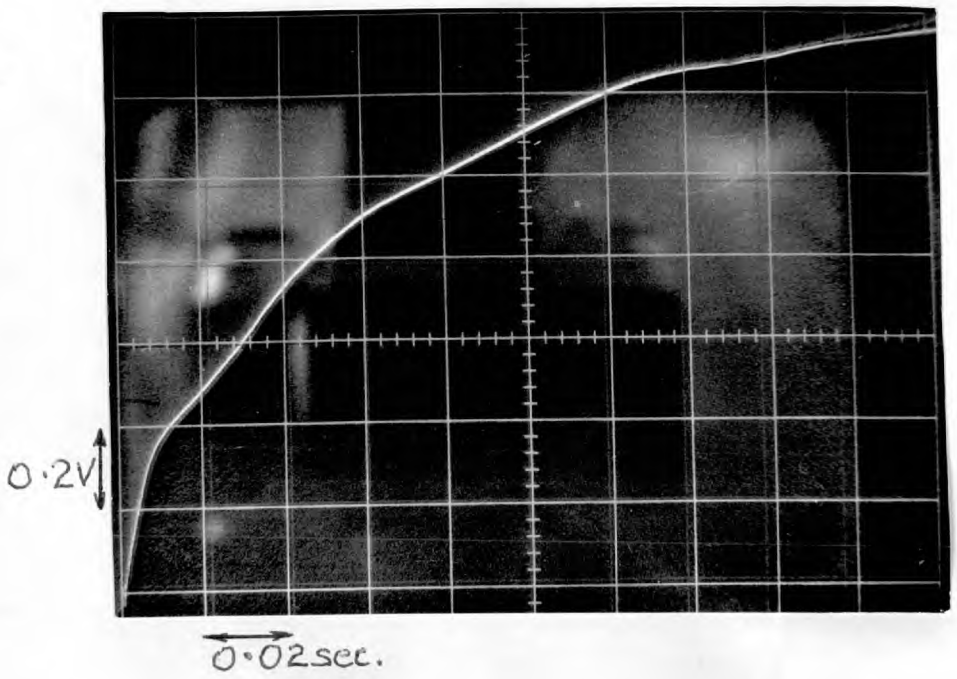
5.2.4. Sodium metaphosphate in sodium chloride-potassium chloride

The sodium trimetaphosphate was mixed with the sodium chloride-potassium chloride and transition times were examined in the temperature range 680° - 780°C. Photographs taken at 680° and 740°C are shown in Fig. 15. Three transition times were obtained; at 680°C the second transition is rather indeterminate, but could be identified on a decay curve. The processes occurred at approximately -0.7V, -1.2V and -1.5V which correspond to the quarter-wave potentials of -0.4V, -0.85V and -1.19V reported by Senderoff (15) for trimetaphosphate dissolved in LiCl-KCl at 500°C.

Assuming that three species are present the transition times can be analysed as shown by Reilly et alia (38) where for the i^{th} species

$$i\left[(\tau_1 + \tau_2 + \ldots \tau_i)^{\frac{1}{2}} - (\tau_1 + \tau_2 + \ldots \tau_{i-1})^{\frac{1}{2}}\right] = \tfrac{1}{2}\pi^{\frac{1}{2}} n_i F C_i D_i^{\frac{1}{2}} \qquad (5.11)$$

(1) 680°C



(2) 740°C

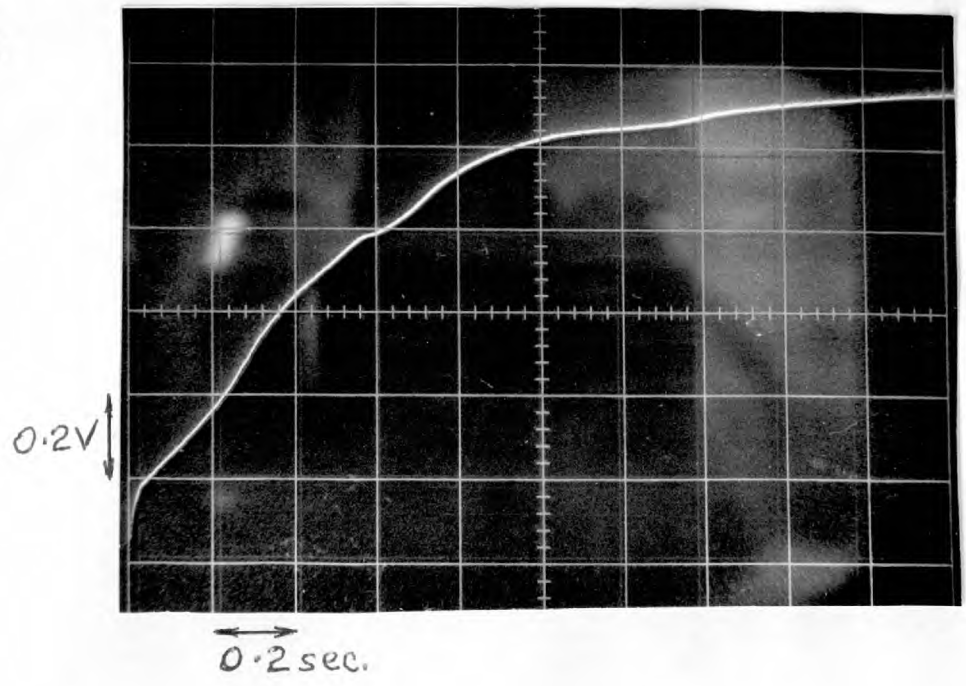


FIG. 15. Transitions for Sodium Metaphosphate in NaCl-KCl

Using this for τ_1, $\tau_1 + \tau_2$, $\tau_1 + \tau_2 + \tau_3$

$$i\tau_1^{\frac{1}{2}} = \tfrac{1}{2}\pi^{\frac{1}{2}} Fn_1 C_1 D_1^{\frac{1}{2}} \qquad (5.12)$$

