

MASS TRANSFER IN THE
ELECTROLYSIS OF FUSED SALTS

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A B S T R A C T

A review is presented of the published studies of the use of molten salt electrolysis in the refining of metals. The expression of the results of transport measurements in fused salts is discussed and the friction coefficient formalism is described.

A theoretical analysis of the behaviour of an anode impurity in electrolysis is given and a solution is obtained for certain simple boundary conditions. A refinability parameter β is obtained which describes the behaviour of the impurity. If β is less than 1 the impurity is concentrated in the anode; if β is greater than 1 the impurity is concentrated in the cathode. It is shown that there is a limit to the refining that can be achieved in any one system by raising the current density. At the limiting current density the refining ratio - the ratio of impurity in the cathode to impurity in the anode - is given by the parameter β . An approximate value of β may be readily obtained from thermodynamic and electrical conductivity data generally available in the literature.

The analysis has been extended to cover the effects of additions of diluting salts, whose cations do not take part in the electrode processes and a solution has been obtained for a simple batch refining process.

The transport of copper, silver and cadmium as anode impurities in lead has been studied, the electrolyte containing the mixed chlorides. The effect of adding sodium chloride to the melt has been investigated in the lead-copper and lead-cadmium systems. The predictions of the theory are confirmed in the lead-copper and lead-silver systems although there are some differences between the predicted and experimental refining ratios. These differences are due to approximations made in estimating β due to lack of data in the literature. The lead-cadmium system shows a considerable deviation from the predicted value and it is suggested that this is due to solution in the melt of cadmium deposited at the cathode.

The investigation has indicated that the ionic species responsible for the transport of copper and cadmium are Cu_2^{2+} and CdCl^+ respectively.

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CHAPTER I

INTRODUCTION

In this Chapter a general review is presented of electrolytic refining using molten salt electrolytes. The refining of lead, the metal chosen for this study, is examined in greater detail.

Three phenomena are used in aqueous electrolytic refining, namely :

- (i) activation overpotential at the cathode,
- (ii) concentration polarisation in the electrolyte,
- or (iii) complexing of the impurities

It was decided to work in systems in which complexing was absent because complexes are not generally as stable in fused as in aqueous media or as well understood. Evidence of complexing in fused salts is obtained from the presence of compounds in phase diagrams and from irregularities of conductance isotherms.

It will be shown in this Chapter that activation overpotential is generally absent where molten metal electrodes are used, and thus only concentration polarisation needs to be considered. In Chapter 2 this phenomenon is treated from the theoretical point of view and its effect on the transport of impurities is studied.

1.1 METALS FROM MOLTEN SALT ELECTROLYSIS

Since the alkali metals were first obtained early in the nineteenth century, there has been considerable interest in the possibilities of winning or refining metals by fused-salt electrolysis. The method has been applied (1.2) for the discovery or for the commercial preparation of many metals, among which are the alkali- and alkaline-earth metals, aluminium, zinc, lead and various refractory metals, as well as rare earth metals and many alloys. Tonnage production by fused salt electrolysis is, however, only carried out at present for the metals aluminium, boron, cerium and rare earths together as "mischmetall", lithium, sodium and tantalum. A list of metals obtained by electrolysis and the salts used is shown in Table I.

The processes for the extraction of metals by fused-salt electrolysis use an inert, or reducing, anode and a mixed halide electrolyte, the feed to the cell being the halide or oxide of the metal. The processes most widely used are those in which the

metal/...

metal is produced in a liquid form and is therefore easily separated from the melt. The method is also used for certain refractory metals solid at the temperature of operation - that are difficult to obtain by other techniques.

Examples of commercial electrowinning processes are the production of aluminium by the Hall-Héroult process, and the production of magnesium, sodium and calcium from their halide salts. Many other electrowinning processes have been proposed from time to time, such as the Ashcroft-Swinburne process for the extraction of zinc.

In the electrowinning process the cell feed is a compound of the required metal, which is reduced within the cell. Electrolysis is an expensive process so that refining is often done at the feed preparation stage and consequently the metal liberated is of such high purity that no further refining is necessary. Magnesium, for instance, is produced to a standard of 99.9% to 99.95% purity. When, however, the cathode metal requires further purification, molten salt electrorefining can be used. Impure metal resulting from other metalwinning processes can also be refined by means of this technique.

Electrorefining differs from electrowinning in that the feed to the cell is an impure metal instead of a compound of the metal and therefore no chemical reduction step takes place within the cell. This impure metal forms the anode of the cell and the pure metal is concentrated in the cathode when the conditions of operation are such that the impurities are not deposited at the cathode. It may be that a cell could refine the feed metal by concentrating the impurities in the cathode, thereby refining the anode. The conditions under which these refining processes take place are described in the next section.

1.2 REVIEW OF MOLTEN SALT ELECTROREFINING

1.2.1 Metals other than lead

Aluminium is the only metal refined by fused salt electrolysis on a tonnage basis. The metal is too reactive to be refined by the controlled oxidation of impurities, and has too high a boiling point to be refined by distillation. Commercially, it is refined by a molten salt refining process often described as the 'three-layer' process. The density of the impure aluminium is increased by alloying with copper so that it forms a

relatively/...

TABLE I COMPOUNDS FROM WHICH METALS HAVE BEEN ELECTROWON

<u>COMPOUND</u>	<u>METAL DEPOSITED</u>
<u>Halides</u>	
BeCl ₂	Beryllium
KBF ₃	Boron
CaCl ₂	Calcium
Rare-earth chlorides	Cerium and rare earths
K ₃ CrF ₆	Chromium
K ₂ HfF ₆	Hafnium
LiCl	Lithium
MgCl ₂ · 1.25H ₂ O	Magnesium
K ₃ MoCl ₆	Molybdenum
K ₂ NbF ₇	Niobium
NaCl	Sodium
K ₂ TaF ₇	Tantalum
ThCl ₄	Thorium
K ₂ TiF ₆	Titanium
UF ₄	Uranium
K ₂ ZrF ₆	Zirconium
<u>Oxides</u>	
Al ₂ O ₃	Aluminium
CeO ₂	Cerium
MoO ₂	Molybdenum
Nb ₂ O ₅	Niobium
Ta ₂ O ₅	Tantalum
WO ₃	Tungsten
UO ₂	Uranium
<u>Minerals</u>	
Chromite (FeCr ₂ O ₄)	Ferro-chromium
Galena (PbS)	Lead
Serpentine (H ₄ Mg ₃ Si ₂ O ₉)	Magnesium
Scheelite (CaWO ₄)	Tungsten

relatively dense molten anode. The electrolyte - basically a mixture of aluminium fluoride and other halides - floats on top of the anode, but its density is greater than that of pure aluminium. Thus the purified aluminium cathode can form a third layer, floating on the electrolyte. The method is adequately described in standard texts (see, for example, Mantell (1)). Details of the electrolyte compositions and conditions used are shown in Table 2.

Attempts have been made to adapt this three-layer method to the refining of magnesium and its alloys (3-5) and experiments have been carried out on a semi-industrial scale (3), using currents of up to 2000 A. The anode density has been increased by additions of copper, zinc or zinc and aluminium together. The process has been shown to work satisfactorily, but it is not yet in general commercial use.

Several electrolytic mixtures have been used in the electro-refining of beryllium. Menzies et al (6) for example, used $\text{LiCl} - \text{KCl} - \text{BeCl}_2$ or $\text{NaCl} - \text{BeCl}_2$ melts. Wong et al (7-10) also used mixtures of LiCl and KCl with BeCl_2 , finding that the purity of the cathode metal increased with the concentration of BeCl_2 in the electrolyte but that the cathode current efficiency fell. Between 450 and 550°C maximum current efficiencies of about 92% were obtained. Wong and O'Keefe (10) developed a two-stage refining process in which the Be flakes from the first-stage cathode were used as feed for the second cell. The resulting Be was spectographically pure, except for 35 p.p.m. of calcium.

Bjorklund et al (11) found that plutonium could be refined electrolytically in baths containing eutectic mixtures of PuCl_3 with alkali chlorides. The anode is a rod from a plutonium reactor, and solid purified metal is deposited on an iron cathode. In the method developed by Mullins et al (12,13), the Lamex process, which operates at a higher temperature so that liquid metal is deposited, a perforated tungsten cathode is used. The electrolyte is a mixture of potassium and sodium chlorides with plutonium fluorides and chlorides. The cell design is illustrated in Fig. 1 taken from reference (12). The impure molten anode is held in a central cylindrical container

and the/...

TABLE 2 ELECTROLYTIC REFINING PROCESSES FOR ALUMINIUM (1)

	Hoopes' Process	Gaddeau Process	Aluminium Industrie A.G.
Electrolyte : wt. %			
AlF_3	30 - 38	23	48
NaF	25 - 30	17	18
BaF_2	30 - 38		18
BaCl_2		60	
CaF_2			16
Density, g/cm^3	2.5 at 1000°C	2.7 at 740°C	2.5 at 740°C
Electrical resistivity $\Omega \text{ cm}$	0.3 at 1000°C	0.75-0.85 at 740°C	1.1 at 740°C
Anode layer: wt. %			
Al	75	67	70
Cu	25	33	30
Density, g/cm^3	2.8 at 1000°C	3.14 at 740°C	3.05 at 740°C
Cathode layer:	Pure Al	Pure Al	Pure Al
Density, g/cm^3	2.29 at 1000°C	2.3 at 740°C	2.3 at 740°C
Cell characteristics:			
Temperature, $^\circ\text{C}$	900 - 1000	740	740
Voltage	5 - 7	6 - 7.5	5.5 - 5.8
Amperage	20,000	25,000	14,000
Current density, A/cm^2		0.40	0.36
Current efficiency, %		96 - 98	93
Purity of product, % Al	99.90 - 99.98	99.99 +	99.99 +

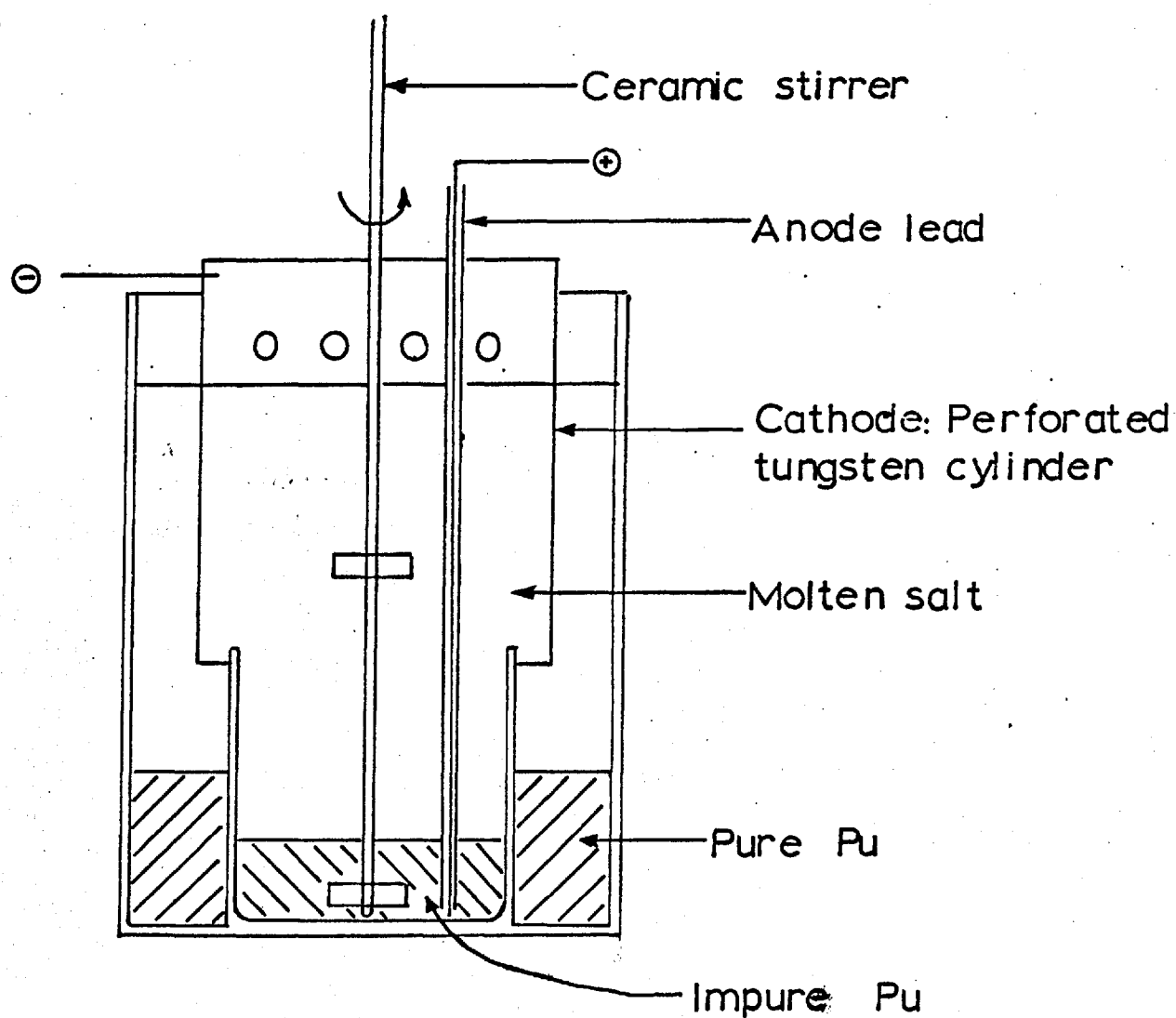


FIG.1 THE LAMEX PROCESS : ELECTROREFINING CELL

and the cathode is a perforated tungsten tube placed above and concentric with the anode compartment. The cathode diameter is larger than that of the anode and the purified Pu flows down the cylinder, being collected in the annular space between the anode compartment and the outer container. The cell has been operated at 740°C under an argon atmosphere, producing 250 g. of pure plutonium in one hour.

Other cells for the separation of plutonium and uranium have been reported (14) with molybdenum or tantalum cathodes, and Benedict and Pigford (15) developed an ingenious method of separating plutonium and other fission products from irradiated uranium by anodic dissolution in a molten mixture of calcium and uranium chlorides. In this case uranium metal is deposited on a manganese cathode and the manganese is subsequently removed by a vacuum distillation. Fission products - mainly Zr, Nb, Mo, Ru and Rh - pass into the anodic sludge and Pu remains dissolved in the melt, from which it is later distilled as a volatile chloride.

Commercial uranium is produced by oxide reduction with magnesium. Sullivan et al (16, 17) developed a method whereby it is subsequently electrolytically refined using $\text{NaCl} - \text{UCl}_3$, $\text{LiCl} - \text{KCl} - \text{UCl}_3$ or $\text{NaCl} - \text{KCl} - \text{UCl}_3$ melts; solid U is deposited on a Mo cathode. Chauvin and his co-workers (18) refined U in a $\text{KCl} - \text{LiCl}$ melt containing up to 30 wt. % of UCl_3 . The cell operates at $450 - 500^{\circ}\text{C}$ under an argon atmosphere and the metal is deposited on a Mo cathode.

Sibert (19) described a method for the production of niobium in which Nb_2O_5 is reduced with carbon at high temperatures, and the product is electrolytically refined using a molten mixture of K_2NbF_7 and alkali chlorides. Steinberg (20) has used a similar method, starting with mixtures of Ta_2O_5 and Nb_2O_5 , in which a molten salt refining process served to separate the niobium from the tantalum.

Impure metallic vanadium has been refined using molten electrolytes of sodium and vanadium chlorides, a laboratory process having been operated at 800°C under a helium atmosphere and with a cathodic current efficiency of about 91% (21). High purity vanadium has also been obtained by electrefining com-

mercially/....

mercially produced metal using an electrolyte of sodium and potassium bromides containing vanadium bromide (22).

The molten salt electrorefining of tungsten, titanium and zirconium has been investigated. Cattoir (23) refined tungsten using melts of LiCl and KCl containing $\text{Na}_2\text{B}_4\text{O}_7$. A series of papers (24) has been published in Russia on the electrolytic refining of titanium using fused chloride mixtures. Kleespie and Henrie (25) studied the transfer of impurities in titanium electrorefining. In his review of the electrolysis of titanium Kroll (26) reported an experimental process for refining. The soluble anode for this process can be made from a range of Ti - containing materials, including 50-50 ferrotitanium. The refining of zirconium has been studied by Baker et al (27) in a sodium chloride melt containing K_2ZrF_6 , and by Smirnov et al (28) in chloride and chloride-fluoride melts. Sheiko et al (29) studied the anodic dissolution of Zr in NaCl - KCl melts.

Nettle et al (32) reported experiments on the refining of hafnium using various molten electrolytes containing HfCl_4 , K_3HfCl_4 or K_2HfCl_6 .

Morachevskii (30) reported that Sazhin and co-workers had studied the purification of antimony by anodic dissolution of the impurities in molten NaCl - KCl.

The electrorefining of thorium has been investigated by Noland (31) using LiCl - KCl mixtures containing ThCl_4 or ThF_4 . The cells were operated under inert atmospheres and used molybdenum cathodes.

1.2.2 The Commercial Electrolytic Refining of Lead

Crude lead is purified commercially by a complex metallurgical process finishing with electrodeposition from aqueous electrolytes.

It may well be that molten salt electrorefining offers a cheaper method. Such a process was developed by Borchers at the turn of the century (2). The cell feed for this process was molten crude lead and the electrolyte was a mixture of lead oxichloride with potassium and sodium chlorides.

The high density of lead ($\sim 10.7 \text{ g/cm}^3$ at 800°K) makes it impossible to use a three-layer process, and so a different cell design was developed (Fig. 2). The cell was operated at

$550^\circ\text{C}/..$

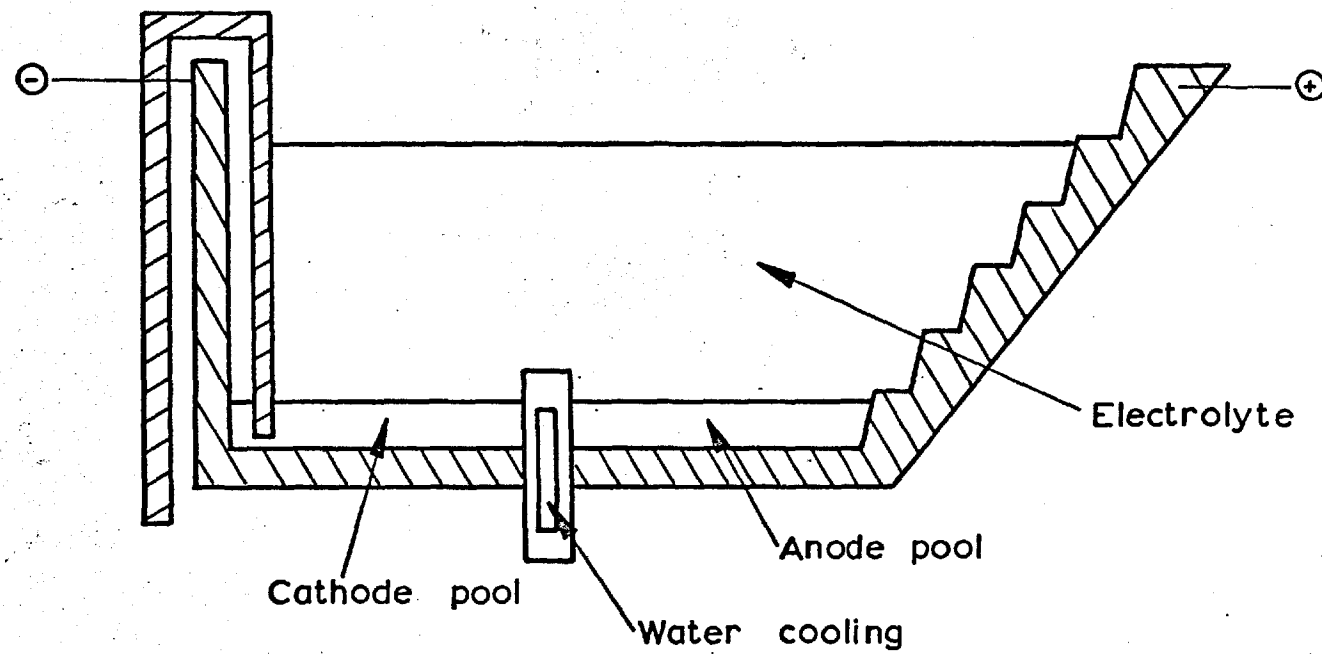


FIG. 2. BORCHER'S CELL

550°C and at a cathodic current density of 1 A/cm². The molten electrodes were separated by a water-cooled insulating joint which was surrounded and protected by a coating of solidified salt. The anode side of the electrolyte cell was sloped and had a series of deep horizontal platforms which served to retain some of the crude molten lead feed. Purified lead was siphoned off from the cathode pool. Borchers' process received no encouragement and is no longer in use owing to the concentration of lead sulphide impurities in the melt causing a rise in operating temperature.

1.2.3 The transference of impurities during electrolytic lead refining

Delimarskii and his co-workers in Russia have carried out extensive investigations into the transfer of impurities from crude lead anodes during molten salt electrolysis. Electrolytes used have included chlorides, silicates, silicate-chloride mixtures and fused sodium hydroxide. Temperatures of operation varied between 350°C and 1000°C.

Refining has been carried out to separate binary alloys of lead with Bi, Sb, As and Sn (33) and also Au (34) using lead chloride and NaCl - KCl eutectic mixtures.

More precise experiments concerning the transfer of Ag and As, which are not completely removed by the furnace refining of crude lead, were carried out by Gitman and Delimarskii (35). Radio-isotopes of Ag and As were used in preparing binary alloys with lead, and mixed chloride melts, PbCl₂ - NaCl - KCl, were used. The electrolyses were performed at differing current densities, with differing silver contents in the anode, and with differing degrees of extraction of lead from it and it was found that most of the silver remained in the anode. The same was found to be true for the alloys containing As, although some As was lost overall - perhaps due to evaporation from the electrolyte as AsCl₃, which boils at 130°C.