$$i(\tau_2')^{\frac{1}{2}} = i\left[(\tau_1 + \tau_2)^{\frac{1}{2}} - \tau_1^{\frac{1}{2}}\right] = \tfrac{1}{2}\pi^{\frac{1}{2}} Fn_2 C_2 D_2^{\frac{1}{2}} \qquad (5.13)$$

$$i(\tau_3')^{\frac{1}{2}} = i\left[(\tau_1 + \tau_2 + \tau_3)^{\frac{1}{2}} - (\tau_1 + \tau_2)^{\frac{1}{2}}\right] = \tfrac{1}{2}\pi^{\frac{1}{2}} Fn_3 C_3 D_3^{\frac{1}{2}} \qquad (5.14)$$

the following results were obtained:-

TABLE 14

Transition times for sodium metaphosphate in NaCl-KCl

$C = 14.8 \times 10^{-5}$ mole.cm.$^{-3}$ as $NaPO_3$

(a) Temp = 740°C

	Seconds			mA.cm.$^{-2}$sec.$^{\frac{1}{2}}$		
imA.cm.$^{-2}$	$\tau_1+\tau_2+\tau_3$	$\tau_1+\tau_2$	τ_1	$i\tau_1^{\frac{1}{2}}$	$i(\tau_2')$	$i(\tau_3')^{\frac{1}{2}}$
29.0	5.0	2.4	0.7	24.5	20.7	20.0
40.8	2.7	1.3	0.4	25.6	20.7	20.5
56.8	1.5	0.7	0.2	25.3	21.9	22.0
66.3	1.0	0.5	0.15	25.6	21.0	19.5
112.0	0.35	0.15	0.05	25.4	19.8	24.0

(b)

Temp.°C	$i\tau_1^{\frac{1}{2}}$	$i(\tau_2')^{\frac{1}{2}}$	$i(\tau_3')^{\frac{1}{2}}$
680	0.018	0.018	0.022
710	0.023	0.020	0.021
740	0.025	0.021	0.021
78C	0.037	0.033	0.025

The first and second transitions have been identified as due to the reduction of the orthophosphate and pyrophosphate ion respectively. By analogy the third transition could arise from the reduction of the tripoly phosphate ion. This was verified by electrolysis of sodium tripolyphosphate in sodium chloride-potassium chloride. Photographs of the transitions are shown in Fig. 16 and results at 750°C are given in Table 15.

TABLE 15

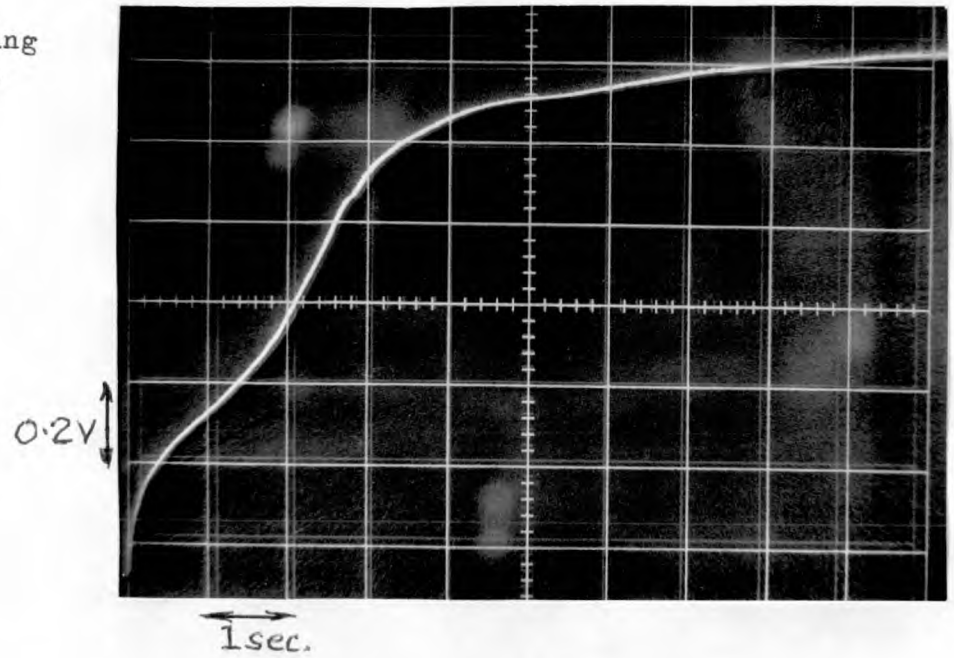
Transition times for sodium tripolyphosphate in NaCl-KCl at 750°C

$C = 9.0 \times 10^{-5}$ mole.cm.$^{-3}$

i mA.cm.$^{-2}$	Seconds			mA.cm.$^{-2}$sec.$^{\frac{1}{2}}$		
	$\tau_1+\tau_2+\tau_3$	$\tau_1+\tau_2$	τ_1	$i\tau_1^{\frac{1}{2}}$	$i(\tau_2')$	$i(\tau_3')^{\frac{1}{2}}$
37.4	-	5.5	3.0	64.6	22.8	-
50.0	5.5	2.8	1.5	61.7	21.9	35.0
57.4	4.6	2.4	1.2	63.8	26.0	34.8
70.0	3.2	1.6	0.9	66.2	22.2	36.6
87.2	1.9	1.0	0.5	61.0	21.7	37.5
102.5	1.4	0.7	0.4	66.0	22.5	35.6
150.0	0.8	0.4	0.2	67.0	28.2	39.0

The three transitions are comparable with those found for the sodium metaphosphate (Table 14).

(1) Charging Curve.



(2) Decay Curve.