Commercial-scale refining of lead from factory crudes was shown to be possible in the eutectic compositions PbCl₂ - KCl - NaCl, PbCl₂ - NaCl and PbCl₂ - PbO (36) at 500°C, with a cathodic current density of 1 A/cm² and varying degrees of recovery as cathodic lead. The cathodic current efficiency was 97-98% and

the elements/...

the elements Bi, As, Sn, Ag and Zn were substantially removed. The removal of Cu and Sb, when present in substantial amounts, was not very satisfactory.

Preliminary experiments into the use of electrolytes containing silica have been reported (37). Four compositions were used - $\text{Na}_2\text{O} \cdot 2\text{PbO} \cdot 3\text{SiO}_2$, $\text{Na}_2\text{O} \cdot \text{PbO} \cdot \text{SiO}_2$, $\text{PbO} \cdot \text{SiO}_2 \cdot \text{PbCl}_2$ and $2\text{PbCl}_2 \cdot \text{PbO} \cdot \text{PbSiO}_3$ - at temperatures between 580 and 1000°C, and varying conditions of electrolysis. The "refining power" of the process was altered by the changing amounts of Na_2O , PbO and PbCl_2 , because such additions "vary the relationship between the electrochemical properties of lead and of the metallic impurities."

The electrolytic separation of bismuth from lead using molten sodium hydroxide has been investigated (38,39). A complex intermetallic compound of the form $\text{Na}_x \text{Pb}_y \text{Bi}_z$ is thought to be formed at the cathode which is subsequently oxidised at the liquid lead anode. Pure Pb was the anode and the Pb-Bi alloy was the cathode; electrolysis produced pure Pb on the cathode and a Pb-Bi alloy with up to 70% Bi on the anode. Obviously such a process can be regarded as an anode purification process for bismuth, as well as a cathode purification process for lead. Delimarskii has also studied the removal of Pb from Bi-Pb alloys using molten chloride electrolytes (50) as a means of obtaining bismuth.

The particular emphasis on the removal of Bi from crude lead was because Bi is the most difficult impurity to remove, since it is similar to lead in many of its properties. The substitution of experimental data into the theoretically derived "refinability parameter", Chapter 2, shows why Bi is so easily removed from Pb by electrolysis.

A further study of the feasibility of the refining of Pb in fused NaOH has been published (41). Cu, Bi and Ag remained in the anode, while As, Sb, Sn and Zn transferred to the electrolyte.

Delimarskii and his co-workers have not produced a theoretical analysis of their experiments.

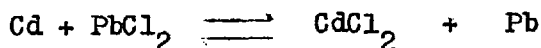
TABLE 3 REFINING OF LEAD USING MOLTEN SALT ELECTROLYSIS
 (after Delimarskii et al)

<u>Melt Composit- ions</u>	Impur- ities Studied	Position of impurities after electrolysis			<u>Ref:</u>
		<u>Anode</u>	<u>Electro- lyte</u> *	<u>Cathode</u>	
PbCl ₂ • NaCl. KCl	Bi, Sb, Sn, As	Bi, Sb, As	[Sn] [As]		33
PbCl ₂ • NaCl.	Au	Au			34
PbCl ₂ • PbO	Ag	Ag, As	[As]		35
	Bi, As,	Bi, As	[As]		36
	Sn, Ag,	Ag, Zn	[Sn]		
	Zn;				
	Cu, Sb	Sb, Cu	Sb, Cu	Cu, Sb	
Na ₂ O. 2PbO. 3SiO ₂	Bi, Sb, Ag, Cu	Bi, Cu, Ag	Cu	Bi, Cu	37
Na ₂ O. PbO. SiO ₂	Bi, Sb, Ag, Cu	Bi, Ag, Cu	Cu	Cu	
[PbO. SiO ₂ . PbCl ₂ 2PbCl ₂ • PbO. PbSiO ₃	Bi, Sb, Ag, Cu	Bi, Sb, Ag	Cu, Ag	Ag, Sb	
NaOH	Bi	Bi			38

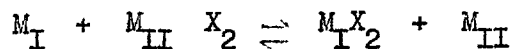
* Square brackets indicate probable volatilisation from the melt.

1.3 METAL - MOLTEN SALT EQUILIBRIA

In a fused salt refining cell the impurity metals in the anode "react" with the electrolyte and a double displacement reaction takes place, i.e.



In fused systems, a strictly reversible equilibrium is established (section 1.4). Consider a system of two divalent metals M_I and M_{II} and a halogen X. The liquid metallic phase consists of an alloy of the two metals and is in equilibrium with the liquid salt phase, which is a mutual solution of the two salts. The equilibrium reaction is :



and the mass action law can be applied.

Considering that the metals form atomic-molecular solutions in the fused salt (and do not dissolve by subhalide compound formation) we introduce the following designations:

$(M_I)_s$	concentration of M_I in the salt phase ;
$(M_{II})_s$	" " M_{II} " " " " ;
$(M_I X_2)_s$	mole fraction of $M_I X_2$ " " " " ;
$(M_{II} X_2)_s$	" " " $M_{II} X_2$ " " " " ;
$(M_I)_m$	mole (atom) fraction of M_I in the metallic phase;
$(M_{II})_m$	" " " " M_{II} " " " "

Considering the salt phase as a homogeneous system, then

$$K = \frac{(M_{II})_s (M_I X_2)_s}{(M_I)_s (M_{II} X_2)_s} \quad (1.1)$$

where K is the mass action law constant which could be derived from thermodynamic data. Unfortunately it is not generally possible to determine all the concentrations by chemical analysis. However the equation may be rewritten in a more practical fashion, using the Nernst distribution law which states that the ratio of the concentrations of the metal in the salt phase to that in the metallic phase should be constant (in terms of activity - the activity

of the/...

of the metal in both phases must be the same when the phases are in equilibrium), i.e.

$$\frac{(M_I)_s}{(M_I)_m} = K_1 \quad (1.2)$$

and
$$\frac{(M_{II})_s}{(M_{II})_m} = K_2 \quad (1.3)$$

by substitution in equation (1.1) we obtain

$$K' = \frac{(M_{II})_m (M_I X_2)_s}{(M_I)_m (M_{II} X_2)_s} \quad (1.4)$$

where
$$K' = \frac{K \cdot K_1}{K_2} \quad (1.5)$$

Putting
$$\begin{aligned} (M_I)_m &= x \\ (M_{II})_m &= (1-x) \\ (M_I X_2)_s &= y \\ (M_{II} X_2)_s &= (1-y) \end{aligned}$$

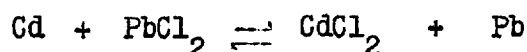
we can rewrite equation (1.5) as

$$K' = \frac{(1-x)y}{x(1-y)} \quad (1.6)$$

All the quantities on the R.H.S. of equation (1.6) can be determined experimentally (e.g. by chemical analysis)

The quantity K' in equation (1.6) is used in Chapter 2 (where it is designated K) and represents a combination of the equilibrium constant from the mass action law and of the constants from the Nernst distribution law. For simplicity, K' is usually referred to as the equilibrium constant, with the understanding that a heterogeneous equilibrium is involved.

It has been found that the quantity K determined from experimental data is not necessarily constant, e.g. for the reaction



The/...

The value of K varied from 4.6 to 22.2. It may be that the solubility of cadmium in CdCl_2 and its variation with composition was not properly taken into account. Attempts have been made to derive more exact formulae than equation (1.6) ⁽⁴²⁾, but it has been found that, despite the sounder theoretical basis, these equations are less accurate and less generally applicable than equation (1.6). Most investigators have therefore employed equation (1.6) for interpreting their data.

Some values of K for equilibria of interest to the present work have been tabulated in Table 4. The data have been extracted from the book by Delimarskii and Markov ⁽⁴²⁾.

TABLE 4. METAL - MOLTEN SALT EQUILIBRIA ⁽⁴²⁾

Reaction	Temp. °C	K^*
$\text{Cd} + \text{PbCl}_2 \rightleftharpoons \text{Pb} + \text{CdCl}_2$	600	12.8 - 43.5
	600	38.5
	600	25
$2\text{Ag} + \text{PbCl}_2 \rightleftharpoons 2\text{AgCl} + \text{Pb}$	800	$1.7 \times 10^{-3} - 2 \times 10^{-3}$
	800	$2.1 \times 10^{-3} - 2.6 \times 10^{-3}$
$\text{Sn} + \text{PbCl}_2 \rightleftharpoons \text{SnCl}_2 + \text{Pb}$	600	0.16 - 0.54
	600	0.24 - 0.42
	550	0.28 - 0.67

* The above values were calculated in terms of atom fractions of components of the metal phase and the mole fractions of components of the salt phase.

1.4 POLARISATION AT LIQUID METAL ELECTRODES IN MELTS

1.4.1 Direct measurement of overvoltages at the electrode.

Direct measurement of overvoltages at electrodes in melts has been systematically carried out by Piontelli and co-workers ⁽⁴³⁾. Overvoltages have been found to be absent, within the approximation permitted by measurement, in the following molten metal/molten salt electrode/...

electrode systems, among others:

- (1) $\text{Pb}(\ell) / \text{PbCl}_2(\ell)$ at 530°C up to 200 amp/dm^2
- (2) $\text{Pb}(\ell) / \text{PbCl}_2 + \text{KCl}$ (various amounts and temperatures, in the range 560° to 670°C)
- (3) $\text{Cd}(\ell) / \text{CdCl}_2 + \text{KCl}$ (various amounts, 590°C)
- (4) $\text{Sn}(\ell) / \text{SnCl}_2 + \text{KCl}$ (various amounts, 350°C)
- (5) $\text{Zn}(\ell) / \text{ZnCl}_2 + \text{KCl}$ (various amounts, 490°C)

Fig. 3 shows values of apparent overvoltages (mV) as a function of the current density (Amp/dm^2) for examples (1) and (3) above. The measurements were made with the reference and polarised electrodes a known distance apart (d , cm). When the results are corrected by subtracting the ohmic drop in the region between the two electrodes, the remaining true overvoltages are zero, in the order of approximation allowed by the experiment.

It will be noted that the overvoltages are zero in both the cathodic and anodic regions. Measurements were made using short pulses so that concentration polarisation effects did not confuse the issue.

Anodic overvoltages have been found in some systems, e.g. Al and Ni ⁽⁴⁵⁾, but not in those systems of interest to the present study.

1.4.2 Overvoltages from exchange current data

The overpotential at the metal electrode/metal ion in solution interface can be estimated from exchange current data according to the equation

$$\eta = - \frac{RT}{nF} \cdot \frac{i}{i_0} \quad (1.7)$$

where

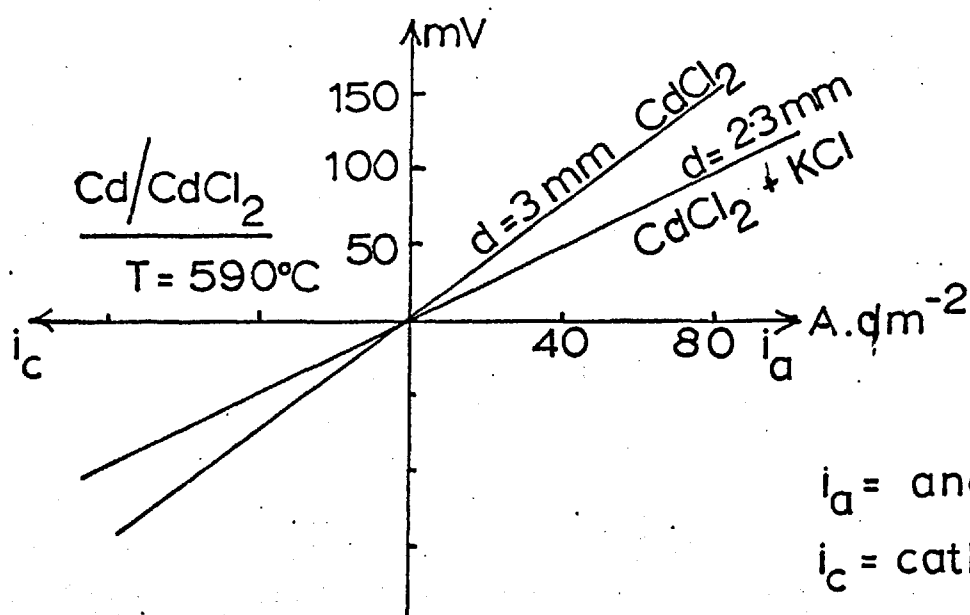
η = overvoltage

i = current density

i_0 = exchange current density

and R, T, n, F have their usual significance.

The /



i_a = anodic current density

i_c = cathodic " "

d = distance between
reference and
working electrodes

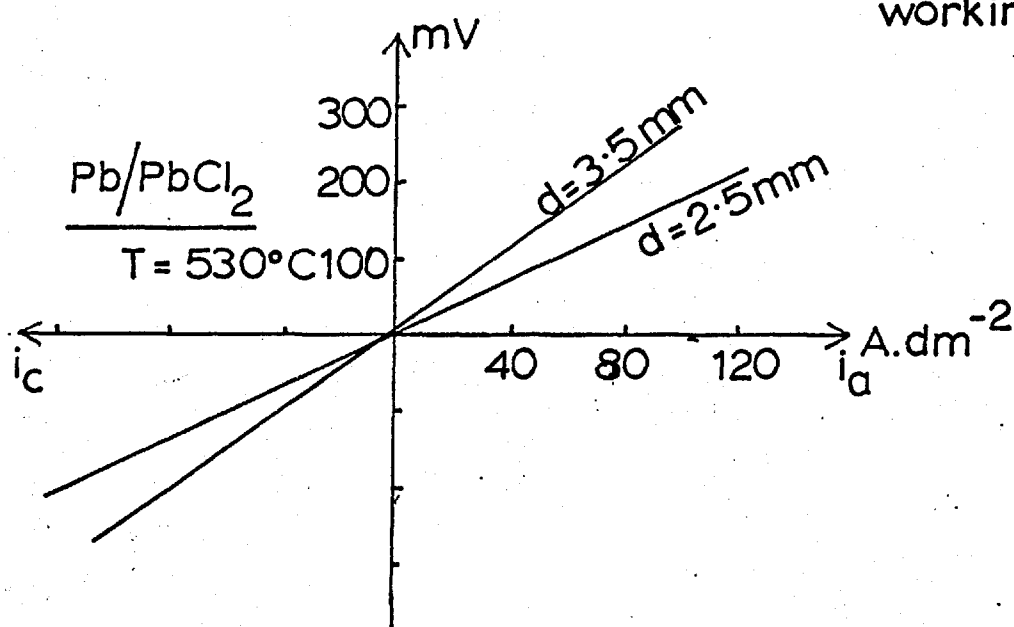


FIG.3 APPARENT OVERVOLTAGE AS A FUNCTION OF CURRENT DENSITY

The overvoltage measured thus relates to the electrochemical - reaction velocity, i.e. the charge transfer resistance. Concentration polarisation is not involved in the experiments performed to measure i_o because the methods concerned use either a.c. or short-pulse d.c. techniques.

Ukshe and Bukun (46) used an a.c. impedance technique to measure the faradaic impedance of lead in molten equimolar KCl-NaCl at 720°C. Extrapolated to infinite frequency, i_o is related to the resistive component of the impedance thus

$$R_p = \frac{RT}{nF} \cdot \frac{1}{i_o} \quad (1.8)$$

The values of i_o obtained are shown in Fig. 4. The anomaly at low Pb^{2+} concentrations was explained as being due to corrosion of the lead working electrode.

Laitinen, Tischer and Roe (47) used the double pulse and voltage step methods to measure exchange current densities in a KCl-LiCl eutectic melt at 450°C. In the double pulse method the charge transfer resistance X was measured from which i_o was obtained by

$$i_o = \frac{RT}{nFA} \quad (1.9)$$

where A is the electrode area.

In the voltage step method the faradaic current is extrapolated back to zero time, thus overcoming the effect of the double-layer charging current which obscures the faradaic current. The exchange current density is calculated from the measured "zero time" $i_t = 0$, the known voltage step V and the total resistance of the system R_T . Similar to equation (1.9) above

$$i_o = \frac{RT}{nFA} \cdot \frac{i_{t=0}}{(-V - i_{t=0} \cdot R_T)} \quad (1.10)$$

The sign of V is given by the European convention; when negative, the current is cathodic (positive). Therefore the quantity on the left is always positive.

The data obtained by Laitinen et al for Cd^{2+} and Pb^{2+} are also shown in Fig. 4.

Recent values of i_o for Pb^{2+} , also at 450°C, obtained by Graves (48) at Imperial College are also shown.

Approximate/...

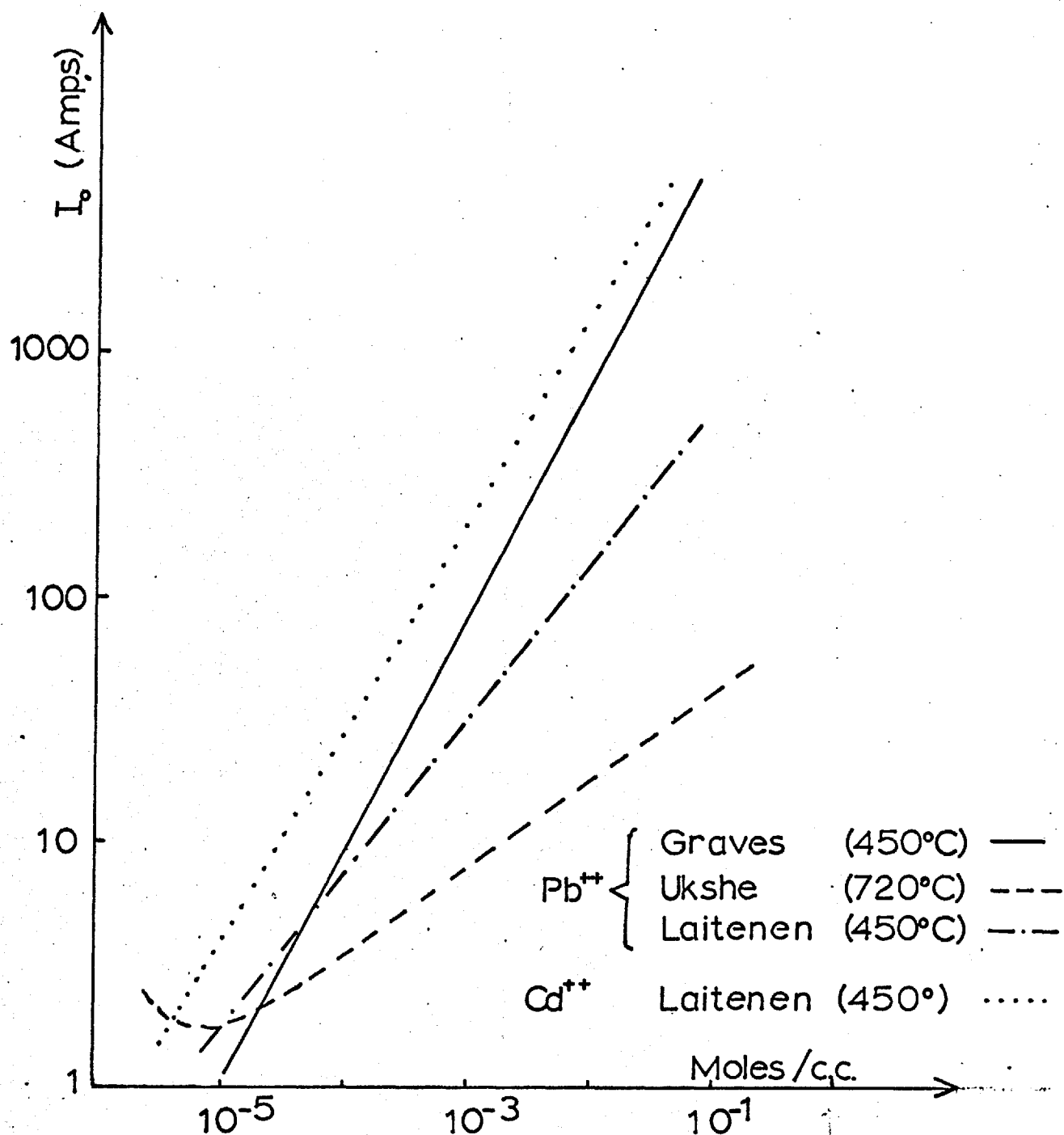


FIG.4 EXCHANGE CURRENT (I_0) vs. CONCENTRATION

Approximate values of i_o for the pure metal salts can be obtained by extrapolation to the concentration in moles/c.c. of the salts at the appropriate temperatures. These values are:

Pb^{2+}	(720°C)	$i_o = 20 \text{ amp/cm}^2$	(Ukshe and Bulam)
	(450°C)	$i_o = 1400 \text{ "}$	(Graves)
Cd^{2+}	(450°C)	$i_o = 200 \text{ "}$	(Laitenen et al)
	(450°C)	$i_o = 2200 \text{ "}$	" " "

Now from equation (1.7) at 800°K, if $n = 2$,

$$\eta = 8.25 \times 10^{-3} \frac{i}{i_o} V. = 8.25 \times \frac{i}{i_o} \text{ mV.}$$

Therefore, if i_o lies between 20 and 1000 amp/cm^2 , the order of magnitude of the overvoltage at the current densities usual in molten salt electrorefining ($\sim 1 \text{ amp/cm}^2$) is likely to be less than 1mV. Although the extrapolation is probably most inaccurate, the conclusions of 1.4.1 tend to be confirmed. Consequently it may be assumed that liquid metal/metal salt exchanges are reversible.

A discussion of the investigations quoted above may be found in Graves' thesis (48).

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CHAPTER 2

THEORETICAL APPROACH

2.1 EXPRESSION OF THE RESULTS OF TRANSPORT MEASUREMENTS

The transport properties of systems are conventionally expressed in terms of diffusion coefficients, electrical conductances, interdiffusion coefficients, transport numbers and electronic conductances. Except for the two last, these terms are proportionality constants in linear equations relating fluxes of matter to the applied forces. Commencing with the equations of irreversible thermodynamics, a method of writing phenomenological equations for the description of electrical and mass transport, based on approaches by Onsager (49) and Klemm (50) and re-expressed by Laity (51,52), was shown by him to give rise to a set of coefficients which tied together the above-mentioned quantities, so that a single physical concept could be applied. Laity expanded this "Friction Coefficient" formalism in the field of molten salt transport (54) and introduced a new formalism, known as the 'L' formalism (53).

These three formalisms will be briefly outlined below.

2.1.1 Conventional Transport Parameters

The net motions of ions or molecules under the influence of applied forces can generally be described by simple linear relationships. The quantities used to characterise these relationships are usually based on the simplest experimental approach. Quantities of use are defined as follows:

Ionic self (tracer) - diffusion coefficient, D_i :

$$C_i v_i = J_i = -D_i \nabla C_i$$

$$J_i + J_k = 0$$

$$J_j = 0$$

where C_i = concentration of ions of species i ,

J_i = flux of ions of species i

D_i = diffusion coefficient of species i

i = either ionic species, k = same species,
but labelled,

j = oppositely charged species.

Equivalent/...

Equivalent conductance, Λ :

$$(v_+ + v_-)F = -\Lambda \nabla \phi$$

Transport number, t_i :

$$t_i = v_i / (v_i + v_j)$$

Ionic conductance λ_i , mobility u_i :

$$t_i \Lambda = \lambda_i = u_i F$$

Two distinct concepts of ionic mobility emerge; diffusional (D_i) and electrical (u_i or λ_i). In electrolytic solutions, these have been found experimentally to be different in value, even when expressed in the same units (cm^2/sec). There is an exception at infinite dilution when the Nernst - Einstein equations holds.

$$\frac{D_i}{RT} = \frac{\lambda_i}{Z_i F^2}$$

The derivation of this relationship relies on the assumption that displacement of an ion by either diffusional or migrational forces occurs by the same mechanism.

The concept of diffusional mobility is the more fundamental of the two. The self-diffusion experiment measures the rate at which the ion moves through a medium in which there is no net movement of species relative to one another. The value of D_i is equal to one-sixth of the mean square displacement per unit time as the ion undergoes random thermal (Brownian) motion. The concept suggested is a simple microscopic model in which the ion, regarded as a sphere, moves in a continuum possessing the viscosity of the bulk fluid. If this is a true description of the system then the Stokes - Einstein equation should hold:

$$D_i = kT / 6 \pi \eta r_i$$

This equation is rigidly applicable to diffusion of spheres whose radii, r_i , are large compared with those of the surrounding liquid. Figures reported for self-diffusion of Na^+ and of Cl^- (55) in NaCl as well as those of Dworkin, Escue and Van Artsdalen (56) for the cations in LiNO_3 , NaNO_3 , KNO_3 and AgNO_3 all give "Stokes radii" r_i 15-35% less than crystallographic values. The consistency of

these/...

these results suggests that even though the crude model described is inadequate, the concept of diffusional mobility could be useful.

In the definition of D_i the reference for v_i is the bulk at rest. A suitable reference for λ_i is less obvious. The moving ion, at finite dilution, when the Nernst-Einstein equation breaks down, encounters a system in which both the solvent and the other ionic species move relative to those of its own kind, as well as to each other. It is doubtful whether a quasi-lattice theory (52,55), similar to the lattice theory of migration in solid ionic crystals, is of much applicability for molten salts. The "porous plug" determinations of transport numbers (57) give results of doubtful meaning (52,58), because of difficulties involved in the use of an external reference.

It can be seen therefore that the attempt to relate phenomenological transport parameters, conceived in different terms and with different dimensions, by means of equations like the Nernst-Einstein and the Stokes-Einstein, is not successful.

2.1.2 Friction Coefficient Formalism

Friction coefficients, r_{ik} , are obtained as the proportionality constants resulting when the thermodynamic force producing a matter flux is written as

$$-V\bar{\mu}_i = -V(Z_i F\phi + \mu_i) = \sum_k^N r_{ik} X_k (v_i - v_k), \quad r_{ik} = r_{ki} \quad (2.1)$$

The thermodynamic force ($\bar{\mu}$) is the sum of the gradients of free energy ($\sum_k^N \mu_k$) and electrical potential ($Z_i F\phi$). In some cases, experiments can be designed to measure the r_{ik} directly. In others, it is best to obtain them indirectly as a combination of conventional transport coefficients, because the latter are obtained from simpler experiments and not because they are more fundamental.

The emphasis in this approach is placed on the relative motion of pairs of species, rather than on the motions of individual ions in an arbitrarily defined frame of reference. The only concept involved is the dissipation of ~~kinetic~~ energy by the interaction between the ion and other species as it moves. The approach is, so far, macroscopic and no microscopic models aimed at predicting friction coefficients have yet been put forward.

The/....

The relationships between friction coefficients and conventional parameters for pure salts are as follows (52):

Equivalent conductance,

$$R_{+-} = \frac{Z_+ (Z_+ + Z_-) F^2}{\chi_{+-}} \quad (2.2)$$

where χ_{+-} = specific conductance, $R_{ik} = r_{ik}/C_T$ and C_T = molar concentration. R_{ik} is preferred for use because it is less concentration dependent than r_{ik} .

Self-diffusion,

$$D_{++} = \frac{(RT/C_T) (Z_+ + Z_-)}{(Z_- R_{++} + Z_+ R_{+-})} \quad (2.3)$$

$$D_{--} = \frac{(RT/C_T) (Z_+ + Z_-)}{(Z_+ R_{--} + Z_- R_{+-})} \quad (2.4)$$

For a three-component system the equations are more complex (52,59).

The implicit expressions are

$$\Delta = \frac{(F^2/C_T) (Z_1 Z_2 / Z_3 + X_{13} Z_2 + X_{23} Z_1) (Z_3 R_{12} + Z_2 X_{23} R_{13} + Z_1 X_{13} R_{23})}{(Z_1 Z_2 / Z_3) R_{13} R_{23} + Z_1 X_{23} R_{12} R_{23} + Z_2 X_{13} R_{12} R_{13}} \quad (2.5)$$

$$P = 1 - t_1 - t_3 X_{13} = \frac{X_{23} (Z_2 R_{13} + Z_3 R_{12})}{Z_1 X_{13} R_{23} + Z_2 X_{23} R_{13} + Z_3 R_{12}} \quad (2.6)$$

$$D_{12} = \frac{(RT/C_T) (Z_1 X_{23} + Z_2 X_{13} + Z_1 Z_2 / Z_3)}{(Z_3 R_{12} + Z_2 X_{23} R_{13} + Z_1 X_{13} R_{23}) (Z_2 X_{13} + Z_1 X_{23})} \quad (2.7)$$

where P is a transport parameter defined in Hittorf experiments.

It should be noted that Sundheim (59) is incorrect in his definition of Δ and P, and Laity for D_{12} (52). In order to obtain the R_{ii} values as well as the R_{ik} it would be necessary to perform three self-diffusion experiments.

It is/...

It is found that the Nernst-Einstein equation results as a special case when all the r_{ik} are equal, or when r_{ik} is the geometric mean of r_{ii} and r_{kk} . When the measured diffusion coefficient of a single species is large enough for its contribution to the equivalent conductance, calculated by the Nernst-Einstein equation, to be greater than the measured conductance, the friction coefficient for that species will be negative. It has been suggested (52) that the occurrence of negative friction coefficients may indicate that the entities chosen to describe the system are not the most suitable. Where, in a fused salt, the entities chosen are the simple ions, negative friction coefficients would therefore indicate association.

2.1.3 'L' Formalism

Self-diffusion would appear to be a more fundamental process than electrical conductance, because it takes place without applied forces. It is seen however to be described by two parameters when using the friction coefficient formalism, whereas electrical conductance is defined by one, which contradicts the above statement. Consequently Laity developed a new formalism (53), which considers the phenomenological equations in reverse, the ionic fluxes being expressed in terms of the thermodynamic forces.

Consider a system composed of two ionic species (i.e. a pure fused salt). The following equations describe adequately isothermal non-viscous transport:

$$-J_i = L_{ii} V\bar{\mu}_i + L_{ij} V\bar{\mu}_j \quad (2.8)$$

$$-J_j = L_{ij} V\bar{\mu}_i + L_{jj} V\bar{\mu}_j \quad (2.9)$$

The Onsager reciprocal relation $L_{ij} = L_{ji}$ has already been applied. There are still three phenomenological coefficients to be identified with experiment. Since i and j are oppositely charged ions, it follows from the definition of equivalent conductance that

$$\frac{\Lambda}{F^2} = \frac{Z_i L_{ii}}{C_i} + \frac{Z_j L_{jj}}{C_j} - \frac{2Z_i L_{ij}}{C_j} \quad (2.10)$$

To relate the self (tracer)-diffusion coefficients (D_i) to these parameters we must assume that $L_{ik} = 0$, where k is the isotope of species i . We then obtain :

$$(2.11)$$

$$\frac{D_i}{RT} = \frac{L_{ii}}{C_i} \quad (2.11)$$

For convenience we may define

$$L'_{ii} = \frac{L_{ii}}{C_i} \quad \text{and} \quad L'_{ij} = \frac{Z_i L_{ij}}{C_j} = \frac{Z_j L_{ij}}{C_i}$$

The new parameters developed in this formalism involve two distinct physical concepts; of diffusional mobility for L'_{ii} and of interference to motion for L'_{ij} .

The final term of equation (2.10) represents the departure from the Nernst-Einstein equation due to the opposing ionic flux. It should be noted that the type of interference is not limited to the type of ionic interference arising from relative motion in an electric field, but can include also that due to diffusion of associated pairs (an idea used in the mechanistic explanation of deviations from the Nernst-Einstein equation).

The friction coefficient formalism was adopted for this work because its usage is more widespread than the 'L' formalism, and because it is simpler to operate in this work.

2.2 THEORETICAL MODEL OF MOLTEN SALT ELECTROREFINING

The experimental investigations of electrorefining reviewed in Chapter I have attempted to determine which impurities can be removed by fused salt electrolysis and how additions to the electrolyte can affect the refining process. In the main, these investigations have been concerned with the chemical aspects of molten salt electrorefining. Hills⁽⁶⁰⁾ developed a simple theoretical model of the process to take account of the bulk transport aspects. This theory, which only takes account of processes in which both electrodes are liquid, shows how the refining ability of a cell is affected by the cell geometry, and by the current density. Definitions of symbols used are given in Appendix A.

2.2.1 Concentration polarisation across the cell

Since activation polarisation effects are generally absent from molten metal electrodes (Section 1.4) any purification effect must be due to concentration polarisation in the electrolyte. It is convenient to use the friction coefficient

formalism/....

formalism of irreversible thermodynamics for the analysis of these polarisation effects. This will first be done for a simple system consisting of one main metal (B), one impurity (C) and a common anion (A). The electrolyte will thus be a binary mixture of the salts BA and CA.

The theoretical model of molten salt electrorefining is illustrated schematically in Fig. 5. The concentration of the impurity in the anode is $[X_C]_a$, in the cathode $[X_C]_c$, and L is the length of the transport path between the two electrodes. In a three-layer cell, this is simply the distance between the anode and cathode layers, but some other suitable mean length must be used for other cell geometries. The impurity is considered to enter the electrolyte as the result of an exchange reaction at the anode surface. Any effects due to the dissolution of metals in their molten salts are neglected.

The friction coefficient formalism (see above) enables the flux of any ion to be related to the gradient of its electrochemical potential by the use of the equation (2.1)

$$-\bar{V}\mu_i = \sum_K^N r_{ik} X_k (v_i - v_k); \quad r_{ik} = r_{ki}$$

Using the modified friction coefficients $R_{ik} = r_{ik}/C_T$, and molar flux densities $\dot{n}_i = v_i X_i C_T$, the above equation becomes

$$-\bar{V}\mu_i = \sum_K^N R_{ik} \left(\frac{X_k}{X_i} \dot{n}_i - \dot{n}_k \right); \quad R_{ik} = R_{ki} \quad (2.12)$$

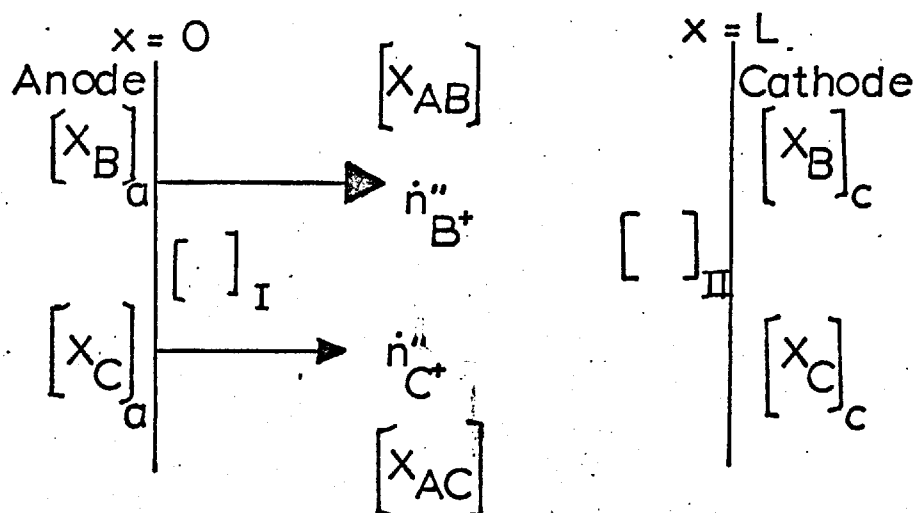
This equation can be used to relate the fluxes of the three ions to the gradients of their electrochemical potentials. Because of the Gibbs-Duhem relationship only two of the equations are independent. In addition the net velocity of the anions (v_A) and hence the flux of the anions ($\dot{n}_A$) is taken to be zero in the system defined above. Thus we have :

$$\bar{V}\mu_A = R_{A-B^+} \dot{n}_{B^+} + R_{A-C^+} \dot{n}_{C^+} \quad (2.13a)$$

$$-\bar{V}\mu_{B^+} = \left\{ R_{A-B^+} \frac{X_{A^-}}{X_{B^+}} + R_{B^+C^+} \frac{X_{C^+}}{X_{B^+}} \right\} \dot{n}_{B^+} - R_{B^+C^+} \dot{n}_{C^+} \quad (2.13b)$$

These equations cannot be integrated directly since no unique

relationship/...



Exchange reaction:

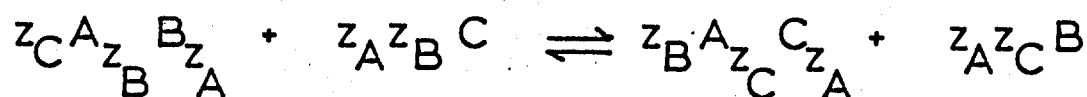


FIG.5 SCHEMATIC MODEL OF MOLTEN SALT
ELECTROREFINING

relationship exists between the concentration of an ionic species and its electrochemical potential. However the concept of local equilibrium allows us to assume a relationship between the concentration of a neutral salt and its chemical potential. Thus the analysis can be conducted in terms of neutral salts, since :

$$\mu_{AB} = Z_B \mu_{A^-} + Z_A \mu_{B^+}$$

Equation (2.13) can then be used to derive the following equation for the gradient of the chemical potential of the neutral salts:

$$\begin{aligned} \nabla \mu_{AB} = & \left\{ \begin{aligned} & Z_B \left(\frac{R}{X_{B^+}} \right) - Z_A \left(\frac{R}{X_{B^+C^+}} \right) \\ & + Z_A \left(\frac{R}{X_{B^+C^+}} \right) - Z_B \left(\frac{R}{X_{B^+C^+}} \right) \end{aligned} \right\} \dot{n}_{B^+} \\ & + \left\{ \begin{aligned} & Z_B \left(\frac{R}{X_{A^-C^+}} \right) + Z_A \left(\frac{R}{X_{B^+C^+}} \right) \end{aligned} \right\} \dot{n}_{C^+} \end{aligned} \quad (2.14)$$

We will assume that the fluxes are in one direction only. This means that only the gradient of chemical potential in that direction need be considered. If we further assume that the molten salts form an ideal solution we can write :

$$\mu_{AB} = \mu_{AB}^0 + RT \ln (X_{AB})$$

$$\text{Thus:} \quad \frac{d(\mu_{AB})}{dx} = \frac{RT}{(X_{AB})} \frac{d(X_{AB})}{dx} \quad (2.15)$$

We can now integrate equation (2.14) formally. Using the stoichiometric relation between the mole fractions of the individual ions, and their proper salts, viz: in terms of X_{AC}

$$\begin{aligned} X_{A^-} &= \frac{Z_B + (Z_C - Z_B) X_{AC}}{Z_A + Z_B + (Z_C - Z_B) X_{AC}} \\ X_{B^+} &= \frac{Z_A (1 - X_{AC})}{Z_A + Z_B + (Z_C - Z_B) X_{AC}} \\ X_{C^+} &= \frac{Z_A X_{AC}}{Z_A + Z_B + (Z_C - Z_B) X_{AC}} \\ X_{AB} + X_{AC} &= 1 \end{aligned} \quad (2.16)$$

We have/....

we have

$$RT \frac{dX_{AC}}{dx} = \left\{ (Z_C^R A^{-B+} + Z_A^R B^{+C+}) \dot{n}''_{B+} \right\} X_{AC} - \left\{ (Z_B^R A^{-C+} + Z_A^R B^{+C+}) \dot{n}''_{C+} \right\} (1 - X_{AC}) \quad (2.17)$$

The implications of this equation are made clear if we recast it in terms of the dimensionless fluxes defined in the list of symbols :

$$L \frac{dX_{AC}}{dx} = (n_B^* + n_C^*) X_{AC} - n_C^* \quad (2.18)$$

In the steady state the fluxes of the two components will be constant, and so we can integrate this equation, across the cell. As the length of the transport path between anode and cathode is L, we have :

$$\begin{aligned} [X_{AC}]_{II} = & \left\{ [X_{AC}]_I - \frac{n_C^*}{n_C^* + n_B^*} \right\} \exp(n_C^* + n_B^*) \\ & + \frac{n_C^*}{n_C^* + n_B^*} \end{aligned} \quad (2.19)$$

Since we assume that equilibrium exists across the electrode surfaces, the composition of the anode and cathode fix $[X_{AC}]_I$ and $[X_{AC}]_{II}$ respectively. Equation (2.19) shows that the fluxes of the two ionic species are not fixed by these compositions as they would be if diffusion were the sole transport mechanism. However equation (2.19) does ~~not~~ represent a definite relationship between the two fluxes, and so one other condition is necessary before they can be calculated.

This condition depends on the mode of operation of the refining cell. We will only consider one mode of operation here - constant current conditions. Thus the required further condition is written:

$$i'' = F (\dot{n}''_{B+} Z_B + \dot{n}''_{C+} Z_C) \quad (2.20)$$

In terms/...

In terms of the dimensionless quantities this becomes:

$$i^* = i'' \left\{ \frac{Z_C^R A^{-B+} + Z_A^R B^{+C+}}{F RT} \right\} L = \frac{Z_B n_B^*}{R^*} B + \frac{Z_C n_C^*}{R^*} C \quad (2.21)$$

Once the ionic fluxes of the two species have been calculated they can be combined with the relevant continuity equations to generate differential equations for the varying compositions of the electrodes. If a batch refining process is being operated, the electrode compositions will vary with time. If a continuous counter-current system is used the electrode compositions will vary with position. In either case variations in the electrode compositions could only be predicted using numerical methods, except in certain special cases (section 2.4). The results would be valid only for restricted sets of conditions. The analysis would be extremely laborious, and would not serve as a simple test from which to predict the behaviour of an impurity, or the effect of varying current density on the performance of the cell.

2.2.2 A simple refinability parameter

One particular set of conditions leads to a situation that can be easily analysed. This occurs when the mass of the anode is very much greater than that of the cathode, and when the cathode is entirely composed of material transported across the cell. Under these conditions no part of the system will be time dependent. Even for this simple situation, it is only possible to obtain a generally valid expression if we postulate that impurity concentrations throughout the system are very much less than unity. We can then determine the ratio between the impurity concentrations in the cathode and in the anode.

The value of this ratio will determine whether the impurity will be concentrated in the anode or in the cathode.

Since $n_C^* \ll n_B^*$, equation (2.19) becomes:

$$\left[X_{AC} \right]_{II} - \frac{n_C^*}{n_B^*} = \left\{ \left[X_{AC} \right]_{I} - \frac{n_C^*}{n_B^*} \right\} \exp(n_B^*) \quad (2.22)$$

As the/....

As the left-hand side of this equation can only be finite or zero, the expression in curly brackets on the right-hand side must tend to zero as the current density increases. Thus :

$$\lim_{n_B^* \rightarrow \infty} \left(\frac{n_C^*}{n_B^*} \right) = [X_{AC}]_I \quad (2.23)$$

When the current across the cell is zero the anode and the cathode will be in equilibrium and their compositions equal. Increasing the current across the cell changes the anode to cathode composition ratio, which will tend to a value determined by equation (2.23). This equation therefore determines the maximum possible composition change between the electrodes and provides a measure of the ability of the system to refine the anode metal. Since we are assuming that the cathode is composed entirely of material transported across the cell, its composition is given by the equation :-

$$\frac{[X_C]_C}{[X_B]_C} = \frac{\dot{n}_{C^+}}{\dot{n}_{B^+}} \quad (2.24)$$

In terms of the dimensionless numbers defined in the list of symbols we have :

$$\frac{n_C^*}{n_B^*} = \frac{R^* \dot{n}_{C^+}}{\dot{n}_{B^+}} = R^* \frac{[X_C]_C}{[X_B]_C} \quad (2.25)$$

As we are assuming that the concentration of the impurity is very much less than unity throughout the system :

$$[X_B]_C = 1 - [X_C]_C \simeq 1 \quad (2.26)$$

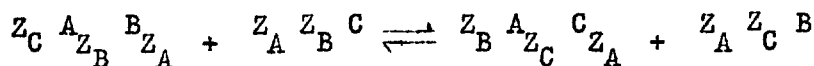
Thus equation (2.23) becomes :

$$\lim_{n_B^* \rightarrow \infty} \left(R^* [X_C]_C \right) = [X_{AC}]_I \quad (2.27)$$

Chemical equilibrium exists at the anode/electrolyte interface, and so we can relate $[X_{AC}]_I$ to the impurity

concentration/...

concentration in the anode. Consider the dissolution, or exchange, reaction:



Since we are assuming that the molten salt mixture is ideal, we can write the equilibrium for the reaction as :

$$\frac{[X_{AC}]_I^{Z_B} (\gamma_B [X_B]_a)^{Z_A Z_C}}{[X_{AB}]_I^{Z_C} (\gamma_C [X_C]_a)^{Z_A Z_B}} = K \quad (2.28)$$

The anode is almost pure B, and so we can say that $\gamma_B = 1$ and $[X_B]_a \approx 1$. Moreover $[X_{AB}]_I \approx 1$. Thus:

$$[X_{AC}]_I = K (\gamma_C [X_C]_a)^{Z_A} \quad (2.29)$$

Generally the anion is univalent in electrorefining processes ($Z_A = 1$), so that if we substitute relationship (2.29) into (2.27) we can determine a simple expression for the limiting ratio between the impurity concentrations in the anode and cathode. This gives:

$$\lim_{n_b \rightarrow \infty} \frac{[X_C]_C}{[X_C]_a} = \frac{\gamma_C K^{1/Z_B}}{R^*} = \beta \quad (2.30)$$

The value of β will determine whether the impurity will concentrate in the anode or in the cathode. If β is less than one, the cathode will be purer than the anode; if β is greater than one, the anode will be purer. β is a logical parameter since

$(\gamma_C K^{1/Z_B})$ measures the tendency of the impurity to enter the melt, and R^* measures the relative resistance to motion of the two metal ions. Thus the value of β provides a simple test as to the behaviour of the impurity.