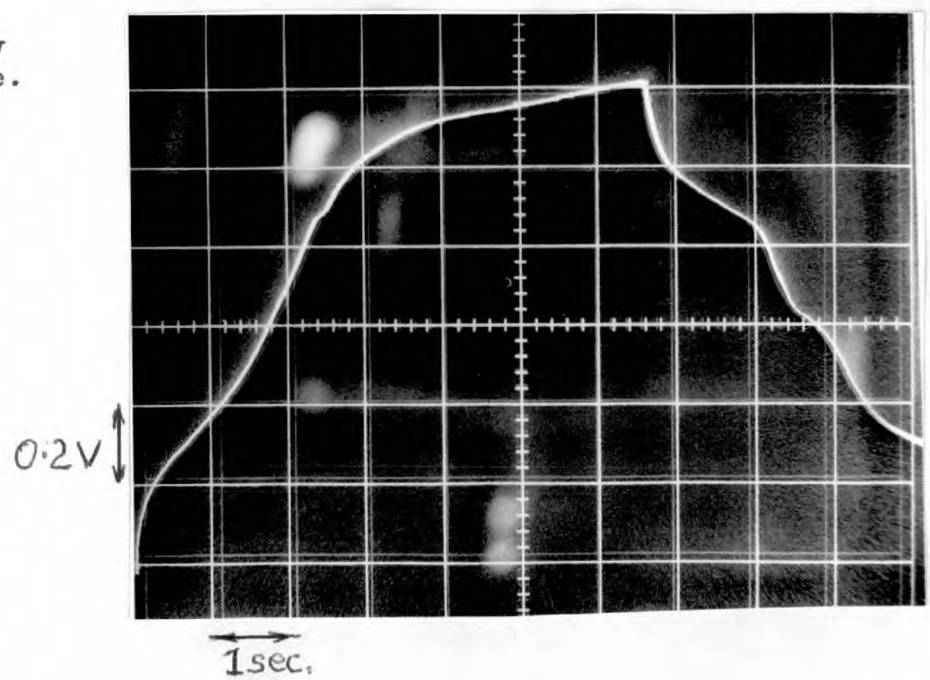


FIG. 16. Transitions for sodium tripolyphosphate in NaCl-KCl at 750°C.

As with the metaphosphate the second transition tends to be less definite than the others. However, by gradual increase of current densities and adjustment of the time scale on the oscilloscope, well-defined first and second transitions can be obtained. All three transitions can be clearly observed under open circuit conditions as shown for the decay curves in Fig. 16.

The dissociation of the tripolyphosphate into pyrophosphate and orthophosphate can be estimated from the transition times. The concentration of the orthophosphate can be obtained from Fig. 11, with an estimated diffusion coefficient at 750°C. This gives a value of 14×10^{-5} mole.cm.$^{-3}$ for the orthophosphate ion.

Assuming the diffusion coefficients of the phosphate ions are equal

$$\frac{i\tau_1^{\frac{1}{2}}}{i(\tau_2')^{\frac{1}{2}}} = \frac{n_1 C_1}{n_2 C_2} \quad \text{and} \quad \frac{i\tau_1^{\frac{1}{2}}}{(i\tau_3')^{\frac{1}{2}}} = \frac{n_1 C_1}{n_3 C_3}$$

It has been found that $n_1 = 2$ and $n_2 = 4$, and by analogy n_3 can be assumed equal to 6. Using these values of the estimated C_1 the following results are obtained:-

C_1 = orthophosphate = 14×10^{-5} mole.cm.$^{-3}$

C_2 = pyrophosphate = 4×10^{-5} mole.cm.$^{-3}$

C_3 = tripolyphosphate = 3×10^{-5} mole.cm.$^{-3}$

This indicates a large measure of depolymerisation.

5.2.5. Diffusion coefficient for the orthophosphate ion in sodium-potassium chloride

From the Sand equation (4.1) $i\tau^{\frac{1}{2}}$ is directly proportional to the concentration of the solute. The diffusion coefficient can be obtained from the slope of the curve. Using the values shown in Fig. 11 a diffusion coefficient of 8.2×10^{-6} cm.^{2} sec.$^{-1}$ was calculated for the orthophosphate ion in sodium chloride-potassium melt at 780°C. This compares with the value of 8.0×10^{-6} cm.^{2} sec^{-1} calculated by Lucas (16) from the first transition of sodium metaphosphate in lithium chloride-potassium chloride eutectic.

The effect of temperature on the diffusion coefficient was examined by determining the transition times for a fixed concentration of sodium orthophosphate in the temperature range 780°-670°C. Results are shown in Table 16.

TABLE 16

Variations of diffusion coefficient with temperature

Concentration = 11.3×10^{-5} mole.cm.$^{-3}$

Temperature °C	$i\tau^{\frac{1}{2}}$ mA.cm.$^{-2}$ sec.$^{\frac{1}{2}}$	D cm.^{2} sec.$^{-1}$
780	56.6	8.2×10^{-6}
760	49.0	6.8
740	47.6	5.8
720	44.5	5.0
690	38.2	2.7
670	34.4	3.0

Over the temperature range used, the relationship between the diffusion coefficient D and temperature can be expressed as:

$$D = D_o e^{-E_D/RT}$$

$$\text{or } \log_e D = -\frac{E_D}{RT} + \log_e D_o \qquad (5.15)$$

A graph between $\log_{10} D$ and $\frac{1}{T}$ is shown in Fig. 17.

An activation energy of diffusion E_D of 18.3 K cal.mole.$^{-1}$ is obtained, which, although high, is consistent with the low value of the diffusion coefficient for the orthophosphate ion.

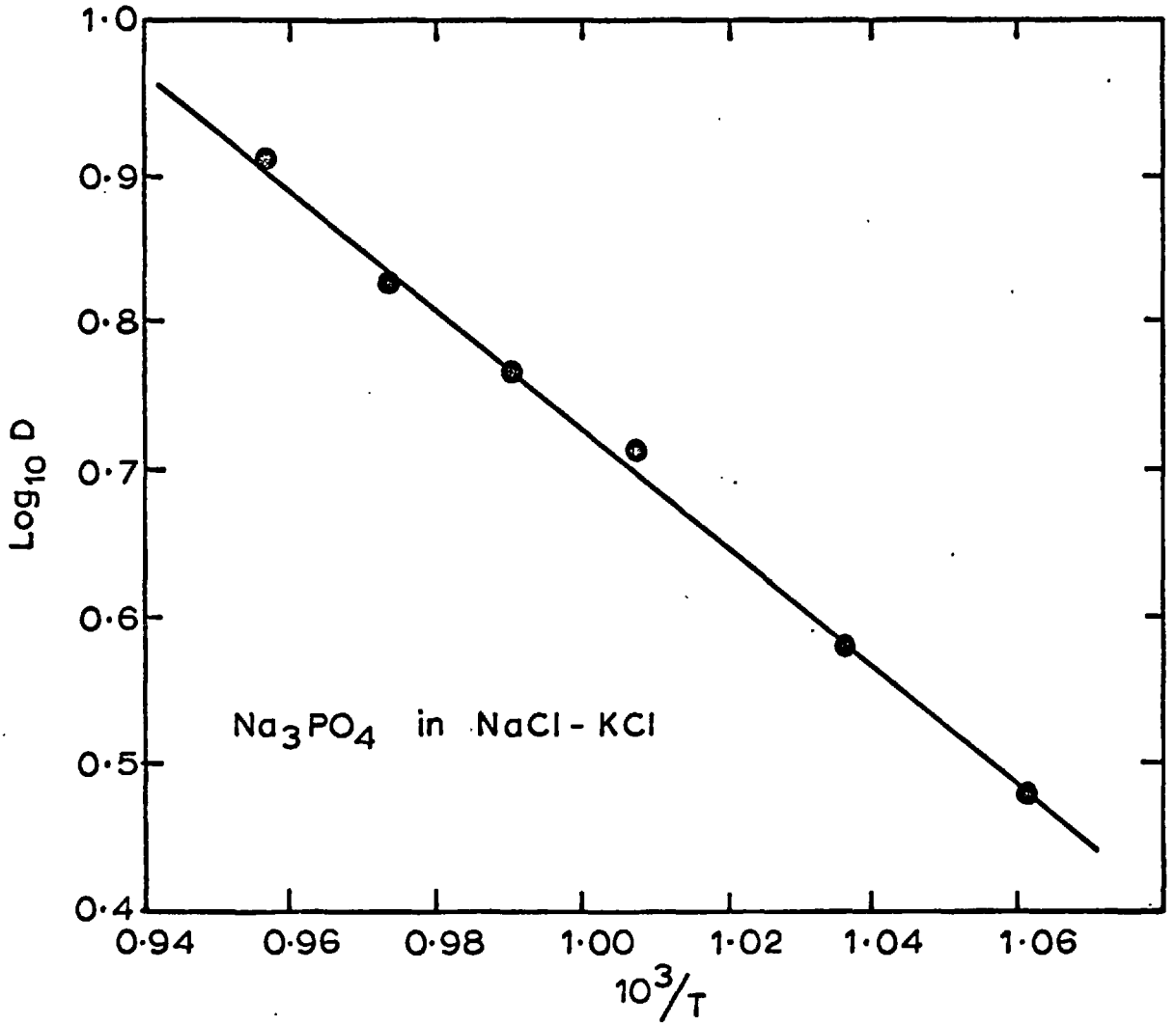


Fig.17. VARIATION OF DIFFUSION COEFFICIENT WITH TEMPERATURE

6. SPECIES IN MOLTEN PHOSPHATES

6.1. Reduction Potentials

It has been established that phosphorus is produced at a cathodic potential of approximately -0.7V to graphite. This corresponds to the reduction of the orthophosphate ion. The pyrophosphate ion is reduced at about -0.4V more cathodic and the tripolyphosphate ion is reduced at -0.8V more cathodic than the orthophosphate ion. Although all three processes are evident when either the metaphosphate or tripolyphosphate are dissolved in sodium-potassium chloride, it would appear that only the processes occurring at -0.7V and -1.5V are present in the molten metaphosphate (See Fig. 9). This would seem to indicate very rapid reaction of the pyrophosphate ion and the most probable reaction is

$$P_2O_7^{4-} + O^{2-} = 2PO_4^{3-} \qquad (6.1)$$

A further reaction is

$$2P_2O_7^{4-} = PO_4^{3-} + P_3O_{10}^{5-} \qquad (6.2)$$

This loss of pyrophosphate would seem to occur even in molten pyrophosphate since Francis (7) obtained decomposition potentials of -1.5V and -2.2V for this melt at 930°C. The -1.5V was identified as the process producing phosphorus and it was suggested that sodium was produced at -2.2V. However there was no evidence that sodium had been produced. In addition, the potential difference between the two processes is almost the

same as that found between the processes occurrring in the molten metaphosphate melts.

6.2. Orthophosphate in metaphosphate melts

In the examination of phosphate glasses by quenching followed by hydrolysis and paper chromatography (32, 33, 37) negligible amounts of orthophosphate have been found in sodium phosphate glasses.

The transition times found by chronopotentiometry for the orthophosphate in sodium metaphosphate melts (Table 6) were used to estimate the amount of orthophosphate present at various temperatures. In order to determine the concentration of the orthophosphate, its diffusion coefficient in the metaphosphate melt must be known; a value of 1×10^{-6} cm.^{2} sec.$^{-1}$ at 780°C was used. This corresponded to the value found for silver ions in molten borates (39) of comparable viscosity to the metaphosphate at that temperature. Diffusion coefficients at other temperatures were then calculated from the Stoke-Einstein equation (4.15). Using the equilibrium values of $i\tau^{\frac{1}{2}}$ (orthophosphate transitions) shown in Table 6 (Section 4.4.) the following results were obtained:

TABLE 17

Concentrations of Orthophosphate in Metaphosphate melts

Temperature °C	D $cm.^2 sec.^{-1}$	$i\tau^{\frac{1}{2}}A$ $cm.^2 sec.^{\frac{1}{2}}$	C $mole.cm.^{-3}$
680	0.34×10^{-6}	0.20	1.93×10^{-3}
720	0.54	0.35	2.61
750	0.77	0.55	3.53
780	1.0	0.85	4.95

The increase of orthophosphate ion can be considered as the measure of depolymerisation occurring in the molten metaphosphate. If the concentrations of the orthophosphate are taken as the equilibrium values of the monomeric phosphate ion, the temperatures correspond to that temperature at which the monomer is thermodynamically stable. This is known as the ceiling temperature T_c (40).