2.2.3 The effect of current density

When no current flows across the cell, the anode and cathode are inequilibrium and therefore of equal composition. As the current density increases, the concentration ratio will tend to β . For a cell in which the impurity concentration is everywhere very much less than unity, the value of β will also determine the way in which the concentration ratio varies with current density.

For such a cell equation (2.21) gives :

$$i^* = Z_B n_B^* \quad (2.31)$$

Substituting equations (2.25), (2.26), (2.29) and (2.31) into (2.22)

$$\left[X_{AC} \right]_{II} - R^* \left[X_C \right]_C = \left\{ \gamma_C K^{1/2} \left[X_C \right]_a - R^* \left[X_C \right]_C \right\} \exp.(i^*/Z_B) \quad (2.32)$$

This equation is indeterminate once the current density reaches an effectively infinite value. At lower current densities it constitutes one relationship between the impurity concentration in the cathode and the concentration of its salt in contact with the cathode. A further relationship is provided by the equilibrium conditions at the cathode - electrolyte interface. This latter condition, which is valid whatever the value of current density, gives:

$$\left[X_{AC} \right]_{II} = \gamma_C K^{1/2} \left[X_C \right]_C \quad (2.33)$$

Substituting this expression into equation (2.32), and rearranging, gives in terms of β

$$\frac{\left[X_C \right]_C}{\left[X_C \right]_a} = \frac{\beta}{1 + (\beta - 1) \exp - i^*/Z_B} \quad (2.34)$$

This equation is plotted for various values of β in Fig. 6. It can be seen that the value of β also determines the rapidity with which the current density reaches an effectively infinite value. When β

is less/....

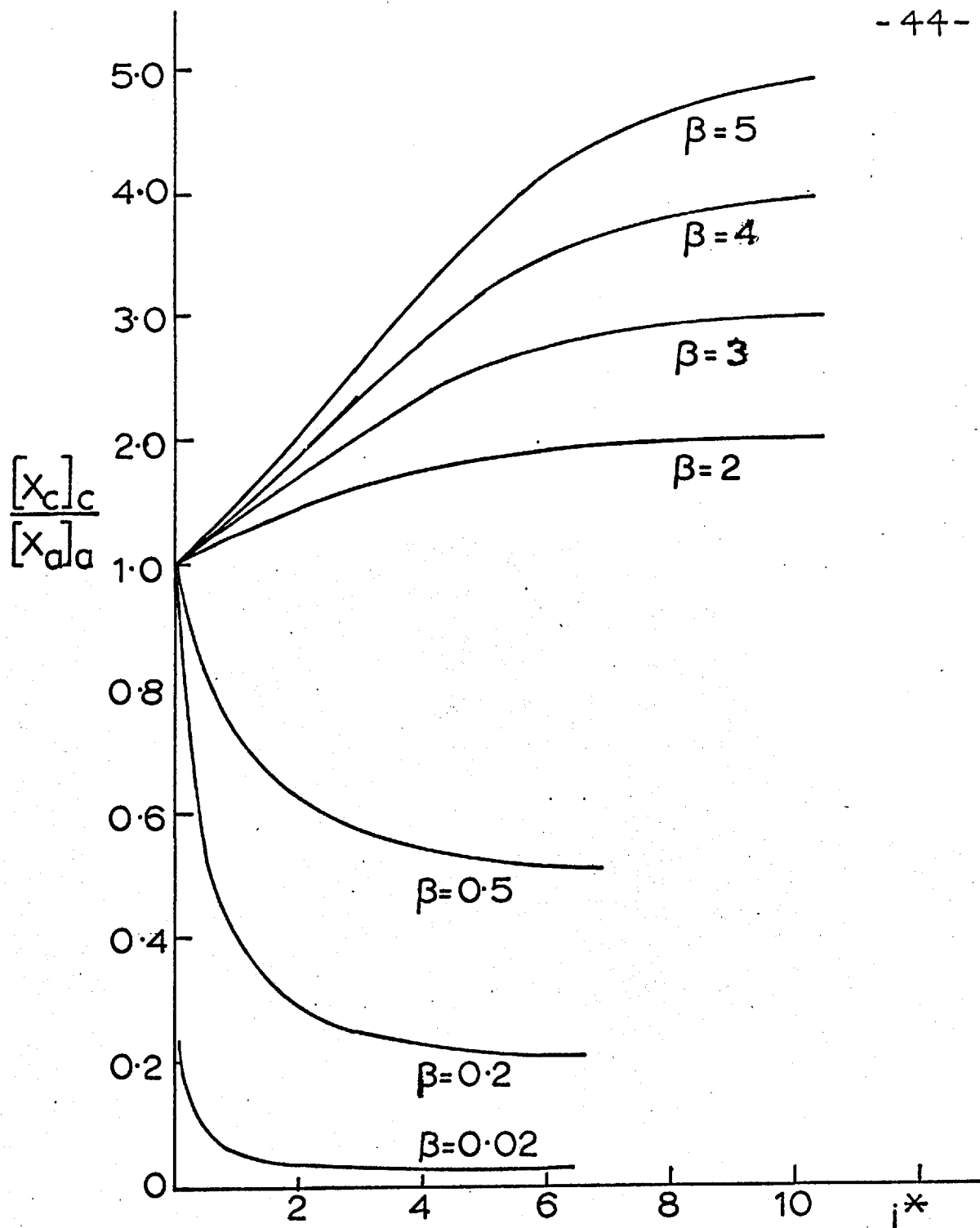


FIG. 6 EFFECT OF CURRENT DENSITY ON REFINING

is less than unity, quite low values of current density are effectively infinite. As β increases, higher and higher current densities are necessary before the concentration ratio reaches its limiting value.

The dimensionless current density is given by equation (2.21)

$$i^* = \frac{(Z_C R_{A^- B^+} + R_{B^+ C^+}) L}{F R T} i'', (Z_A = 1)$$

With any one impurity, main metal and electrolyte, the values of the friction coefficients are fixed. The value of i^* can, however, be increased by increasing the current density and by increasing the transport path length between the electrodes. Under certain conditions these changes can improve the refining ability of the cell, but the extent of the improvement to be gained is often limited.

For example, when $\beta = 0.2$ the dimensionless current density has reached an effectively infinite value when it is equal to 4. The actual value of the current density when this occurs is given by rearranging equation (2.21)

$$i'' = \frac{F R T i^*}{(Z_C R_{A^- B^+} + R_{B^+ C^+}) L} \quad (2.35)$$

If we take the following values for the factors in equation (2.35) we can calculate an order of magnitude value for the effectively infinite current density.

$$\begin{aligned} Z_C &= Z_B = 1 \\ R_{A^- B^+} &= 10^{10} \text{ joule sec. cm. mole}^{-2} \text{ (see ref: 54)} \\ L &= 1 \text{ cm} \\ F &= 10^5 \text{ coulomb mole}^{-1} \\ R &= 10 \text{ joule mole}^{-1} \text{ (deg. K)}^{-1} \\ T &= 10^3 \text{ deg. K.} \end{aligned}$$

Therefore

$$i'' = 0.4 \text{ A/cm}^2$$

Most of the processes discussed in Chapter I are operated at higher current densities than this. Very little improvement in the/.....

the refining ability of a cathode - refining cell ($\beta < 1$) can be achieved, therefore, by increasing the current density or the transport path length. Thus such a cell should be operated with the shortest possible transport path length in order to keep the power loss to a minimum. Fig. 6 shows, however, that an anode refining cell ($\beta > 1$) would not normally operate at effectively infinite current density and so it should be possible to increase its refining ability by increasing the current density or the transport path length.

2.2.4 Calculations of refinability parameters for the lead system.

In the following Chapters experiments and results are described concerning the refining of small amounts of impurities in lead, under the conditions defined above in the derivation of the refinability parameter. The calculation of the value of β will now be discussed taking the copper-lead system as an example.

Friction coefficients in molten salt mixtures have not yet been determined, through lack of sufficient information, and so we must estimate the friction coefficient ratio, R^* . This ratio is given by the following equation :

$$R^* = \frac{Z_B R_{A^-C^+} + R_{B^+C^+}}{Z_C R_{A^-B^+} + R_{B^+C^+}}, \quad (Z_A = 1) \quad (2.36)$$

As we are assuming that the friction coefficients are not functions of composition, the R_{+-} friction coefficients can be determined from the pure salt conductivity data. This may be done using the formula

$$R_{+-} = \frac{(Z_+ + Z_-) F^2 Z_+}{\chi} \quad (2.37)$$

(where χ is the specific conductance of the molten salt).

No data exists from which it is possible to calculate the R_{++} coefficients. However, it is likely that interactions between ions of like sign will be less important than those between ions of unlike sign (54). Thus we can assume that the R_{++} coefficients are very much smaller than the R_{+-} coefficients. This being so, R^* can be estimated from the following equation :

$$R^* = \frac{Z_B R_{A-B^+}}{Z_C R_{A-B^+}} \quad (2.36A)$$

The following values (and those used in Table 4) for specific conductances have been taken from Klemm's review (72) of transport properties of molten salts

$$\begin{aligned} \left[\chi_{\text{PbCl}_2} \right] 800^\circ\text{K} &= 1.57 \quad \text{ohm}^{-1} \text{ cm}^{-1} \\ \left[\chi_{\text{CuCl}} \right] 800^\circ\text{K} &= 3.52 \quad \text{ohm}^{-1} \text{ cm}^{-1} \end{aligned}$$

Using equation (2.37) we get

$$\begin{aligned} \left[R_{\text{PbCl}_2} \right] 800^\circ\text{K} &= 3.52 \times 10^{10} \quad \text{joule sec. cm. mole}^{-2} \\ \left[R_{\text{CuCl}} \right] 800^\circ\text{K} &= 0.53 \times 10^{10} \quad \text{joule sec. cm. mole}^{-2} \end{aligned}$$

Therefore

$$R^* = 0.301$$

The value of the exchange constant, K, can be calculated from the free energy of formation of copper and lead chlorides, and from the latent heat of melting of copper (71).

Thus, for the reaction :



it follows that -

$$K_{800^\circ\text{K}} = 2.72 \times 10^{-3}$$

The activity coefficient of copper in lead at zero dilution, and at 1263°K, 5.68⁽⁷³⁾. If we assume that the solution of copper in lead is regular, we get :

$$\left[\gamma_{\text{Cu}} \right]_{800^\circ\text{K}} = 5.68^{1263/800} = 15.5$$

Therefore/....

Therefore

$$\gamma_{\text{Cu}}^{\text{K}} = 0.81$$

Therefore $\beta = 2.68$

It will have been seen that several assumptions have been made which may not be fully justified in all cases. However there is a measure of agreement between the predicted results of molten salt electrorefining, as shown by values of β in Table 4 and the practical results of Delimarskii and co-workers (Table 3). It should be borne in mind that the derivation of β considers a melt containing the chlorides of the two metals, whereas Delimarskii's experiments involve several impurities present together and melts of differing compositions.

2.2.5 Variation of concentration across the cell

The equation describing the variation of the impurity component across the cell is

$$L \frac{dX_{\text{AC}}}{dx} = (n_{\text{B}}^* - n_{\text{C}}^*) X_{\text{AC}} - n_{\text{C}}^* \quad (2.18)$$

This differential equation was integrated in 2.2.1 in order to obtain the impurity salt concentration $[X_{\text{AC}}]_{\text{II}}$ at the cathode interface. The general solution for $[X_{\text{AC}}]_{\text{x}}$ at a distance x ($0 \leq x \leq L$) from the anode is given by

$$[X_{\text{AC}}]_{\text{x}} - \frac{n_{\text{C}}^*}{n_{\text{B}}^* + n_{\text{C}}^*} = \left([X_{\text{AC}}]_{\text{I}} - \frac{n_{\text{C}}^*}{n_{\text{B}}^* + n_{\text{C}}^*} \right) \exp. (n_{\text{B}}^* + n_{\text{C}}^*) \frac{x}{L} \quad (2.38)$$

If we assume, as above, that $n_{\text{C}}^* \ll n_{\text{B}}^*$, then

$$i^* = Z_{\text{B}} n_{\text{B}}^* \quad (2.31)$$

and $\frac{n_{\text{C}}^*}{n_{\text{B}}^*} = R^* [X_{\text{C}}]_{\text{C}} \quad (2.35)$

At/....

TABLE 4. REFINABILITY PARAMETERS FOR IMPURITIES IN LEAD AT 800°K

METAL	χ_{800} (72) cm	$R_{A^- B^+}$ $\times 10^{10}$	R^*	$\left[\gamma_c\right]$ 800 (73)	K_{800} (71)	β	Refining according to Delmars- kii Table No: 3
Pb ²⁺	1.57	3.52					
Cu ⁺	3.52	0.530	0.301	15.5	2.72 $\times 10^{-3}$	2.68	Partly
Ag ⁺	3.98	0.480	0.272	5.06	7.48 $\times 10^{-5}$	0.161	Yes
Cd ²⁺	1.74 [†]	3.21	0.912	3.22	102.6	35.9	-
Zn ²⁺	0.120	46.6	13.2	11.8	2240	42.2	No
Sn ²⁺	2.17 [†]	2.58	0.732		13.2	5	Yes
Bi ³⁺	0.54	20.7	3.92		1×10^{-7}	10^{-8}	Yes

† Extrapolated values

-----000-----

At infinite current density

$$\lim_{n^* \rightarrow \infty} (R^* \left[X_C\right]_C) = \left[X_{AC}\right] I \quad (2.27)$$

This implies that at high current densities $\left[X_{AC}\right]_x$ tends towards $\left[X_{AC}\right] I$, and the concentration gradient in the electrolyte tends towards zero.

Now with (2.31) and (2.25) equation (2.38) reduces to

$$\left[X_{AC}\right]_x = \left(\left[X_{AC}\right] I - \frac{n^* C}{n^* B}\right) \exp. \left(\frac{i^* x}{Z_B L}\right) + \frac{n^* C}{n^* B} \quad (2.39)$$

At any current density we have

$$\frac{[X_C]_C}{[X_C]_a} = \frac{\beta}{1 + (\beta - 1) \exp. (-i^*/Z_B)} \quad (2.34)$$

and at the anode

$$[X_{AC}]_I = \gamma_C K^{1/Z_B} [X_C]_a \quad (2.29)$$

Substituting in (2.39) we obtain

$$[X_{AC}]_x = [X_{AC}]_I \left[\exp. \left(\frac{i^*}{Z_B} \cdot \frac{x}{L} \right) + \frac{(1 - \exp. \left(\frac{i^*}{Z_B} \cdot \frac{x}{L} \right))}{1 + (\beta - 1) \exp. (-i^*/Z_B)} \right] \quad (2.40)$$

Equation (2.40) describes $[X_{AC}]_x$ in terms of known or defined factors. Fig. 7 shows the variation of $[X_{AC}]$ with x for the case where $\beta = 5$ over a range of i^* up to a value of $i^* = 10$. It can be seen that as i^* increases the concentration gradient in the bulk of the electrolyte tends to disappear as predicted above for the limiting case of $i^* = \infty$. In other terms the "boundary" layer thickness is decreasing as current increases.

2.3 MOLTEN SALT ELECTROREFINING WITH AN "INERT" DILUTING SALT

We shall consider a system in which an electrolyte AD, having the same anion as metals B and C, is added to the melt previously considered (2.2). The cation D does not take part in any of the electrode reactions. Hence we can put the velocity of the cations D^+ as zero, as we did the velocity of the anions A. The change in concentration of D^+ ions is a secondary effect at relatively low current densities so that we may ignore the effect of the true concentration polarisation which is set up in the cathode compartment. Difficulties in analysis do not warrant the extra work at this stage, although it would be necessary with high concentrations of dilutant.

From the general equation for mass transport using the friction coefficient formalism

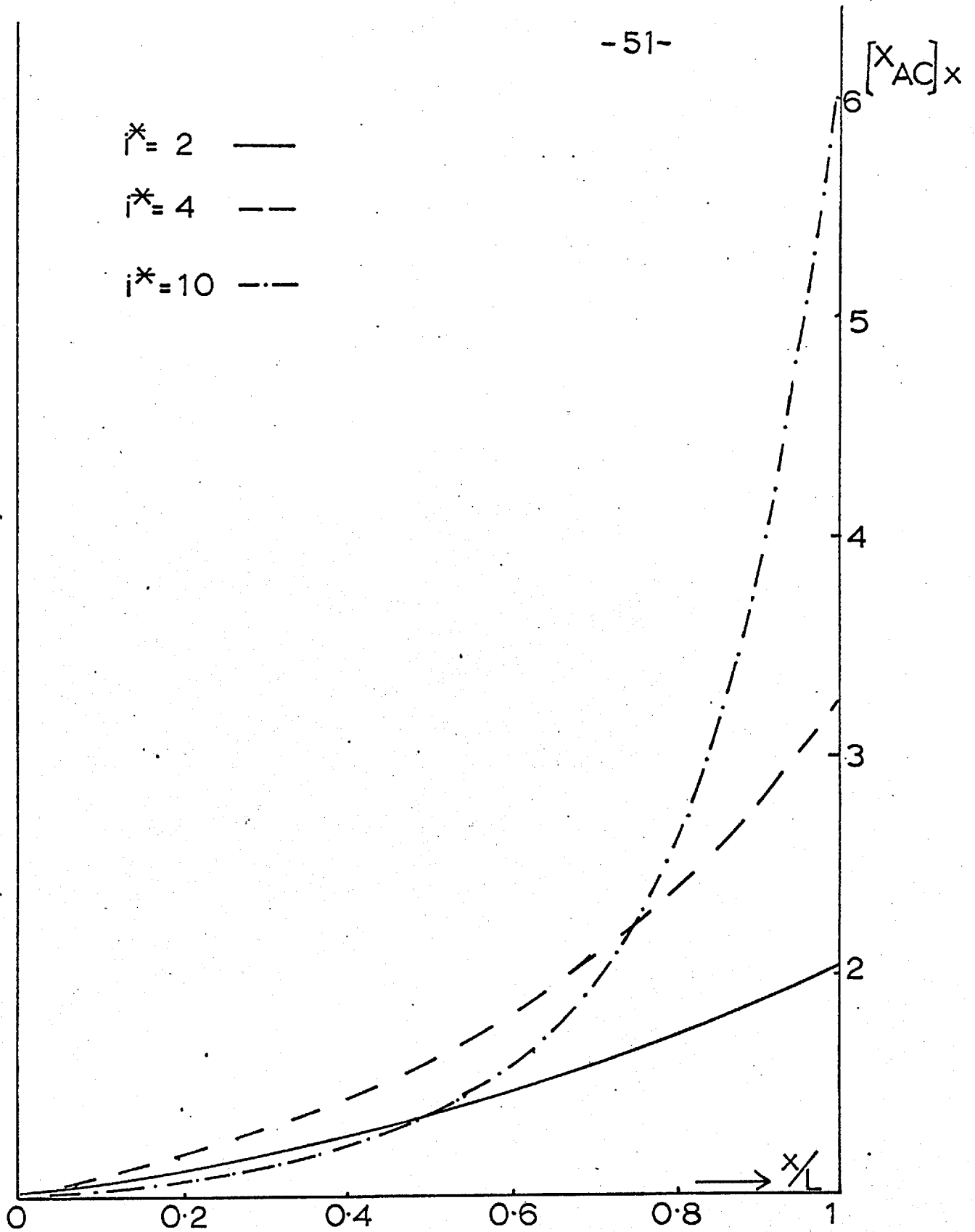


FIG. 7 IMPURITY CONCENTRATION GRADIENT

$$-v_{\mu_i} = \sum_{k=1}^n R_{ik} \left(\frac{X_k}{X_i} \dot{n}_i'' - \dot{n}_k'' \right)$$

we obtain, since $v_A = v_D = \dot{n}_A'' = \dot{n}_D'' = 0$,

$$v_{\mu_{A^-}} = R_{A-B^+} \dot{n}_B'' + R_{A-C^+} \dot{n}_C''$$

$$v_{\mu_{C^+}} = R_{B^+C^+} \dot{n}_B'' - \dot{n}_C'' \left(R_{A-C^+} \frac{X_{A^-}}{X_{C^+}} + R_{B^+C^+} \frac{X_{B^+}}{X_{C^+}} + R_{D^+C^+} \frac{X_{D^+}}{X_{C^+}} \right)$$

As in section 2.2 the concept of local equilibrium allows us to assume a relationship between the concentration of a neutral salt and its chemical potential. Thus

$$\mu_{AC} = Z_C \bar{\mu}_{A^-} + \bar{\mu}_{C^+} \quad (Z_A = 1)$$

whence

$$\bar{v}_{\mu_{AC}} = \dot{n}_B'' (Z_C R_{A-B^+} + R_{B^+C^+}) + \dot{n}_C'' \left[R_{A-C^+} \left(Z_C - \frac{X_{A^-}}{X_{C^+}} \right) - R_{B^+C^+} \frac{X_{B^+}}{X_{C^+}} - R_{D^+C^+} \frac{X_{D^+}}{X_{C^+}} \right] \quad (2.41)$$

Making, as above, the assumption that we are dealing with linear fluxes and that the molten salts form an ideal solution, then

$$\mu_{AC} = \mu_{AC}^0 + RT \ln (X_{AC})$$

and thus

$$\frac{d\mu_{AC}}{dx} = \frac{RT}{(X_{AC})} \cdot \frac{d(X_{AC})}{dx} \quad (2.42)$$

In a four component system the stoichiometric relations between the mole fractions of the individual ions and the mole

fraction/

fraction of salt AC are given by the following equations where

$$X_F = (1 - X_{AD}) = (X_{AC} + X_{AB}),$$

$$\left. \begin{aligned} X_{A-} &= \frac{Z_D + X_F (Z_B - Z_D) + X_{AC} (Z_C - Z_B)}{Z_D + Z_A + X_F (Z_B - Z_D) + (Z_C - Z_B) X_{AC}} \\ X_{B+} &= \frac{Z_A (X_F - X_{AC})}{Z_D + Z_A + X_F (Z_B - Z_D) + (Z_C - Z_B) X_{AC}} \\ X_{C+} &= \frac{Z_A X_{AC}}{Z_D + Z_A + X_F (Z_B - Z_D) + (Z_C - Z_B) X_{AC}} \\ X_{D+} &= \frac{Z_A (1 - X_F)}{Z_D + Z_A + X_F (Z_B - Z_D) + (Z_C - Z_B) X_{AC}} \end{aligned} \right\} \quad (2.43)$$

whence

$$\left. \begin{aligned} \frac{X_{A-}}{X_{C+}} &= \frac{Z_D + X_F (Z_B - Z_D) + X_{AC} (Z_C - Z_B)}{X_{AC}} \\ \frac{X_{B+}}{X_{C+}} &= \frac{(X_F - X_{AC})}{X_{AC}} \\ \frac{X_{D+}}{X_{C+}} &= \frac{(1 - X_F)}{X_{AC}} \end{aligned} \right\} \quad (Z_A = 1) \quad (2.44)$$

Substituting relations (2.44) and (2.42) in equation (2.41)

$$\begin{aligned} RT \frac{d(X_{AC})}{dx} &= \dot{n}_B (Z_C R_{A-B+} + R_{B+C+}) X_{AC} - \\ &\dot{n}_C (Z_B R_{A-C+} + R_{B+C+}) (X_F - X_{AC}) - \dot{n}_C (Z_D R_{A-C+} + R_{D+C+}) (1 - X_F) \end{aligned} \quad (2.45)$$

When $X_F = 1$, i.e. there is no diluting salt, equation (2.45) reduces to the same as equation (2.17) for the three component system.