The concentration of the monomer and the ceiling temperature are connected by the following equation:-

$$\text{Log}_{10}[m_1] = \frac{\Delta H_p}{2.303RT_c} - \text{Log}_{10}\frac{A_p}{A_d} \qquad (6.3)$$

Where ΔH_p = heat of polymerisation

A_p = frequency factor for polymerisation

and A_d = frequency factor for depolymerisation.

$[m_1]$ = conc. of monomer - molar

The entropy of polymerisation is given by

$$\Delta S^{\circ}_{p} = R \log_{e} \frac{A_p}{A_d} \quad (\text{for } [m_1] = 1M) \qquad (6.4)$$

Fig. 18 shows the relationship between monomer concentration and melt temperature. From this, the heat of polymerisation is 19.1 Kcal.mole.$^{-1}$ and $\frac{A_p}{A_d}$ is $10^{-4.5}$ which would give an entropy of polymerisation of about -20 cal.mole.$^{-1}$. These values are comparable with those found for polymeric reactions (40). For depolymerisation the heat of reaction is endothermic and the entropy becomes positive

$$\text{i.e. } \Delta G_d = 19.1 \times 1000 - T \times 20 \qquad (6.5)$$

this gives equilibrium at T = 950°K and depolymerisation can occur in the temperature range used for molten phosphates.

For the orthophosphate ion in sodium metaphosphate, 1M is approximately equivalent to 5 per cent by weight. Using the values determined from equation (6.3) 1M concentration occurs at a temperature of about 900°K, whereas the equilibrium concentration at 640°K is 10^{-2}M.

A possible explanation for the large variation between the chronopotentiometric and the chromatographic values of the orthophosphate present in the molten phosphate is the removal of the monomer by polymerisation during quenching.

The formation of monomer has been assumed to occur from a

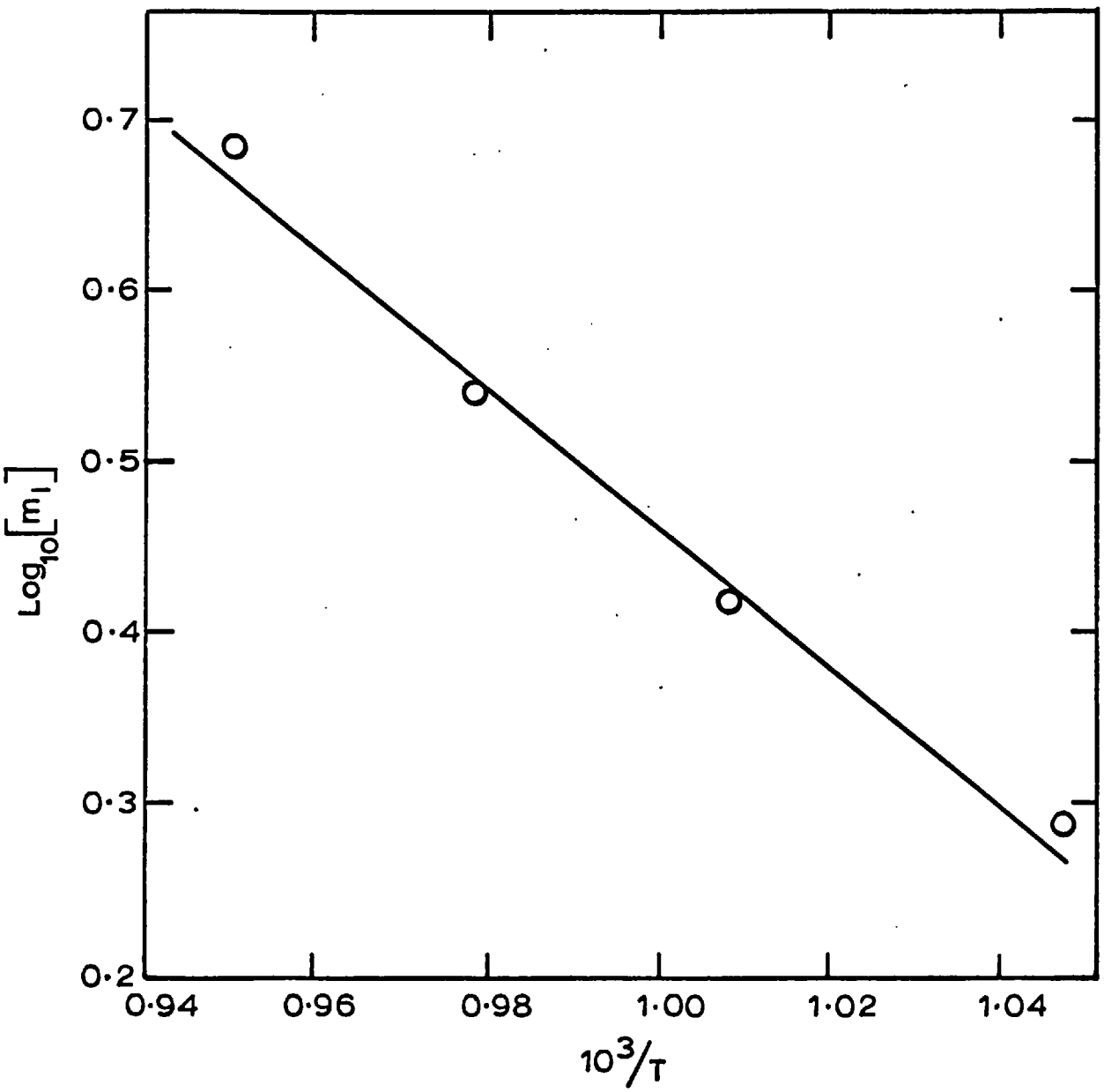


Fig.18. VARIATION OF MONOMER CONCENTRATION WITH TEMPERATURE.

series of reactions of the type (40)

$$m_n \underset{k_p}{\overset{k_d}{\rightleftharpoons}} m_{n-1} + m_1 \qquad (6.6)$$

or overall

$$\sum m_n \rightleftharpoons \sum m_{n-1} + m_1 \qquad (6.7)$$

If this can be related to the prior chemical reaction occurring in metaphosphate melts the values of the equilibrium constant K_d and velocity constants k_d and k_p can be estimated.