Using the defined dimensionless fluxes, we obtain

$$\frac{L d (X_{AC})}{dx} = n_B^* X_{AC} - n_C^* (X_F - X_{AC}) - n_C^* \frac{(Z_D^R A^{-C+} + R_{D+C+})}{Z_B^R A^{-C+} + R_{B+C+}} (1 - X_F)$$

If we put $\frac{(Z_D^R A^{-C+} + R_{D+C+})}{(Z_B^R A^{-C+} + R_{B+C+})} = Q$ and rearrange

$$\frac{L d (X_{AC})}{dx} = (n_B^* + n_C^*) X_{AC} - n_C^* (Q + X_F(1 - Q)) \quad (2.46)$$

The coefficient $(Q + X_F(1 - Q))$ represents the effect produced by adding a diluting salt (c.f. eq. 2.18). It is equal to 1 when $X_F = 1$.

In the steady state the fluxes of the two components B and C will be constant and so we can integrate equation (2.46) across the cell.

Equation (2.46) is similar in form to equation (2.18) and so, by comparison, we obtain :

$$n_B^* \lim_{B \rightarrow \infty} (R^* [X_C]_c) = \frac{[X_{AC}] I}{Q + X_F (1 - Q)} \quad (2.47)$$

As before the equilibrium relationship at the anode relates $X_{AC} I$ to $[X_C]_a$, since

$$\frac{[X_{AC}] I^{Z_B} (\gamma_B [X_B]_a)^{Z_C}}{[X_{AB}] I^{Z_C} (\gamma_C [X_C]_a)^{Z_B}} = K \quad (2.48)$$

X_B and $[X_B]_a$ are approximately = 1 as before but, in this case,

$[X_{AB}] I$ is not. Therefore

$$[X_{AC}] I = \frac{1}{K} \gamma_B^{1/Z_B} \gamma_C^{Z_C/Z_B} [X_{AB}] I^{Z_C/Z_B} [X_C]_a \quad (2.49)$$

Substituting/....

Substituting the expression (2.49) into equation (2.47) we obtain

$$\lim_{n_B^* \rightarrow \infty} (R^* \left[\frac{X_C}{X_C} \right]_c) = \frac{(K^{1/z_B} \gamma_C) \left[\frac{X_{AB}}{X_{AB}} \right] I^{z_C/z_B} \left[\frac{X_C}{X_C} \right]_a}{Q + X_F (1 - Q)}$$

This equation may be further simplified since $X_{AB} \approx X_F$ if $X_{AC} \ll X_{AB}$ whence :

$$\lim_{i_B^* \rightarrow \infty} \left(\frac{\left[\frac{X_C}{X_C} \right]_c}{\left[\frac{X_C}{X_C} \right]_a} \right) = \left(\frac{K^{1/z_B} \gamma_C X_F^{z_C/z_B}}{R^* (Q + X_F (1 - Q))} \right) = \beta' \quad (2.50)$$

Thus we obtain a modified refinability parameter, β' , which is equal to the parameter β obtained for the simple three component system modified by a term which is a constant for given anode conditions. The factor Q can be estimated if we make the approximation $R_{BC} \ll R_{AC}$ which is justified by available information (see above). Thus we obtain

$$Q = \frac{Z_D R_{AC} + R_{DC}}{Z_B R_{AC}}$$

Further, because the diluting salt cations are stationary the velocity of the impurity cations relative to them must be the same as the velocity of the impurity cations relative to the stationary anions. Therefore the friction coefficient R_{DC} must be of the same order of magnitude as R_{AC} . Thus the expression for Q can be reduced to

$$Q = \frac{Z_D + 1}{Z_B}$$

The effect of the diluting salt therefore depends on

(1) its concentration = $(1 - X_F)$

and

(2) the valency of the cation.

The term

$$\frac{X_F^{z_C/z_B}}{Q + X_F (1 - Q)}$$

is/...

is always a positive fraction so that the refining ratio is always reduced, i.e. refining is improved by the addition of a diluting salt. It would also seem possible to reduce the refinability parameter from a number greater than unity to a number less than unity, and so to change the system from anode - to cathode - refining.

The effect of current density on the ratio $\left[X_C \right]_C / \left[X_C \right]_a$ may be obtained by replacing β by β' in equation (2.34).

2.4 BATCH REFINING PROCESS

A batch process is one in which electrolysis continues until the anode is entirely transported or, more probably, until the tolerable limit of impurity is reached in the cathode.

Consider a system with a refinability parameter β which is operating at a current density i in the region where i^* is effectively infinite. Let the number of moles of impurity metal in the anode at any time be C_a ($= C_a^0$ at $t = 0$) and the total number of moles of metal in the anode M_a ($= M_a^0$ at $t = 0$). ~~when~~

Equation (2.23) applies under these conditions, and with equation (2.29) and the definitions of n_B^* , n_C^* , R^* and β , gives

$$\begin{aligned} \frac{n_C}{n_B} &= \beta \left[X_C \right]_a \\ \text{but } n_C dt &= dC, \quad n_B dt = dM \text{ and } \left[X_C \right]_a = C_a/M_a \\ \therefore dC &= \beta \frac{C_a}{M_a} dM_a \end{aligned} \quad (2.51)$$

Now, at time t ,

$$M_a = M_a^0 - \frac{it}{F}$$

$$\therefore dM = - \frac{i dt}{F}$$

and thus

$$\frac{dC}{C_a} = \frac{-\beta i dt}{F (M_a^0 - it/F)}$$

By integration/...

By integration we obtain

$$\log C_a = +\beta \log (M_a^o - it/F) + \log (C_a^o / (M_a^o)^\beta)$$

or

$$C_a = C_a^o \left(\frac{(M_a^o - it/F)}{M_a^o} \right)^\beta = C_a^o (1 - n)^\beta \quad (2.52)$$

where $n = \frac{it/F}{M_a^o}$ = the fraction of the anode that has been transported.

Further we have

$$\left[\frac{X}{C} \right]_a = \frac{C_a}{M_a} = C_a^o (1 - n)^\beta \cdot \frac{1}{M_a^o - it/F}$$

so that

$$\left[\frac{X}{C} \right]_a = \frac{C_a^o}{M_a^o} (1 - n)^{\beta-1}$$

$$= \left[\frac{X}{C} \right]_a^o (1 - n)^{\beta-1} \quad (2.53)$$

The change in the composition of the cathode with time is determined from the relationship

$$C_a + C_o = C_a^o$$

$$\therefore C_o = C_a^o (1 - (1 - n)^\beta) \quad (2.54)$$

and we may derive

$$\left[\frac{X}{C} \right]_o = \frac{\left[\frac{X}{C} \right]_a^o}{n} (1 - (1 - n)^\beta) \quad (2.55)$$

From equation (2.53) it is possible to calculate how much of the anode phase can be transferred before a solid phase appears if the phase diagram is known (cf. the LANEX process described earlier) or how far an anode-refining process can be allowed to go before an unacceptable amount of impurity is transferred.

Equation (2.55) shows how much of the anode can be transferred before the tolerable limit of the impurity is reached in the cathode.

The treatment above could quite simply be extended to cover the case in which some of the pure metal is used to start the cathode (see Section 5.2.1).

CHAPTER 3

EXPERIMENTAL METHODS

3.1

FOREWORD

The purpose of the experimental programme was to investigate the predictions of the theory described in Chapter 2; in particular to verify the predicted effect of changing the current density on the refining action of the cell. Secondly it was intended to compare the limiting refining ratio measured experimentally with calculated values of β for several different systems. The design of the experimental cell used had therefore to meet the following requirements:

- (1) the initial mass of the cathode had to be very small or zero, in order to simulate the cathode continuity condition used in the theory
- (2) the transport path along which the concentration changes occur had to be such that transport occurred in one direction only
- (3) the mass of the anode had to be large enough for its composition to be sensibly constant during any one experiment.

3.2

PRELIMINARY CELL

3.2.1 Preliminary Cell Design

Fig. 8 illustrates the cell design for preliminary experiments. The cell was constructed of Pyrex and was to be used between 500 and 600°C. The outer compartment, 60 mm. o.d., contained the anode, and the inner, 23 mm. o.d., contained the cathode. A 1.5 mm i.d. precision bore capillary (obtained from J. A. Jobling Ltd.) vertically attached to a side arm of the inner tube presented a small cathode surface area to the electrolyte. The ratio of anode to cathode surface area was thus approximately 1600:1, and correspondingly the ratio of cathodic current density to anodic current density was 1600:1. The electrode leads consisted of tungsten tips brazed on to Kanthal wire. The tungsten tips were sealed in glass except for about 1 mm. which protruded from the end. A hollow stirrer was fitted in the cathode tube to keep the cathode material homogeneous in composition and to prevent a build-up of transported material at the depositing interface. Samples of the cathode material could be removed when required by sucking up into a sampling tube (Fig. 9a) which was inserted through the hollow stirrer which was normally

stoppered/...

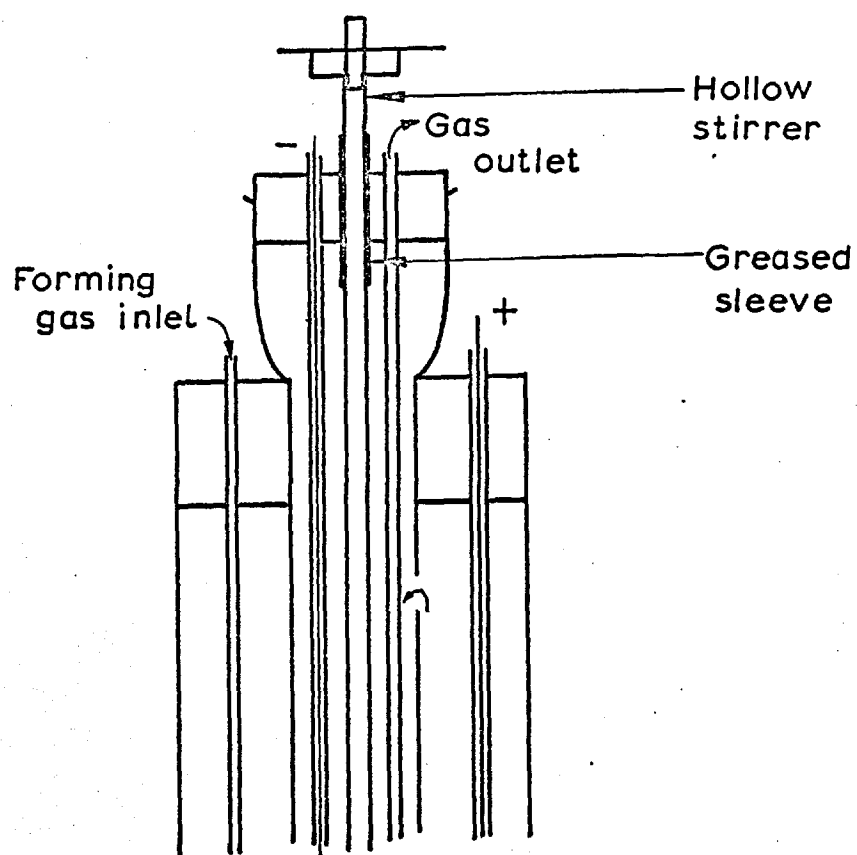
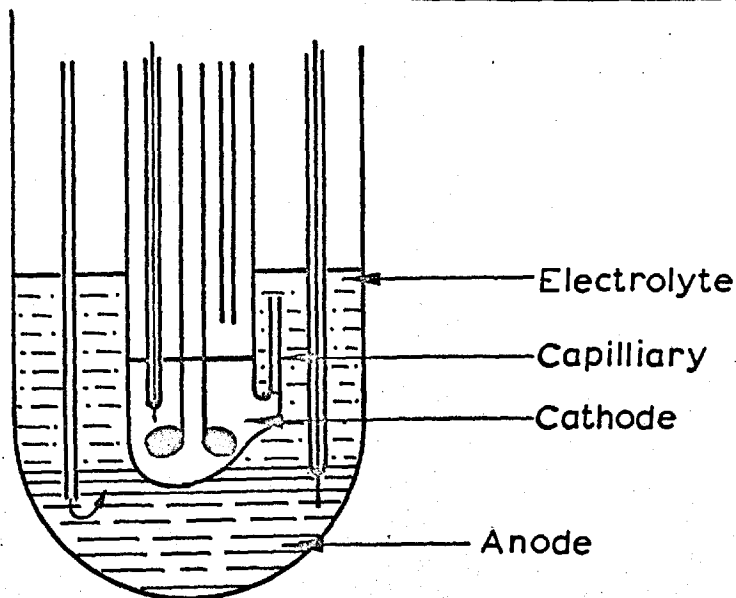


FIG.8
PRELIMINARY CELL



stoppered. An atmosphere of dry forming gas (90% N_2 , 10% H_2) was introduced through a tube which dipped below the surface of the anode. The gas stirred the anode and electrolyte and was forced to exit over the cathode phase, thus keeping the system free from oxidation. The stirring kept the conditions at the anode end of the capillary constant. The cell was 45 cm. in height so that the top projected out of the furnace while the bottom fitted inside the stainless steel tube in the hot zone. The cathode stirrer was chain-driven from an electric motor using "Meccano" cogged wheels and chain. The speed of rotation was geared up from 3 r.p.m. to 10 r.p.m.

3.2.2 Procedure with Preliminary Cell

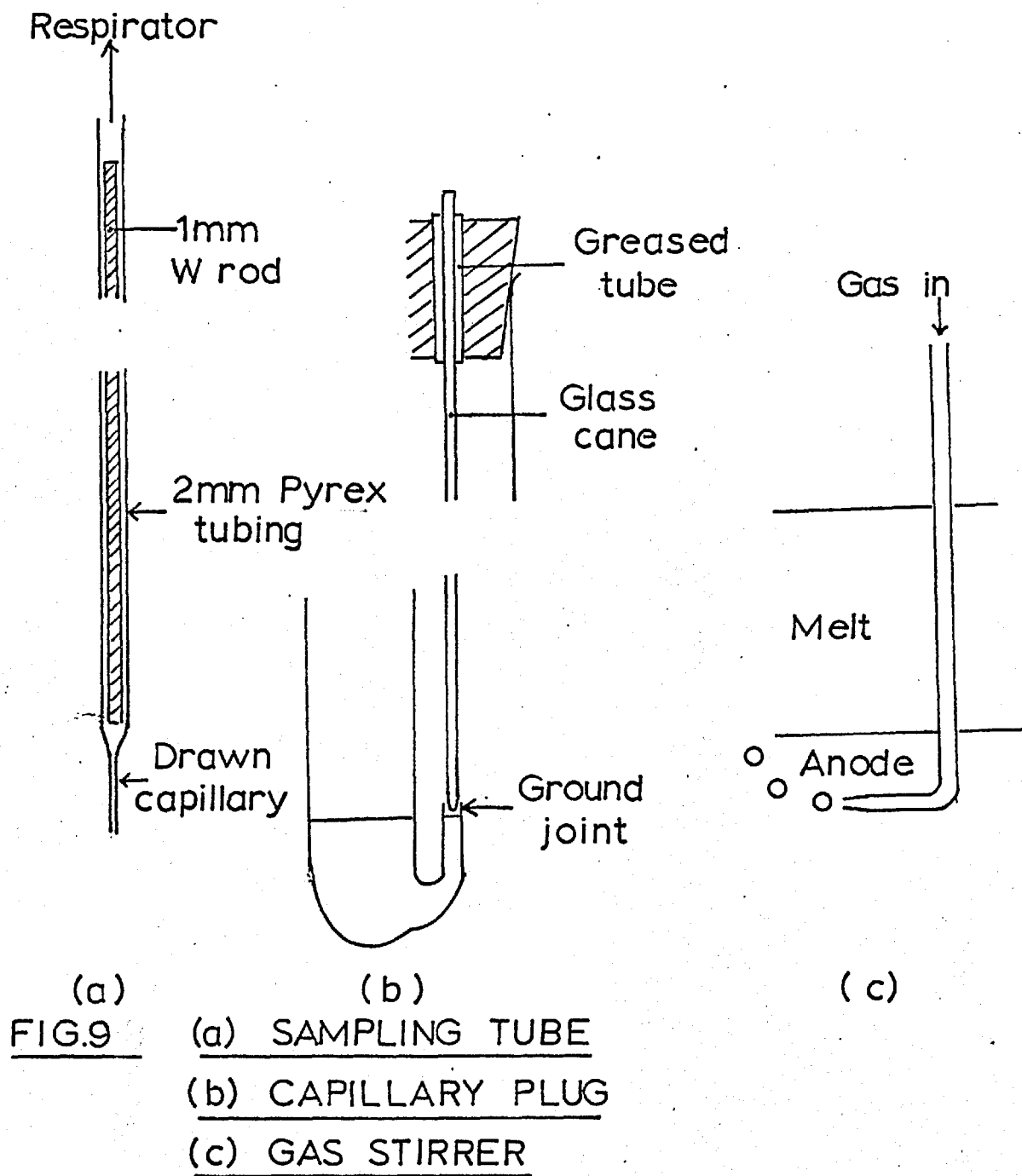
The anode tube was loaded with the calculated amounts of metals and salts necessary for equilibrium. These were heated under dry forming gas and melted. The melt was stirred and kept at constant temperature for 24 hours to ensure that thermodynamic equilibrium had been set up, before experiments were started. This preliminary procedure utilised as a stopper a rubber bung which contained gas inlet and outlet tubes and a thermocouple tube. When experiments were performed this was replaced by another bung which contained the cathode tube. This cathode tube contained a calculated quantity of pure lead metal such that with the tube in position, the capillary side arm was partially filled with salt. The length of this capillary path was measured by a conductance bridge. It was assumed that the great majority of the resistance of the system was caused by the narrow capillary and since the conductance of the mixture and the resistance of the cell were known, it was possible to calculate the length of the diffusion path in the capillary. Runs were performed with and without current and samples of anode, cathode and electrolyte were taken for analysis. Anode samples were obtained through a tube which dipped below the metal surface.

3.2.3 Modification to Preliminary Cell

The electrode leads as described above were difficult to make and did not have a long life. In later experiments tungsten rods sealed in glass were used.

It was also found that some electrolyte appeared in the cathode compartment. This could have occurred via the gas phase

or/....



or through the capillary and was undesirable because of the possibility of the exchange of metals between the metal and salt phases. Transport via the gas phase was therefore prevented by using separate gas trains for the inner and outer compartments. Several methods were tried to prevent the transference of electrolyte via the capillary during the setting-up stage. In the first a plug was fitted in the top of the capillary by means of a ground glass joint and a glass rod with a ground end (Fig. 9b). This proved unsatisfactory in preventing transference of salt. In later experiments the cathode compartment was filled with excess lead so that the capillary was completely filled with metal, which was removed by sucking up into a tube through the stirrer until the conductance bridge indicated that there was a suitable diffusion length of salt in the capillary. This procedure also eliminated the possibility of gas bubbles in the capillary.

It was also noted when the conductance bridge was used that the violence of stirring by gas bubbling disturbed the capillary length. Some salt may indeed have entered the cathode compartment by this method. A gas stirrer which produced less disturbance was designed (Fig. 9c). This consisted of a tube with a right angle bend and a drawn-down tip to give finer bubbles. The tip was at right angles to the radius of the tube to impart some circulatory motion to the melt. This arrangement was still not completely satisfactory in that some disturbance of the capillary length was still noted, though not as much as previously. It was found that, with these modifications, no chloride entered the cathode compartment.

Experiments using the preliminary cell were performed on the lead - copper - chloride system, with results detailed in Chapter 4.

3.3 THE FINAL CELL

Although some results were obtained from the system described in section 3.2., it was apparent that the initial mass of the cathode was too great for sensible changes in its composition to occur during moderately - lengthed experiments. This was even more serious because the current densities used (10 A/cm^2) and 5 A/cm^2) corresponded to very high values of i° (550 and 275 respectively). According

to the/....

to the theory, the refining effect will only vary with the dimensionless current density as the latter varies between 0 and 10. Thus it was not possible to use the first experimental apparatus to show how current density altered the refining effect.

3.3.1 Design of the Final Cell

A new cell was designed in which the initial mass of the cathode was zero. This cell is illustrated in Fig. 10. The cathode compartment consisted of a vertical 1.5 mm bore capillary tube with a 0.030 inch tungsten (or tungsten-molybdenum) wire sealed in the bottom. The initial metal was deposited on the bare wire, only the tip of which extended beyond the seal. Otherwise the apparatus was similar to the previous design except that the anode and the electrolyte were mechanically stirred. This was found to be necessary since bubbling gas through the anode could splash metal into the cathode capillary. A glass stirring rod with two sets of angled paddles, connected by a rubber band drive to an electric motor, was used. The speed of rotation was about 10 r.p.m.

3.3.2 Procedure

The calculated quantities of lead, impurity metal and lead chloride, the latter having been dried at 130°C for at least six hours and under vacuum at 450°C, were melted and allowed to come to equilibrium at 800°K, under an atmosphere of dry forming gas. The head containing the cathode, anode connector etc. was placed in the apparatus, and the cell was evacuated to remove all traces of gas from the capillary. The length of the capillary was then measured by determining the anode-cathode resistance using a Wayne Kerr Universal Bridge B221. This was possible because most of the cell resistance was due to the narrow capillary. In early experiments a Pye Conductance Bridge or a Cintel Bridge was used.

It was found that copper diffused slowly into the glass wall of the capillary during a run, giving rise to a deep copper-ruby colour. The shorting effect due to this alternate current path through the glass was investigated (see section 3.7) and was found to be small during the time of each individual experiment. The colour was not apparent in the cases when sodium chloride was added to the electrolyte.

The/...

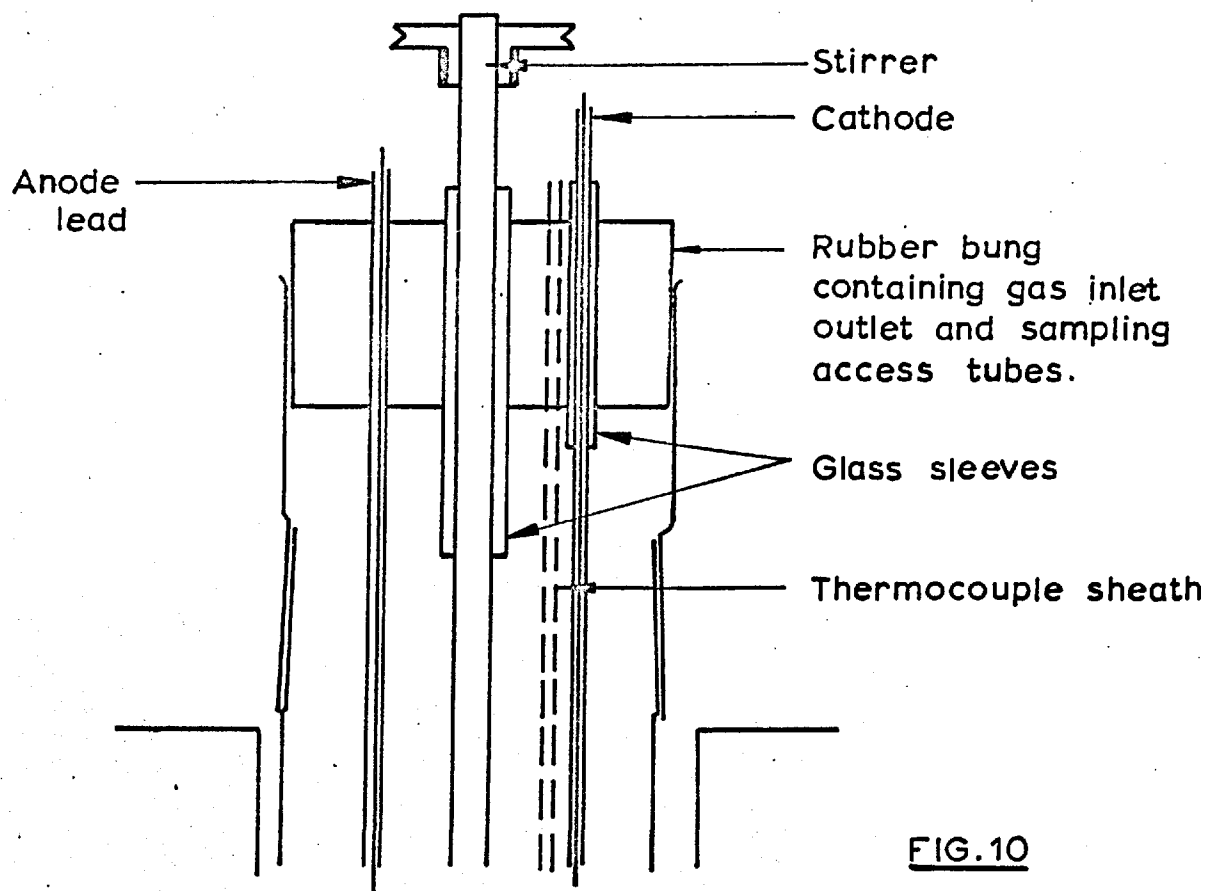
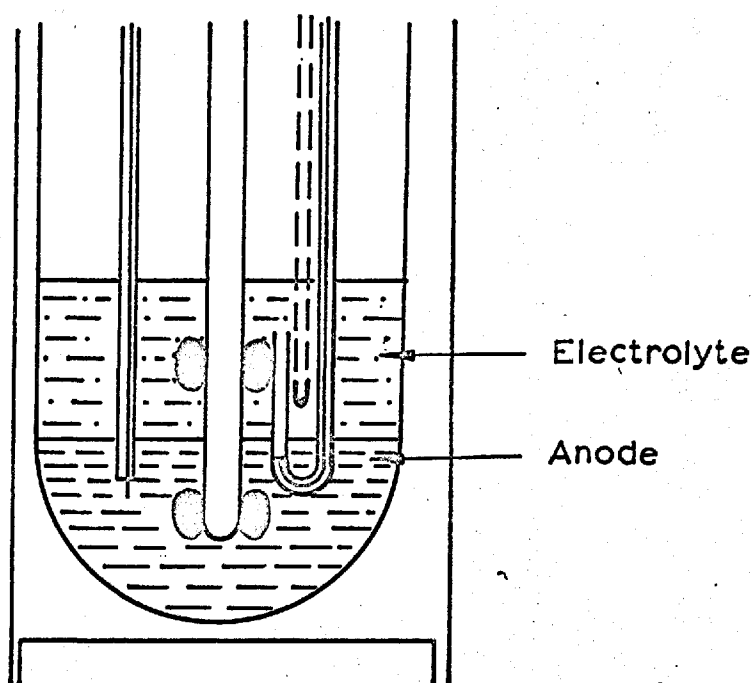


FIG.10

FINAL CELL DESIGN



The anode contained about 200 g of lead and 1 g of impurity metal. Since the total mass of the deposited cathode was about 20 mgm., the anode composition could be taken as constant during any one run.

Once the cell had been set up in this way, a known constant current was passed through the cell for a known time, and the entire cathode analysed together with samples of the anode and the electrolyte. Anode and electrolyte samples were obtained by use of the device described above (Sect. 3.5.1) which was now inserted through a sample access tube (Fig. 9a). The samples were then analysed according to the techniques described below.

From the anode and electrolyte compositions the value of the partition coefficient ($\gamma_C K^{1/2}_B$ in the theory) could be determined. The cathode current efficiency could also be calculated from the total weight of the cathode deposit. From the results of several runs graphs could be constructed of the refining ratio $[Xc]_c/[Xc]_a$ against the dimensionless current density.

The value of i^* was calculated from the measured current density using the R_{A-B^+} (R_{12}) friction coefficient determined from the pure salt conductivity. Specimen calculations are shown in Appendix B.

Runs could not be performed with $i^* < 0.8$ since the time required to deposit sufficient metal for analysis was too long, being in excess of 24 hours. Runs were performed with i^* up to 300.

3.3.3 Measurement of Electrolyte Conductivity

The conductivity of the electrolyte was measured by a simple comparative technique. The prepared cathode was cleaned and fitted in a rubber bung, which was then inserted in a flask (of the type used for filtration under reduced pressure) so that the capillary was immersed in standard potassium chloride solution. The flask was evacuated, using a water pump, until no further bubbles emerged from the capillary. The vacuum was released and the resistance between the cathode connection and a platinum foil electrode in the solution was then measured using the Wayne Kerr bridge. The length of the capillary could then be calculated

because/...

because the conductivity of the KCl solution was known.

When the cathode was subsequently used, after having been washed and dried, it was filled in the manner described in the previous section. The resistance was measured and hence, since the length of the capillary was known, the conductivity of the melt could be estimated.

3.4 FURNACE ASSEMBLY

3.4.1 Design and Construction

The furnace (Fig. 11) was designed to have a 4" constant temperature zone in a 3" i.d. vertical tube furnace. It is difficult to establish such a long constant temperature zone in a tube of reasonable length without special precautions, especially with such a wide tube. The element was therefore "tap-wound" so that some control of the temperature at various points along the winding was possible.

The furnace case was 15" in diameter and 20" long. Two concentric silica tubes 24" long were positioned in the centre of the case. The outer "winding-tube", W, was $4\frac{1}{2}$ " o.d. and 4" i.d.; the inner "furnace" tube, F, was $3\frac{3}{4}$ " o.d. and $3\frac{1}{4}$ " i.d. The element was Kanthal Al S.W.G. 16 wire wound over the centre 16" of the tube with 10 windings per inch and with taps at six locations between the two mains terminals, M. This provided seven sections, two $2\frac{1}{2}$ " long at both ends and three 2" long in between them. The total resistance was 40 ohms. The case was filled with vermiculite, V, as insulation. A stainless steel tube, S, 3" o.d., $2\frac{1}{2}$ " i.d., and approximately 6" long was placed inside as shown. Insulating bricks, B, were cut to fit inside F and S. The entire assembly was supported by a bracket, Z, attached to the bottom of the case. The temperature control thermocouple, C, was placed between F and W. All spaces between tubes, bricks and thermocouple tubes were plugged with asbestos wool to prevent convection.

3.4.2 Temperature Measurement and Control

The temperature measuring thermocouple was platinum - platinum 13% rhodium (supplied by Johnson, Matthey Co. Ltd.) and it was connected to a Tinsley potentiometer. A maximum of 18 mV could be read on the x 0.01 scale to an accuracy of 1 μ V or 0.22%,

whichever/...

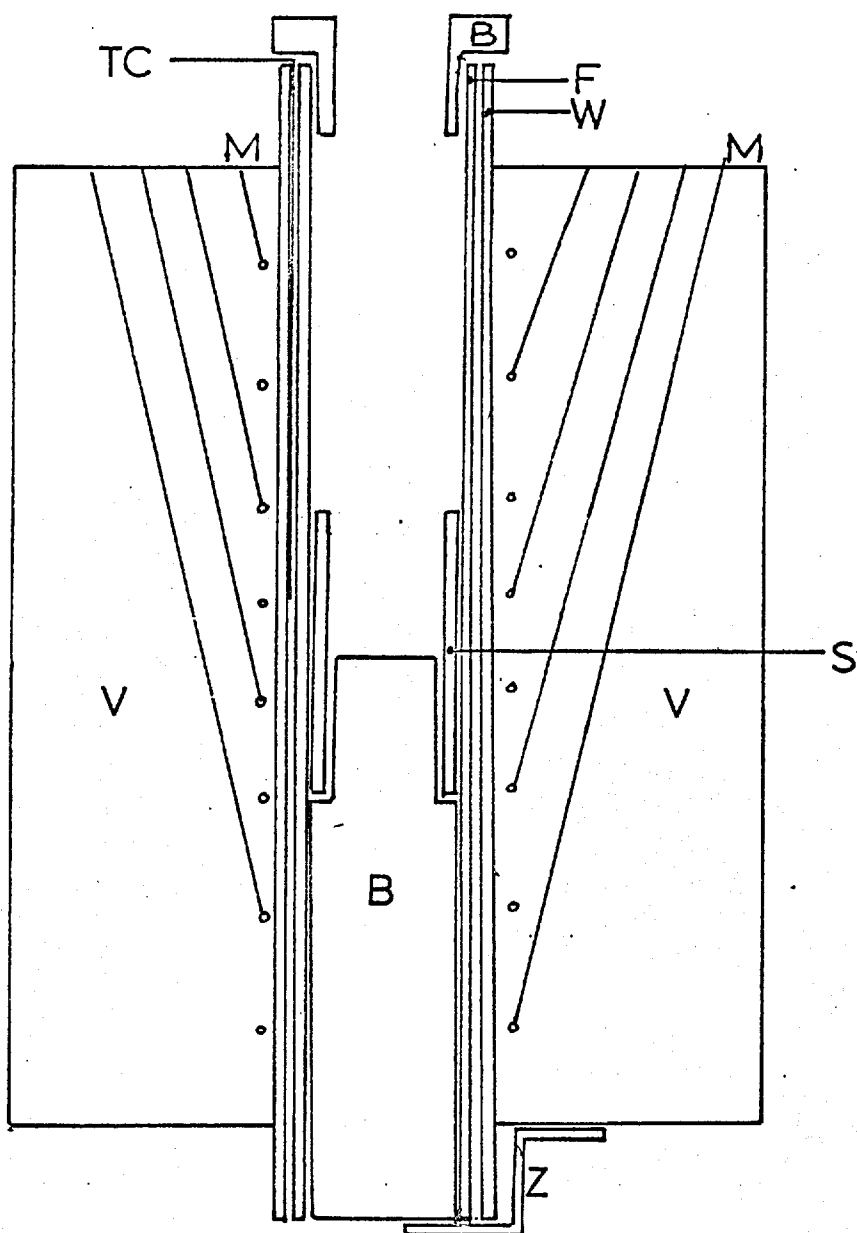


FIG. 11 FURNACE ASSEMBLY

whichever was the greater.

Temperature control was achieved by a "high-low" circuit (Fig. 12). Power was supplied by a Variac auto-transformer; the output leads being connected across the furnace plus an auxiliary resistance of about 7.5 ohms. The auxiliary resistance was in parallel with the micro-switch of a Smith's Mark IV proportional controller. The current necessary to maintain the furnace at the temperature of operation (3 - 3.5 amp) was low enough for the micro-switch of the controller to be used directly, as opposed to control by operation of a mercury or hot-wire switch. A Sorensen A.C. voltage regulator (Model LT-1000-25; input, 190-260 v., 45-55 c.p.s.; output 220 v.) was used to supply constant voltage to the auto-transformer to eliminate the effect of mains voltage variations. The temperature control thermocouple was constructed from chromel-alumel wire.

3.5 DIRECT CURRENT SUPPLY

A circuit was constructed to supply a constant direct current to the cell. Fig. 13 illustrates the circuit schematically. The value of the current was determined by measuring the voltage across a standard 1 ohm. resistance, using a Tinsley potentiometer, which could be read to an accuracy of 1 μ V on the x 0.01 scale.

Two double-throw switches were used so that the current could be switched through the cell or through a by-pass resistance while the resistance of the cell was measured using a conductance bridge.

Initially the laboratory 230 V D.C. supply was used but this retained some A.C. ripple and it was replaced by a Heayberd constant voltage unit which provided 350 V D.C. and a maximum of 120 mA.

3.6 MATERIALS

3.6.1 Lead Metal

Analcar lead metal was obtained from Hopkin and Williams Ltd. The maximum limits of impurities were stated to be (given as %)

Ag	0.0005	Total foreign metals	
Cu	0.001	(as sulphates)	0.02
Fe	0.001	As	0.0001
			(1 ppm)

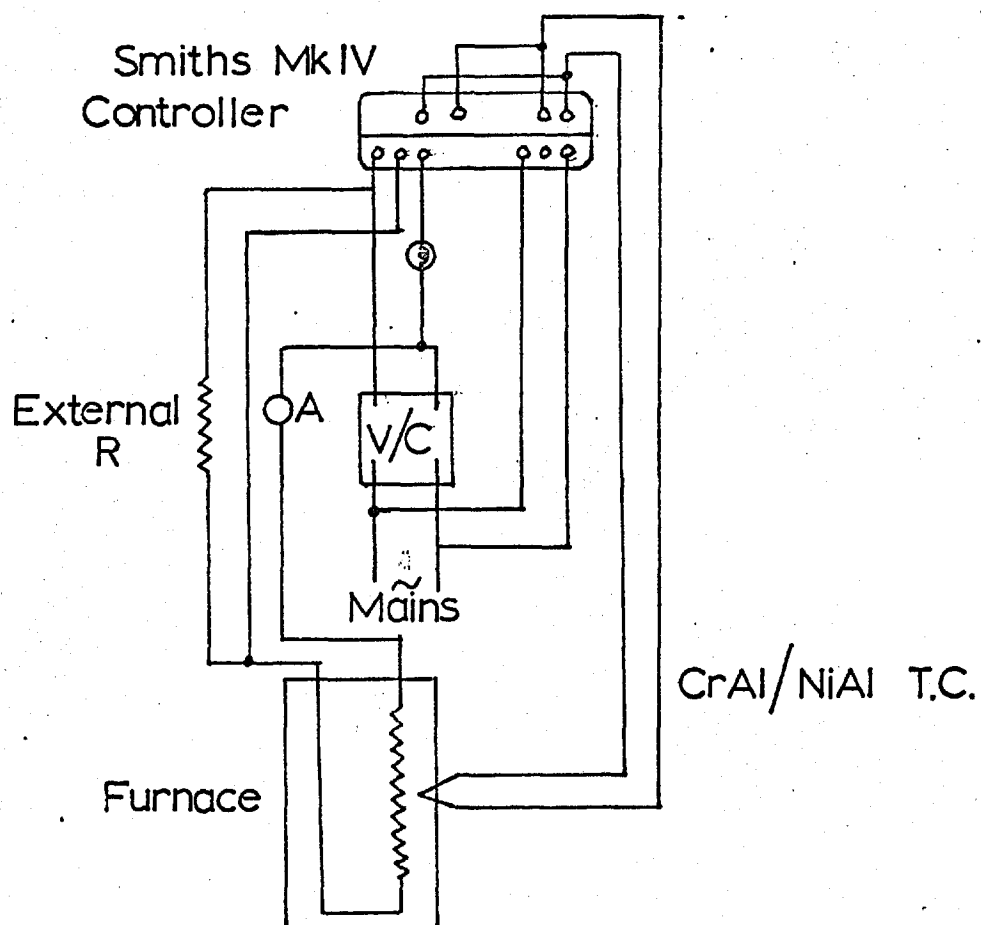


FIG. 12 HEATING AND TEMPERATURE CONTROL

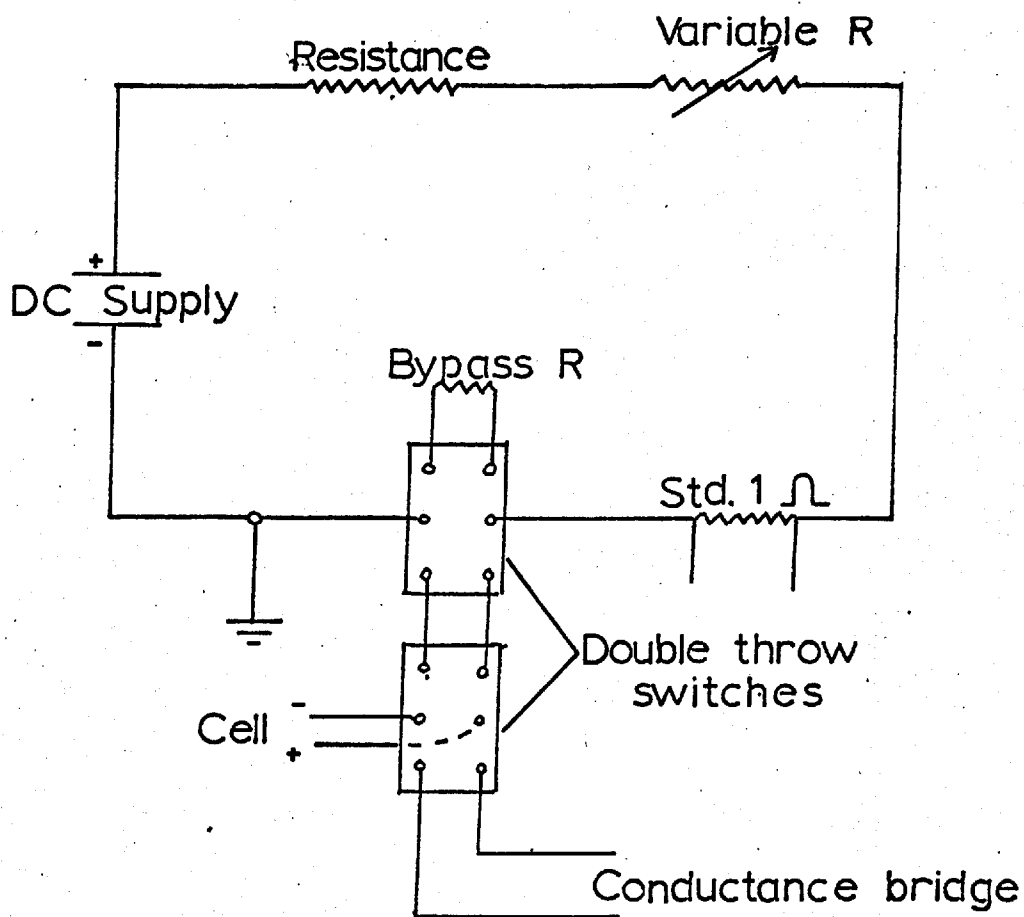


FIG. 13 CIRCUIT DIAGRAM

3.6.2 Cadmium Metal

Spec. pure cadmium metal obtained from Johnson Matthey Ltd. was used in making up lead -cadmium alloys.