Using the results shown in Fig. 10, $\frac{d(i\tau^{\frac{1}{2}})}{di}$ is approximately equal to -0.8

$$\text{Hence} \frac{\pi^{\frac{1}{2}}}{2} \cdot \left(\frac{1}{K_d(k_d+k_p)^{\frac{1}{2}}} \right) = 0.8 \qquad (6.8)$$

By comparison with the theoretical curves derived by Delahay and Berzins (29) these results would be given by $K_d = \frac{1}{10}$ $k_d = 10$ sec.$^{-1}$ $k_p = 100$ sec.$^{-1}$ for the depolymerisation reaction, assuming a first order reaction. The loss of monomer on cooling is due to the polymerisation reaction and the half-life period for a first order reaction is given by

$$t_{\frac{1}{2}} = 2.303 \log_{10} 2/k_p \qquad (6.9)$$

This gives a $t_{\frac{1}{2}}$ value of 7×10^{-3} secs.

The maximum rate of cooling when quenching the phosphate glasses was quoted as 400°C per second by Meadowcroft (37). Thus to drop from 1000K to 640°K would take about one second which may well be above that rate required to remove the monomer by polymerisation. The rate of reaction also agrees with Van Wazer's (17) estimate that liquid sodium phosphates in the viscosity range of 1 poise will equilibrate in a fraction of a second.

7. CONCLUSIONS

7.1. Sodium phosphate glasses are cationic conductors.

7.2. In the highly polymerised sodium metaphosphate melts it is the low polymer phosphate ions that appear at the cathode and can be reduced at potentials more anodic than the sodium ion reduction.

7.3. The orthophosphate, pyrophosphate and tripolyphosphate ions are reduced at increasingly cathodic potentials; the processes occur at intervals of approximately 0.4V.

7.4. In the electro-reduction of phosphate ions the pentavalent phosphorus is reduced to trivalent phosphorus. The final electrode products, however, may result from further chemical reactions cf. the production of phosphorus occurring in the reduction of the orthophosphate ion.

7.5. There is considerable depolymerisation of phosphate melts, particularly above 750°C.

7.6. Depolymerisation is greatly increased by dissolving the phosphates in halide melts.

8. FUTURE WORK

8.1. Diffusion coefficients in molten sodium metaphosphate

Polarographic studies (10, 11) have been carried out on metal oxides dissolved in molten metaphosphate. However, these established the electro-reduction processes for the metal oxide and did not give data on the solvent. It is proposed to determine the diffusion coefficients for metal ions in the metaphosphate using chronopotentiometry.

8.2. Examination of glassy melts by chronopotentiometry

Phosphate glasses can be examined by hydrolysis followed by paper chromatography. Silicates and borates, however, do not retain their structure on hydrolysis. Chronopotentiometry carried out on sodium borates and silicates may indicate the presence of lower polymers as in the case of the phosphates.

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Technical note

Transport measurements in molten sodium metaphosphate

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Technical notes

Transport measurements in molten sodium metaphosphate

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541.135.3

Molten metaphosphates have been employed as solvents in studies of electrode processes and reactions.[1-4] The limiting electrode processes are generally thought to be the formation of phosphorus at the cathode and the evolution of oxygen at the anode.[3,4] Molten sodium metaphosphate should behave as a cationic conductor, in common with the other polyoxyanionic melts, e.g. silicates and borates. In this investigation the transference number of the sodium ion has been determined by measurements of the Na–P ratios of phosphate glasses in the anode and cathode compartments of electrolysis cells.

The experiments were carried out under atmospheric conditions using a Hittorf method. The anolyte and catholyte (each ~3 g) were kept in separate alumina pots in a vertical tube furnace; the pots were connected by a porous aluminosilicate 'U' bridge which was impregnated with sodium metaphosphate (see Fig. 1). Platinum anodes and tungsten cathodes were used. Anhydrous sodium trimetaphosphate was supplied by Albright and Wilson (Oldbury).

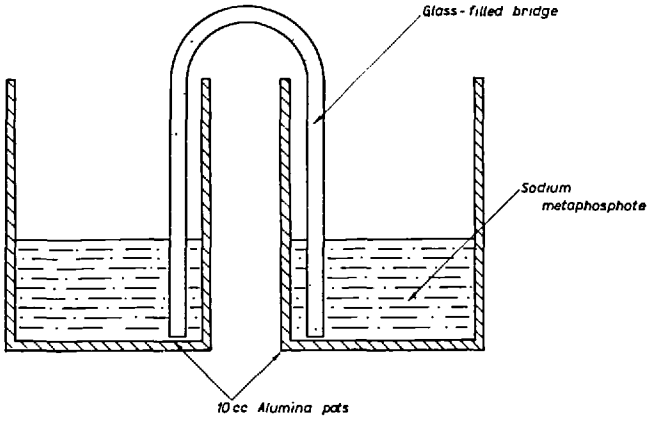


Fig. 1 Electrolysis cell

The temperature of the furnace was raised to 700°C (measured by a chromel–alumel thermocouple). After one hour at this temperature the electrodes were lowered into the melts and electrolysis commenced. At an applied emf of 4 V the current was ~35 mA. Milliammeter readings were taken every 15 min during electrolysis in order to determine the total charge passed. The current was sufficiently constant for an external coulometer not to be necessary for these preliminary measurements. After electrolysis and after removing the bridge and electrodes from the hot furnace the alumina pots were removed separately and the melts poured on to aluminium sheets. The anode and cathode glasses were analysed by hydrolysing with 0·1 N sulphuric acid and by titrating the resulting solutions with sodium hydroxide[5] using pH as the indicator. Typical results are shown in Fig. 2.