3.6.3 Silver Metal

Silver metal, pure foil for assay (99.9% minimum) obtained from Hopkin and Williams Ltd. was used in making up lead-silver alloys.

3.6.4 Copper Metal

Analar copper metal foil obtained from Hopkin and Williams Ltd. was used in making up lead-copper alloys. The maximum limits of impurities (%) were stated to be:

Acid insoluble matter	nil	Bi	0.0005
Sn	0.001	Pb	0.002
Ag	0.001	As	0.0002 (2 ppm)
Fe	0.01		

3.6.5 Lead Chloride

Originally some 99.99% $PbCl_2$ provided by Associated Lead Manufacturers Ltd. was used. In later experiments $PbCl_2$ was prepared by precipitation from a solution of Analar $(Pb(NO_3)_2)$. The Analar $Pb(NO_3)_2$ was obtained from Hopkin and Williams Ltd. and its purity was given as,

pH of solution not less than 3.8

Max. limits of impurities (%)

Chloride	0.01	Fe	0.001
Cu	0.001	Alkalis (as sulphates)	0.1

Some runs were performed using G.P.R. $PbCl_2$ (minimum assay 99%, nitrate not more than 0.005%) which had been dried at $160^\circ C$ and heated under vacuum.

The mean weight loss after drying was found to be 0.035 wt. %. Gravimetric analysis of the material for $PbCl_2$ content (as the sulphate) showed that, within the limits of accuracy of the technique, the dried material consisted only of the chloride.

3.6.6 Cadmium Chloride

Initially G.P.R. anhydrous $CdCl_2$, which had been dried at $120^\circ C$ and heated under vacuum, was used. In later experiments $CdCl_2$ was prepared from Analar $CdCl_2 \cdot 2\frac{1}{2} H_2O$ obtained from Hopkin and Williams/....

and Williams Ltd. The purity was given as :

pH of solution not less than 4.0

Maximum limits of impurities (%):

Sulphate	0.01	Zn	0.005
Nitrate	0.002	Alkalies and other metals	
Fe	0.001	(as sulphates)	0.1
Pb	0.01	Ammonium (NH ₄)	0.01
Cu	0.001	As	0.00002
			(0.2 ppm)

3.6.7 Sodium Chloride

Analar sodium chloride, 99.9% NaCl after ignition, obtained from Hopkin and Williams Ltd., was used in making up ternary chloride electrolytes. The maximum limits of impurities (%) were stated to be

Free acid	0.05 ml N/1	Heavy metals (Pb)	0.001
Free alkali	0.05 ml N/1	Barium (Ba)	0.003
Sulphate (SO ₄)	0.003	Calcium + magnesium (Ca + Mg)	0.005
Nitrate (NO ₃)	0.002	Potassium (K)	0.01
Phosphate (PO ₄)	0.005	Ammonium (NH ₄)	0.001
Iron (Fe)	0.0005	Arsenic (As)	0.0001

3.6.8 Precision Tubing

1.5 mm precision bore pyrex tubing was obtained from J. A. Jobling Ltd. One batch was tested for the value and constancy of the area of cross-section. Mercury was sucked into the tubing, which was then placed horizontally and the length of the mercury column measured. The mercury was tipped out and weighed. From this weight, the length and the density of mercury at room temperature, it was possible to calculate a mean value of the area of cross section and the standard deviation for this batch. It was found that the mean area was

$$1.713 \times 10^{-2} \text{ cm.}^2 \quad (\pm 0.5\%)$$

If the tubing had been of accurate 1.5 mm diam. the area would have been

$$1.767 \times 10^{-2} \text{ cm.}^2$$

The difference of the area was thus 3.1% which was equivalent to an error of 1.5% in the dimensions of the tubing. This was within the stated limits of accuracy of the tubing, and this error was

taken/...

taken into account in the calculation of the errors in experimental results.

3.7 DIFFUSION OF COPPER INTO THE WALLS OF CONTAINERS

The diffusion of copper into the glass of container envelopes, as shown by the copper-ruby coloration (3.6.2), could have led to an alternative current path through the walls of the cathode capillary. The effect was investigated for both cells.

3.7.1 The Preliminary Cell

A used, and therefore coloured, cathode with the capillary closed off was filled with lead and immersed in an anode container filled with molten lead and electrolyte. The resistance between two tungsten electrodes dipping into the respective melts was found to be between 21 and 22 k ohms when measured on a Cintel bridge. Since the resistance of the cathode capillary path was of the order of 40 ohm it was concluded that the amount of current passing through the walls of the cell was negligible.

3.7.2 The Final Cell

The diffusion of copper into the capillary walls was investigated by comparing the change in length of the capillary path (as calculated from the change in measured resistance) with a change in length estimated from the current flowing. The tests were performed with current flowing in order to give a closer approximation to experimental conditions. If copper was diffusing into the capillary walls sufficiently to reduce the glass resistance significantly then the capillary length (estimated from measured resistance) would decrease at a greater rate than expected.

At a current of 1 mA approximately 3.84 mg/hour of lead is deposited. If the density of molten lead at 800°K is taken as 10.7 g/cc, the rate of change of capillary length expected is:

$$\frac{3.84 \times 10^{-3}}{10.7 \times 1.765 \times 10^{-2}} = 2.03 \times 10^{-2} \text{ cm/hr.}$$

Experiments were performed at a current of 1.08 mA (expected rate of change of length = 0.22 mm/hr.) and for times of up to 4 hours. The results are shown in Table 5 and Fig. 14. The initial steep part of the curve represents the filling of the pinch around the wire. Further allowance must be made because the electrode lead wire protruded beyond the pinch seal. The diameter of this/....

of this wire was 0.030" and this leads to an estimated rate of change of length, with a current of 1 mA, of 2.71×10^{-2} cm/hr., or, at 1.08 mA, 0.29 mm/hr.

TABLE 5 CHANGE OF CAPILLARY LENGTH WITH TIME

	<u>TIME</u> (Hours)	<u>COND.</u> $\Omega^{-1} \times 10^2$	<u>LENGTH</u> (CM)
Expt. 1	0	1.627	1.72
T = 800°K	0.35	1.728	1.62
$\gamma(\text{ = 1.57$	0.50	1.788	1.56
i = 1.08 mA	0.75	1.806	1.54
	1.75	1.820	1.53
	2.00	1.871	1.49
	2.25	1.878	1.48 (5)
	2.50	1.880	1.48 (5)
	2.75	1.918	1.45 (5)
	3.00	1.930	1.44 (5)
	3.25	1.940	1.43 (5)
Expt. 2	0	2.140	1.34
T = 810°K	0.33	2.249	1.27
$\gamma(\text{ = 1.62$	0.50	2.324	1.23
i = 1.08 mA	0.75	2.307	1.24
	1.12	2.331	1.23
	1.50	2.376	1.20
	1.75	2.337	1.22
	2.25	2.574	1.11
	2.50	2.612	1.10
	2.75	2.628	1.09
	3.00	2.560	1.12
	4.00	2.688	1.05

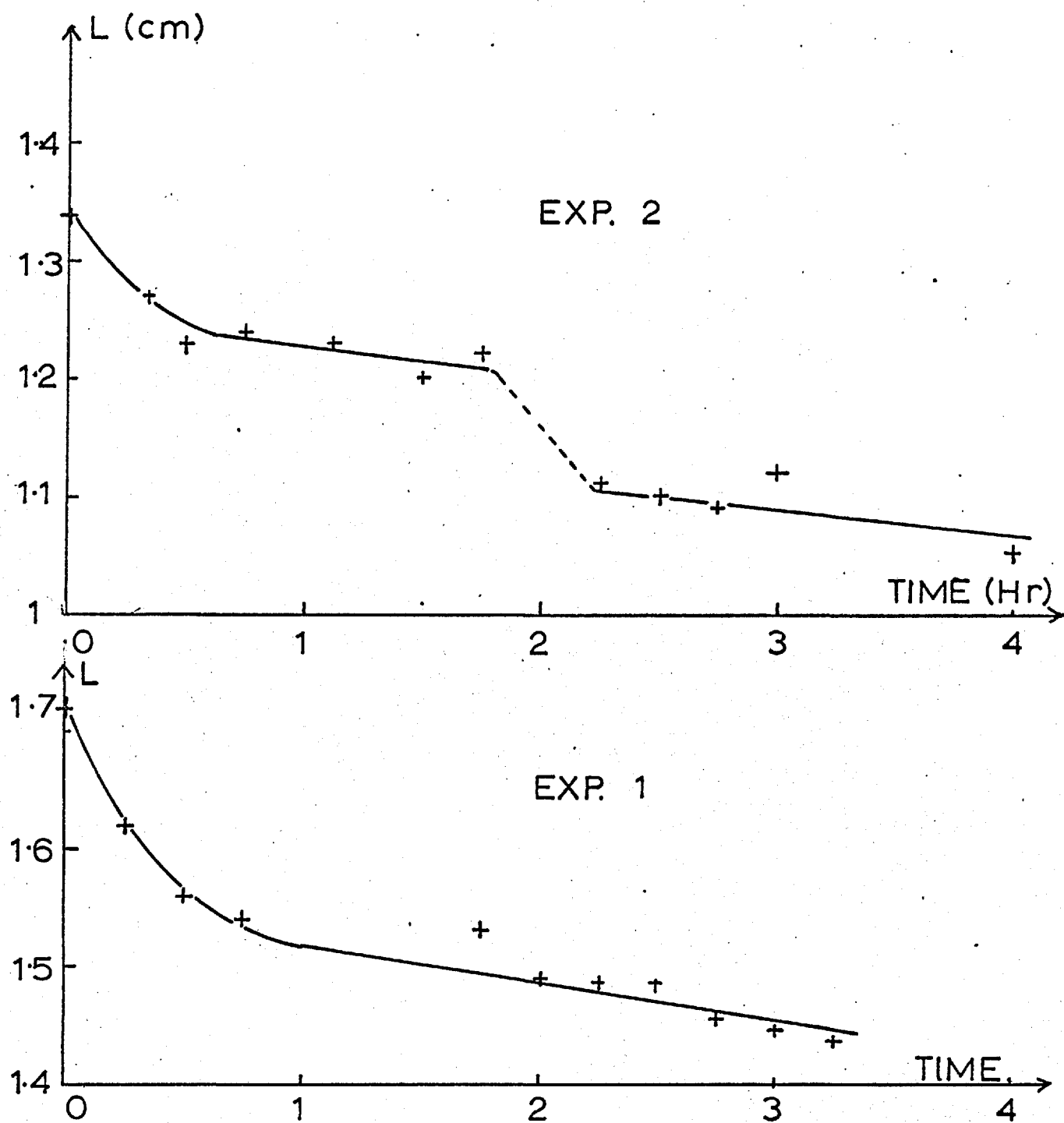


FIG. 14 . CAPILLARY LENGTH vs TIME

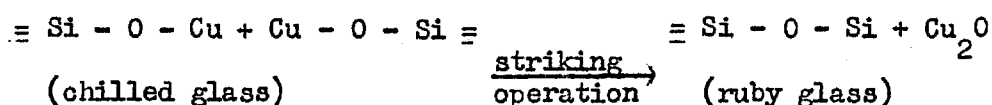
The first experiment was not carried out for a sufficient time for the metal to fill the capillary over the tip of the lead wire and the rate was found to be 0.30 mm/hr. A further experiment was carried out to confirm this result.

The second experiment indicated clearly the three stages of (i) filling the pinch seal, (ii) filling the volume around the wire and (iii) filling the capillary above the wire. The rates of filling during stages (ii) and (iii) were found to be 0.29 and 0.21 mm/hr. respectively. It was therefore concluded that diffusion of copper through the capillary walls did not give rise to a significant reduction in the resistance of the alternative current path.

Copper coloured glass was extremely difficult to seal to the lead wires, perhaps due to partial devitrification, so that the capillaries were always made of fresh glass. There was, therefore, no chance of the capillary becoming of comparatively low resistance due to repeated use, though this might have occurred in the preliminary cell. The fragility due to the copper in the glass may have been the cause of several failures of the containing envelope which occurred during the heating or cooling processes.

The red coloration was drastically reduced when NaCl was present in the melt and it was concluded that copper diffusion occurred to an even smaller extent in experiments using ternary (NaCl - containing) electrolytes.

It has recently been suggested (61) that the red colouring centres in copper ruby glasses are particles of cuprous oxide of colloidal size dispersed in the glass and that they are produced during the striking operation by the decomposition of cuprous silicate radicals present in the chilled glass, thus :



3.8

ANALYSIS FOR COPPER IN THE PRESENCE OF LEAD

A spectrophotometric technique was used for the analysis of copper in the presence of lead (62). The colouring agent was cuprizone (bis-cyclohexanone oxalyldihydrazone).

The reagent solution is made up by dissolving 0.1 gm of the cuprizone in 20 ml of a hot mixture of equal volumes of alcohol and water. The solution is filtered if necessary and cooled before use.

A suitable aliquot of the test solution (containing 0 - 100 μg Cu) is transferred to a 25 ml standard flask. The solution is buffered by the addition of 5 ml of a 10% aqueous solution of copper-free ammonium citrate (from Hopkin and Williams Ltd.) and 3 drops of strong ammonia solution. One drop of a 0.05 aqueous solution of neutral red followed by the dropwise addition of 50% aqueous NaOH solution (or concentrated HCl) until the indicator colour is just yellow. One ml of the reagent solution is added and the volume is adjusted to 25 ml with distilled water. An absorptiometric determination of the Cu present can then be made, at a wavelength of 595 m μ .

There is no interference with quantities of up to 10,000 μg of Pb in each aliquot. Other ions which might interfere are also suppressed. A list is available in the Hopkin and Williams monograph.

In alkaline solutions a blue complex is produced in the presence of copper, the intensity of the colour being such that, under favourable conditions, one part of copper can be detected in 25×10^6 parts of solution. The coloured complex is not formed in acid solutions while in strongly alkaline media the colour fades rapidly. The most suitable pH range in which to carry out the determination is about pH 7 to pH 10 and ammonium citrate may be employed as a complexing agent to prevent precipitation of the hydroxides of certain foreign metals. The coloured complex may, under suitable conditions, remain stable for several days.

A Unicam SP600 spectrophotometer was used and the first calibration curve is shown in Fig. 15, which illustrates that the Beer-Lambert law is obeyed throughout the range of interest. Subsequent recalibrations with known solutions agreed with this

initial/....

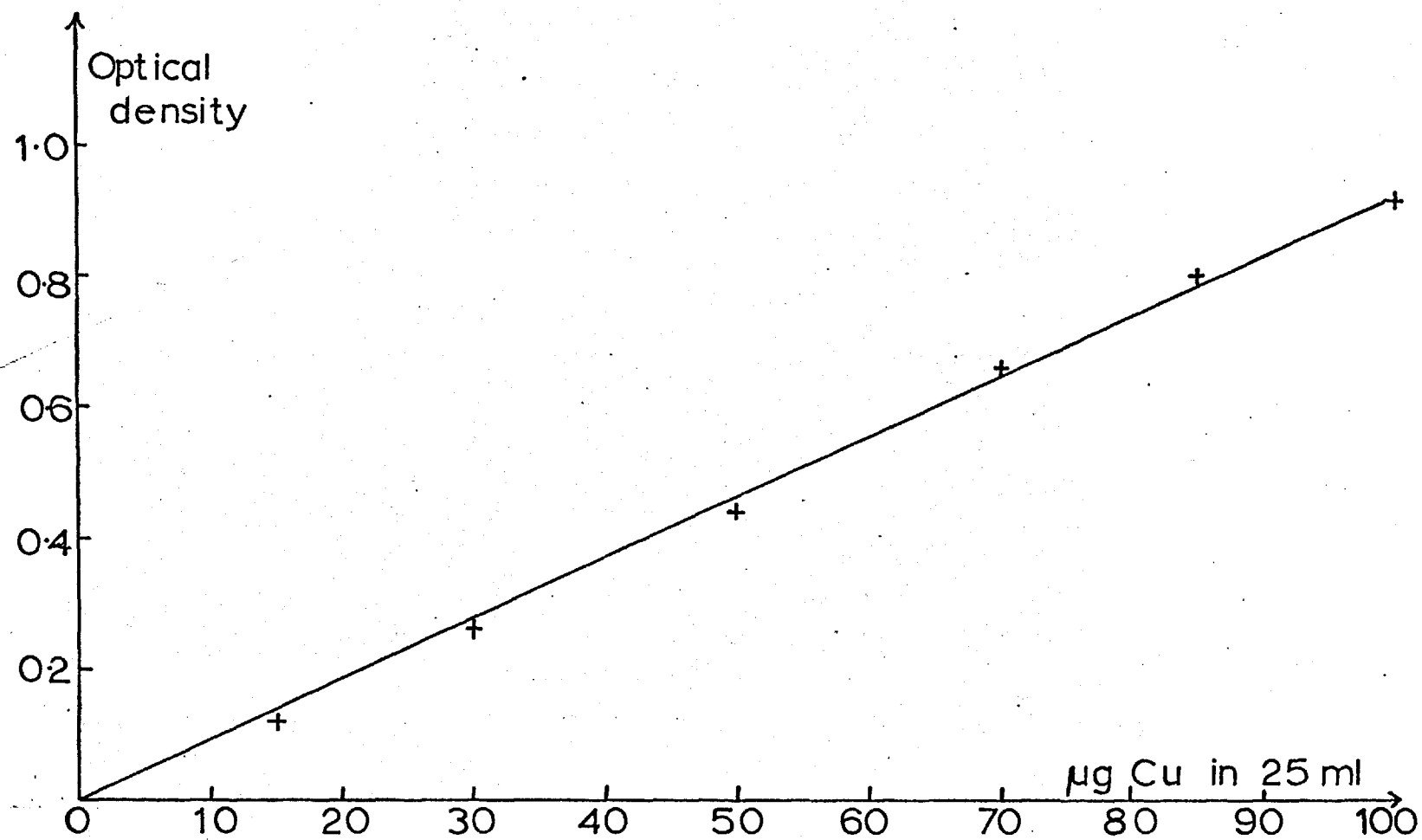


FIG. 15 CALIBRATION: Cu BY SPECTROPHOTOMETRY

initial result within the limits of experimental error.

The spectrophotometer is used with batches of 4 cells, one of which is a "blank". Three aliquots of each test solution were therefore taken and treated as above. The three results were averaged and an approximate analytical error calculated for each sample.

3.9 ANALYSIS FOR CADMIUM IN THE PRESENCE OF LEAD

The technique adopted for the analysis of small amounts of cadmium in lead was that of polarography. The method of Shai-kind⁽⁶³⁾ was adapted to suit the requirements of the system to be analysed. Since no bismuth was present it was possible to dispense with the time-consuming evaporation necessary for the removal of salts of that element. The final procedure was as follows:

- (1) The sample was dissolved in dil. HNO_3 .
- (2) Conc. H_2SO_4 was added carefully.
- (3) The solution was evaporated on a low temperature hotplate (about 80°C) until thick white fumes of H_2SO_4 were freely evolved.
- (4) After cooling, the solution was diluted carefully so that 5 ml. conc. H_2SO_4 would be contained in about 100 ml. of solution.
- (5) The solution was mixed thoroughly and allowed to stand for at least one hour.
- (6) The precipitate of PbSO_4 was filtered through a sintered glass crucible, washed with 1:100 H_2SO_4 and then ethyl alcohol. (For treatment of precipitate, when required, see 3.12).
- (7) The filtrate was placed in a 100 ml. flask and 10 ml. of 4N NH_4Cl and one drop of methyl orange indicator were added.
- (8) The solution was neutralised with a few drops of NH_4OH and then 10 ml in excess was added.
- (9) 2 ml. of 0.5% gelatin solution was added and the flask was made up to 100 ml. using distilled water.
- (10) A polarogram was taken for Cd in the normal manner and was repeated twice.

The/....