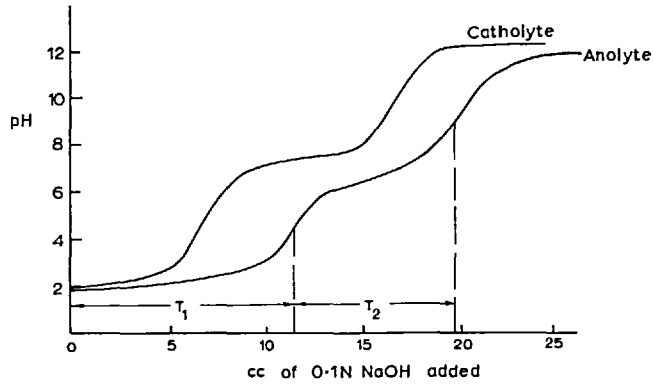


Fig. 2 Typical titration curve for hydrolysed glass. 10 cm^3 of 0·1 N H_2SO_4 was used to hydrolyse 0·100 g glass

$$R = Na\text{–}P = \frac{10 - T_1 + T_2}{T_2}$$

The changes in the Na–P ratios (R) of the anolyte and catholyte glasses on electrolysis can be related to the movement of sodium ions from the anolyte to the catholyte and the loss of phosphorus (by electrolysis) from the catholyte. On the basis of previous work, the electrode reactions for the metaphosphate composition may be assumed to be for the transfer of one electron

Anode $\quad \frac{1}{2}Na_2O.P_2O_5 - e \rightarrow Na^+ + \frac{1}{2}P_2O_5 + \frac{1}{4}O_2\uparrow$

Cathode $\quad \frac{1}{10}Na_2O.P_2O_5 + e \rightarrow \frac{1}{5}Na^+ + \frac{1}{5}P + \frac{3}{5}O^{2-}$

Thus if the transport number of the sodium ion is unity, the overall cell reaction will be

$$\frac{3}{5}Na_2O.P_2O_5 \rightarrow (\underset{\text{Catholyte}}{\frac{3}{5}Na_2O + \frac{1}{5}P}) + (\underset{\text{Anolyte}}{\frac{1}{2}P_2O_5 + \frac{1}{4}O_2\uparrow})$$

and the catholyte will become more basic and the anolyte more acidic.

In calculations based on the postulated cell reaction above, however, it was necessary to allow for the acid–base reaction between the alumina containers (the base) and the acid constituent, P_2O_5, of the melts. A precipitate containing only aluminium and phosphate was obtained when the *electrolysed* glasses were hydrolysed. The quantity of aluminium in a typical sample of electrolysed glass (determined by the 8-hydroxyquinoline method) was 12 wt per cent. This result is consistent with the formation of $Al_2O_3.2P_2O_5$ (this actually contains 14 per cent of aluminium, but the agreement is satisfactory having regard to the difficulties inherent in the precipitation, which is very dependent on pH). The presence of tungsten and an oxidizing atmosphere leads to the formation of

$Al_2O_3.2P_2O_5$ even without electrolysis. Because of this reaction the glasses were more basic than originally expected. There was no P_2O_5 in the gases evolved from the anolyte; phosphorus is therefore not lost in this way. The attack on the alumina crucibles mainly occurs at the three-phase boundary. The quantity of alumina removed during electrolysis was determined and the calculations shown below performed.

If a and c are the moles of $NaPO_3$ ($= \frac{1}{2}(Na_2O.P_2O_5)$) in the anolyte and catholyte respectively before electrolysis and n is the number of Faradays of electricity passed during the electrolysis, then the R values after the electrolysis should be

$\frac{a - nt^+}{a - 4m_a}$ for the anolyte and $\frac{c + nt^+}{c - 0{\cdot}2n - 4m_c}$ for the catholyte, where m_a and m_c are the moles of alumina lost from the anode and cathode pot respectively. The R values for the glasses after electrolysis were determined and t^+ (the transport number of the sodium ion) was calculated. The values obtained are shown in Table 1.

Table 1 Analysis of anode and cathode glasses after electrolysis

Faradays passed $\times 10^3$, n	Moles of glass used $\times 10^3$, a	Moles of alumina lost $\times 10^3$, m_a	R (from titration)	nt^+ (calculated from R)	t^+
Anolyte					
3·60	29·4	1·37	1·09	3·4	0·95
5·39	39·7	1·96	1·14	5·1	0·95
6·25	29·0	1·55	1·00	6·2	0·99
5·38	25·5	1·76	1·10	5·2	0·97
2·84*	31·7	—	0·92	2·5	0·90
n	a	m_c	R	nt^+	t^+
Catholyte					
3·60	30·7	1·86	1·52	3·5	0·97
5·39	31·3	2·33	1·74	5·0	0·93
6·25	31·6	2·05	1·72	6·3	1·01
5·38	25·2	1·86	1·83	5·4	1·00
2·84	25·9	0·74	1·28	2·7	0·96

*A platinum crucible was used as the anolyte container for this run. The low value of t^+ obtained may result from the electrochemical oxidation of the platinum and the subsequent reaction with the melt; this is equivalent to some phosphorus removal. During the run 54 mg of platinum were lost.

If the result using a platinum crucible is disregarded, a mean value of 0·97 is obtained for t^+. Thus the molten phosphate glass (1 : 1 acid : base ratio) can be regarded as a wholly cationic conductor.

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Discussions and contributions

Quality control of electrolytic tough pitch copper

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Report of discussion at April, 1967, general meeting (Chairman: Mr. R. H. MacWilliam, President), contributed remarks and authors' reply. Paper published in *Transactions/Section C (Mineral processing & Extractive metallurgy)* vol. 75, December, 1966, pp. C269–85

Dr. G. Armstrong Smith first apologized for the absence of his co-author, Mr. K. E. Mackay, who very much regretted being unable to attend the meeting in person. Introducing the paper, Dr. Armstrong Smith said he would like to make two minor corrections: on page C278, top of second column, the signs of the multiple correlation coefficients should be reversed. It was one of those things which could be looked at either way, but as selenium and sulphur decreased elongation their multiple correlation coefficients should be negative, not positive; lead, conversely, should be positive. On page C279, line 9, 1300 should read 130.

The paper was an account of some of the measures used for the control of quality of electrolytically refined copper falling into the higher commercial brackets by present-day standards. It was thought opportune to review the subject because of the remarkable advances in quality achieved by a significant number of primary producers over the last few years. Quality had improved to an extent where its determination was posing problems of no small magnitude but, unless one had sufficiently accurate and dependable means of assessing it, there could be little control of one's product and, perhaps as important, the effect of small changes to plant practice could not be properly evaluated. At the same time, he thought numerous fabricators were finding it increasingly difficult to distinguish between different consignments or even different brands, although differences did exist. To some, the small differences involved might appear academic; to others they were not so, and he felt that their importance was bound to grow.

Imitating the historian's penchant for dividing everything into ages or epochs, one was tempted to think of the evolution of high-grade copper as falling into three periods. First, the pre-1913 era, when it could be said that the term 'refined copper' was very much a euphemism by today's meaning of the phrase. Kelvin, it would be remembered, blamed the poor performance of the early trans-Atlantic cables on impure copper, thus creating a demand for high-conductivity metal.

1913 could be taken as marking the start of a second era when the International Electro-technical Commission decided to adopt a standard value for the resistivity of high conductivity copper, calling it the International Annealed Copper Standard (I.A.C.S.). That standard still held today as the datum value against which they measured conductivity. (In passing, it might be noted that the unfortunate use of a density of 8·89 g/cm^3 for wrought tough pitch copper by the Commission meant that per cent mass conductivity was usually not now the same as per cent volume conductivity and that difference sometimes gave rise to some confusion.) The establishment of a conductivity standard did have important consequences in that refiners strove to reduce impurities and obtain better control of their refining processes to meet the specification. By the mid 1950s there could have been few major brands not averaging 101 per cent conductivity or higher.

The third and present stage owed its origin, in the main, to a demand from the fine-wire fabricators for copper pure enough to soften or recrystallize at an acceptably low temperature. No fixed date could be set to that new era but, so far as the industry was concerned, it might conveniently be put at 1959 when the Institute of Metals at its Autumn Meeting in Stockholm organized a symposium on problems connected with fine-wire manufacture. Since then, and especially during the last 3–5 years, the focus of attention on impurities deleterious to softening had brought about a quite astonishing improvement both in purity and consistency of much of the copper on the market. Other factors undoubtedly played their part in that change, such as adoption of automated fabrication processes, more sophisticated applications of copper and, not least, a growing awareness by progressive primary producers of the prestige value attached to a brand that earned a reputation for consistent purity. But, relatively small as the demand for fine wire had been and still was, it was enough to change drastically refinery standards of purity and to promote the development of practical tests, such as the spiral-elongation and others, for gauging the effect of impurities.

The spiral-elongation test described in the paper had much to recommend it and appeared to be ousting others in copper circles, at any rate outside the U.S.A.; but he was personally still of the opinion that attempts to create a rigid standard value for the test such as was done for electrical conductivity were likely to fail. There were too many factors operating against that. Both fabricator and producer needed to choose empirically those conditions for the test that would give them the most profitable data for their domestic needs.

Oscar Wilde said of truth that it was rarely pure and never simple. Reversing those adjectives, it could be stated that, however high the grade, copper was never pure and the assessment of its purity rarely simple. But the purity of the top grades of commercial etp copper did seem to be approaching an asymptotic point where progressively greater effort was required to produce progressively smaller improvements. Whether much further advance was practicable, he thought was open to question. It was hoped, however, that the present paper would give some idea of the efforts now being made to maintain and, where possible, to improve the quality of primary electrocopper.

A. B. Ashton* said that he spoke from the point of view of the fabricator. He was glad that Dr. Armstrong Smith had put things in an historical perspective. He would add that copper production had originally evolved as an art and it was only in the present century that technology had grown upon that art. Copper presented a marked contrast in that respect with aluminium for the latter metal was entirely a product of the technological age. He regarded the present paper as something of a milestone in the application of technology to copper production.

In passing he would like to take the opportunity to compliment not only the authors but copper refiners in general. It was remarkable that so many primary producers in different parts of the world, operating under different climatic conditions, with widely different grades of labour and often remote from centres of scientific aid, had succeeded in producing high-conductivity copper to very high standards of uniformity and purity. There were some differences in trace impurity contents, however, and, under modern conditions of usage, those differences were significant. Modern conditions were becoming more and more sophisticated and were such that quite small trace impurities were important practically.

The paper devoted, very properly, much of its space and time to analytical procedures and emphasized that the properties of coppers were influenced significantly by quantities of impurities which were very near the limits of available instruments. That in itself was a comment on the high qualities which primary producers were attaining. The account of the analytical procedures was so thorough that it gave one a confidence in the conclusions drawn in the paper in respect of those compositions. It was very interesting to see that the paper named selenium as the 'naughty boy' of the whole family of impurities and that too was an indication of progress because not long ago it was firmly believed by all copper fabricators that silver was the principal element influencing the recrystallization behaviour.

The account of the method of measuring electrical conductivity rightfully stressed the many precautions which had to be taken in measuring that property. He could not help raising a little cudgel on behalf of the fabricator in one respect. The paper pointed out that in the results given in Table 2 (p. C273) there

*Frederick Smith and Co., Manchester.