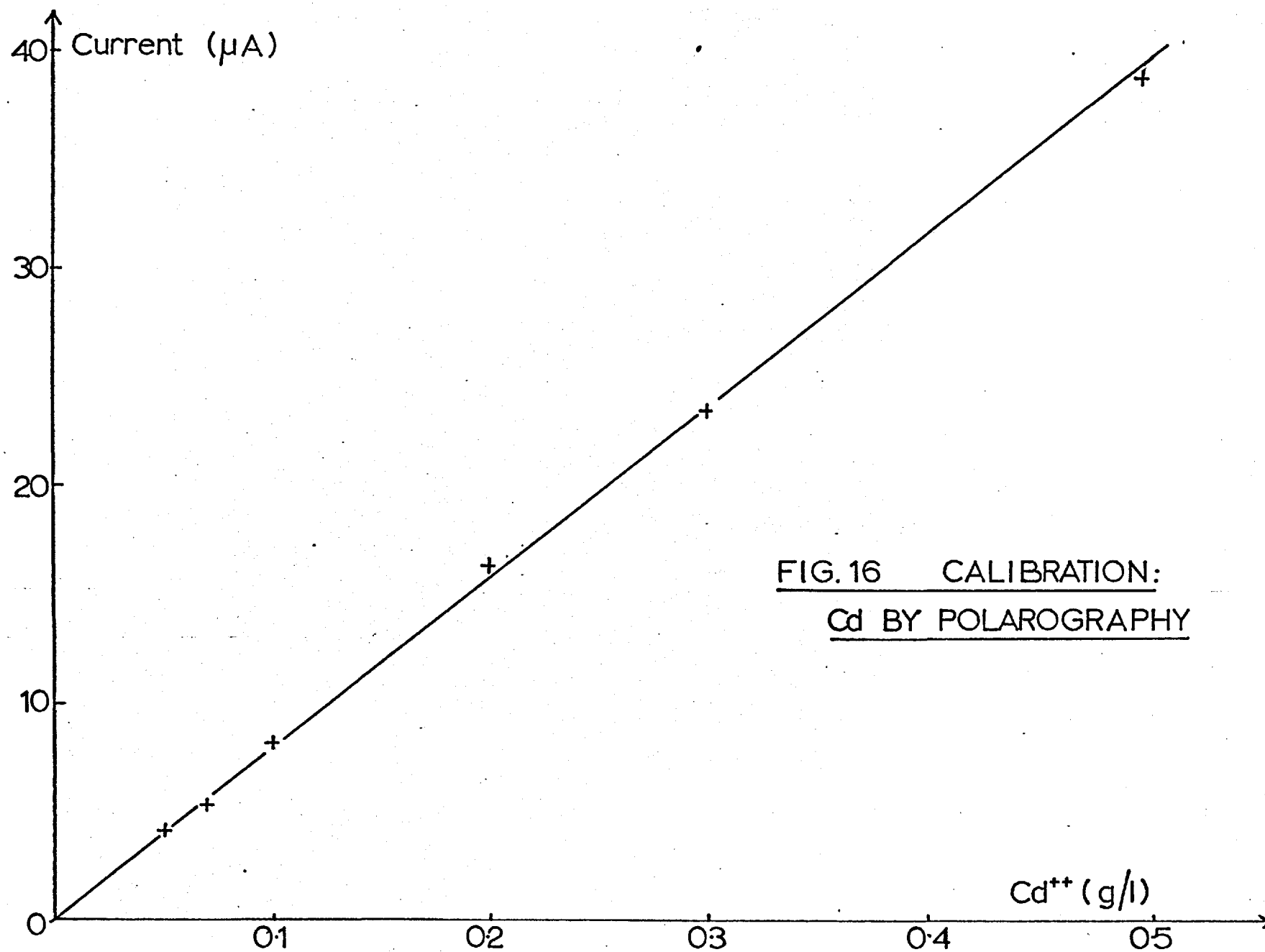


FIG. 16 CALIBRATION:
Cd BY POLAROGRAPHY

The half-wave potential for Cd^{2+} under these conditions is -0.82 volts. The instrument used was a Tinsley Type 19/2 polarograph.

It is necessary to follow the above rigorous removal of lead from the system, even when it is not required for gravimetric analysis, because a Pb^{2+} wave appears at about -0.6 volts and may interfere with the Cd^{2+} wave particularly at very low concentration of the latter ion. The presence of Pb^{2+} in the filtrate may be shown by a cloudy white coloration or precipitate, due to a basic lead salt, when the ammonia solution is added. The presence of very small amounts of lead, even after careful treatment, set some limitation on the amount of Cd^{2+} that could be detected.

Standard solutions containing known amounts of Cd^{2+} , up to 0.5 g/l, were used to calibrate the analysis. The calibration, shown in Fig. 16, did not alter over a period of three years.

3.10 ANALYSIS FOR SILVER IN THE PRESENCE OF LEAD

The analysis of silver in the presence of large excesses of lead and in the small quantities expected was found to be most easily performed by atomic-absorption spectrophotometry.

A theoretical description of the atomic-absorption technique of analysis ⁽⁶⁴⁾ and of its application to the analysis of solutions ⁽⁶⁵⁾ may be found in the literature. The quantitative determination of some noble metals, including silver, has been described ⁽⁶⁶⁾. A monograph on the subject has been published ⁽⁶⁷⁾.

The experimental details are, briefly, as follows:

A collimated beam of monochromatic light of the appropriate wavelength for the element under analysis (3281 Å for silver) traverses a flame and is focussed on the entrance slit of a spectrophotometer. The spectrophotometer is set to zero at the appropriate wavelength with the shutter closed. Distilled water is then sprayed into the flame and the instrument is balanced on the "check" position, i.e. the signal from the lamp is made to correspond to zero on the optical-density scale. A solution of the metal is then sprayed into the flame; this reduces the signal from the lamp, owing to absorption in the flame. The reduction in signal is conveniently expressed as an optical density, which can be read directly

from the/.....

from the spectrophotometer. Optical density measurements are made at various concentrations of the metal and a calibration graph is plotted.

A standard Hilger and Watts hollow-cathode lamp was used as a line source. Power for the lamp was obtained from a FA41 stabilised-supply unit. A Uvispek H700 spectrophotometer fitted with a Hilger H1100 atomic-absorption attachment was used. The burner was of the Meker type. Samples were prepared for analysis by solution in nitric acid.

The analysis was performed by Dr. Riley of the Analytical Services Laboratory at Imperial College.

The effect of iron and lead has been examined (66) and no interference has been found even with large amounts. It should be noted (67) that the slope of the calibration graph often changes slightly from day-to-day, due to variations in atomiser efficiency, and in all subsequent work it is necessary to include tests on a standard solution in order to apply an appropriate correction to the optical densities measured.

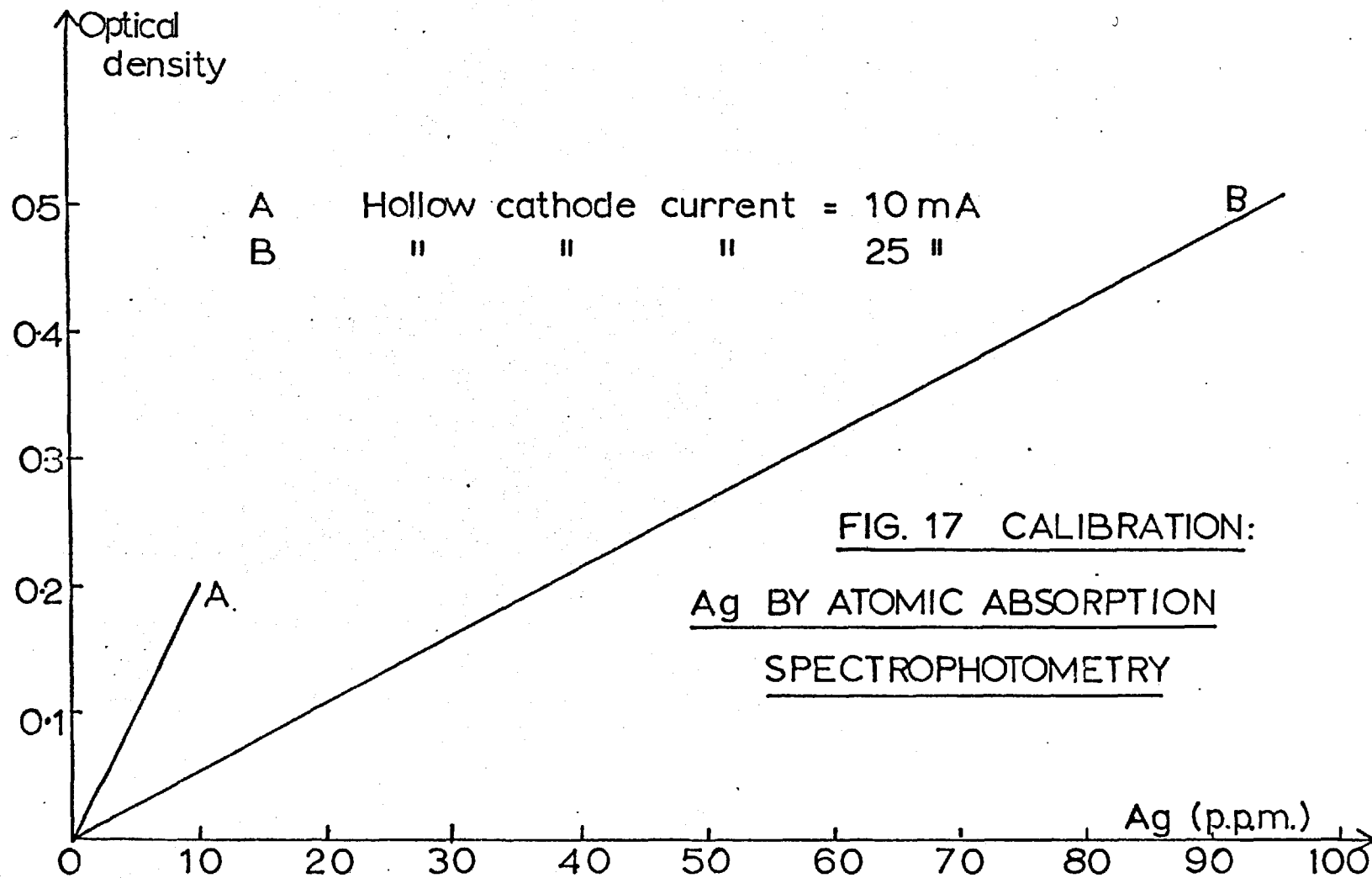
The calibration graphs obtained by Lockyer and Hames(66) and Russell, Shelton and Walsh(65) are shown in Fig. 17. The variation is accounted for by the different hollow-cathode currents used.

3.11 GRAVIMETRIC DETERMINATION OF LEAD CHLORIDE AS SULPHATE

In order to determine the composition of ternary electrolytes which contained NaCl in addition to the chlorides of the two metals in the anode it was necessary to analyse for both lead chloride and the impurity chloride. The standard procedure for gravimetric determination of Pb as the sulphate(68) was adapted for this purpose.

This technique provides a separation from the numerous elements which form soluble sulphates. Hydrochloric and nitric acids exert a solvent action upon lead sulphate, hence, if these are present, the solution must be evaporated with sulphuric acid until dense white fumes are evolved. $PbSO_4$ is slightly soluble in dil. H_2SO_4 , although with the very dilute acid (0.5%, V/V), the solubility (about 5 mg/litre at 10 - 20°C) is less than in water (about 45 mg/litre at 10-20°C) owing to the common ion

effect/...



effect. It is almost insoluble in ethyl alcohol.

The weighed sample is dissolved in the minimum quantity of dil. HNO_3 and about 3-4 ml. of pure conc. H_2SO_4 is added. The mixture is evaporated on a low-temperature hotplate until thick white fumes of H_2SO_4 are freely evolved. This ensures complete removal of HNO_3 and conversion of the lead salt to sulphate. After cooling, the mixture is carefully diluted (the final solution should contain about 5 ml. conc. H_2SO_4 in 100 ml. of solution), mixed thoroughly and allowed to stand for at least one hour. The precipitate of PbSO_4 is filtered through a weighed sintered glass Gooch crucible (the filtrate is retained for further analysis), and is washed three or four times with 1% (by volume) H_2SO_4 , then with ethyl alcohol until free from sulphate, and then dried at 130°C to constant weight. The precipitate is weighed as PbSO_4 .

This procedure was followed when ternary electrolytes were used for the systems containing Cu or Cd as an impurity. The filtrate from the above process was used in the described way for the analysis of Cu (3.8) or of Cd (3.9). The NaCl content was determined by difference.

3.12 ANALYSIS OF EXCESS CADMIUM METAL IN THE SALT

Gas volumetric techniques have been used successfully in this laboratory (69,70) for direct determination of a metal in the presence of salt.

A diagram of the gas volumetric flask (50 ml. capacity) is shown in Fig. 18. The arm (B) could be attached to a horizontal capillary tube, of 2.17 mm mean diameter and 150 cm. long, containing a mercury bead which enabled gas volumes of up to 5 ml. to be read off.

The flask was completely filled with N HCl which had been saturated with hydrogen by bubbling the gas through it and a gelatin capsule containing the powdered sample was introduced by rotating the sidearm (A). The capsule was 20 mm long, 8 mm diam. and was supplied by Parke, Davis & Co. A few minutes elapsed before acid penetrated the capsule and gas evolution began, by which time the mercury bead had regained a steady position. The distance of the bead was noted after several hours, when dissolution was complete.

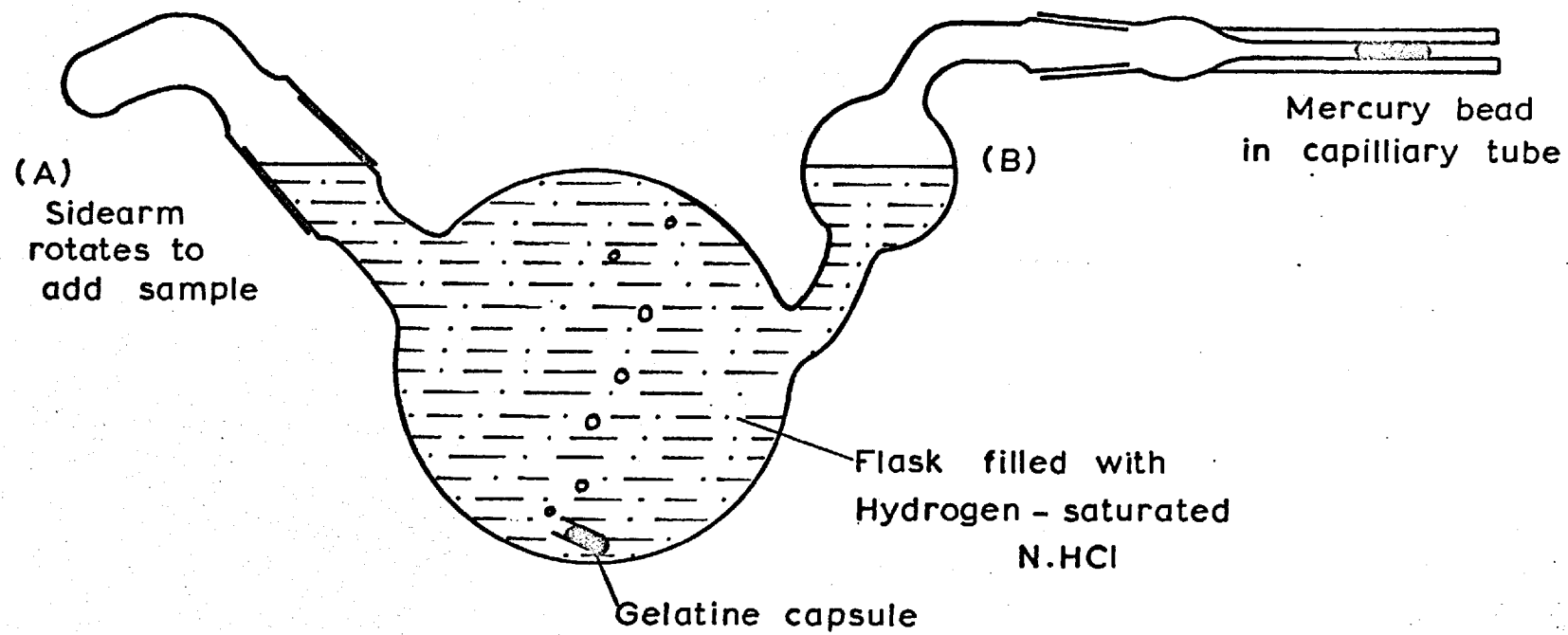


Fig.18. Gas Volumetric Apparatus

Two runs were performed using spectrographic pure cadmium metal and showed that the technique worked satisfactorily. Two analyses were then undertaken with samples of PbCl_2 - CdCl_2 electrolyte. No excess cadmium metal was found in either case and it was assumed that the solubility was negligibly small, as might be expected from the facts that

- (1) CdCl_2 formed only a small part ($\sim 20\%$) of the melt (the metal is assumed to dissolve mainly in its own salt by "subchloride" formation).⁽⁷⁶⁾
- (2) The addition of foreign salts is known to reduce the solubility of metals in their chlorides.

For reason of (2) above it was further assumed that the solubility of Cd metal in PbCl_2 - CdCl_2 -NaCl melts was also negligible.

CHAPTER 4

RESULTS

4A. THE LEAD - COPPER SYSTEM

The experimental apparatus described in Chapter 3 was used to investigate the transfer of three impurities in the electrolytic refining of lead using lead chloride and lead chloride-sodium chloride electrolytes. The impurities were copper, silver and cadmium. The effects of a number of variables on the refining ratio (ratio of impurity in cathode deposit to impurity in anode) were studied. The variables investigated were, temperature, current density, time, path length and amount of sodium chloride in the melt.

4.1 RESULTS USING THE PRELIMINARY CELL

The first system chosen for investigation was lead containing traces of copper, since the predicted value of β for this system was about 0.2 in the first calculations of refinability parameter (γ_c was not at first included in the parameter). Thus, sensible changes in the refining effect achieved by the cell would result from experimentally possible changes in the current density. The change of concentration of copper in the cathode with time for various current densities is shown in Fig. 19. The results obtained showed that more copper was transferred than lead. This was later found to agree with the predictions when activities in the liquid alloy were taken into account. However, a serious defect in the experimental technique was exposed. The current densities used (5 and 10 A cm⁻²) correspond to very high values of i^* (275 and 550 respectively) and it was apparent that the initial mass of the cathode (c. 70 g.) was too great for sensible changes in its composition to occur during experiments at low values of i^* unless experiments were carried out for several hundred hours. According to the theory, the refining effect will only vary with the dimensionless current density as the latter varies between 0 and 10. Thus it was not possible to use this first experimental apparatus to show how current density altered the refining effect. However, some useful information was obtained before the final cell was designed and used.

4.1.1 The Value of the Equilibrium Constant K

The analysis of both the copper concentration in the anode and the copper chloride concentration in the melt made possible the calculation/...

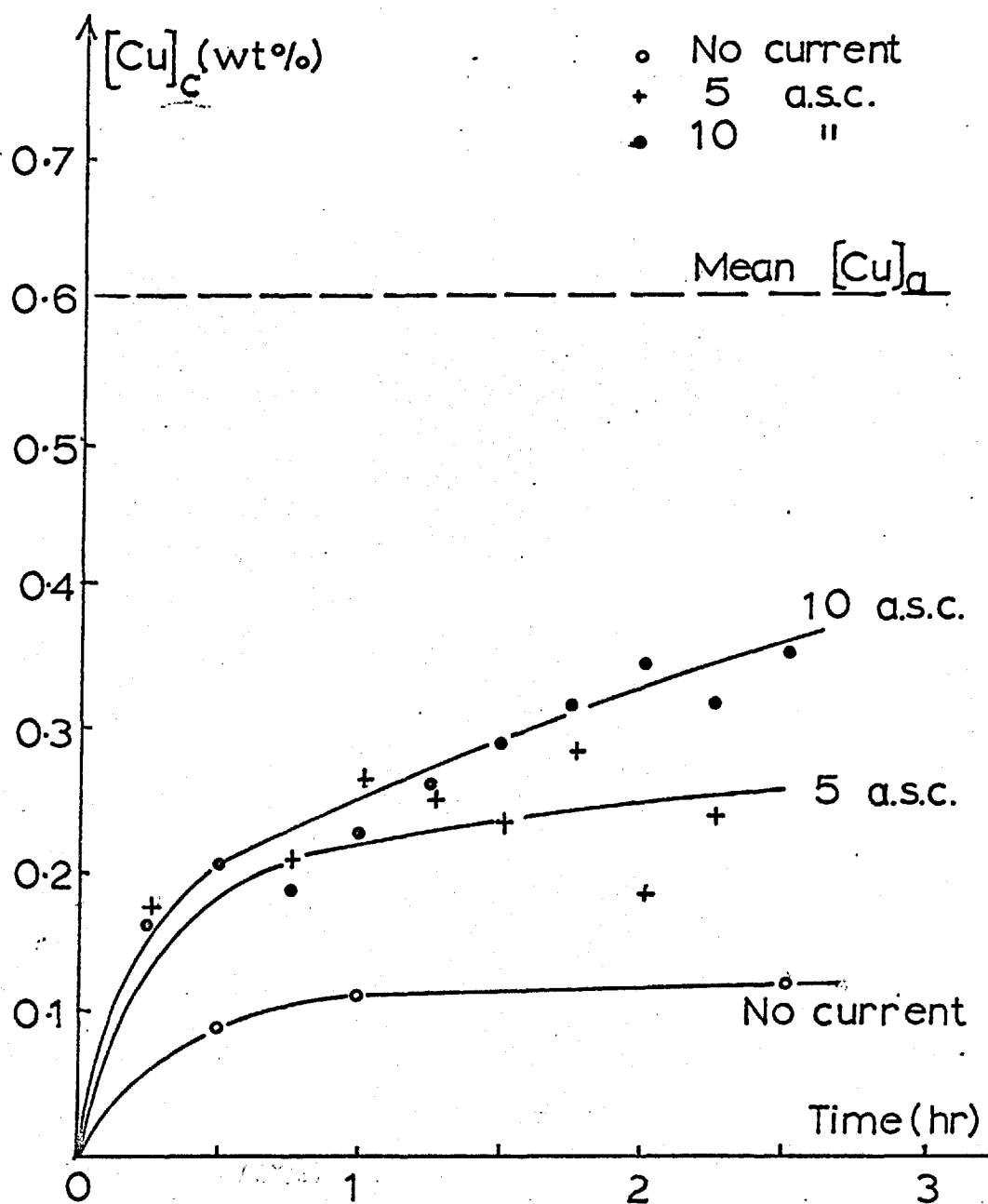


FIG. 19 EFFECT OF CURRENT ON TRANSFER OF
COPPER

calculation of an experimental value of the equilibrium constant K^+ . The temperature at which these experiments were performed varied between 560°C and 565°C and the results of analyses for three analyses of anode and electrolyte are shown below. In all cases the anode was 170 g. of lead and the electrolyte 350 g. of PbCl_2 .

EQUILIBRIUM CONSTANT K IN PRELIMINARY CELL

$[\text{Cu}]_a$ wt. %	$[\text{Cu}]_e$ wt. %	$[\text{Cu}]_a$ g.	$[\text{CuCl}]_e$ g	K^*
0.250	0.485	0.403	2.65	11.9
0.323	0.633	0.556	3.45	10.4
0.579	1.20	0.985	4.20	12.0

* Mean value of $K = 11.4 \pm 0.7$ (6%)

4.1.2 The Diffusion Coefficient of Copper in the Melt.

It was found that the system took a long time to come to thermodynamic equilibrium when no current was passed; a long run (about 140 hr.) was therefore performed with no current flowing in order to establish the nearness of a model which assumed a simple process of diffusion of Cu down the capillary (the melt, anode and cathode being stirred). The temperature was $550^{\circ} \pm 3^{\circ}\text{C}$ over the period of the run.

Considering a simple diffusion model, we obtain the following equation to describe the rate of increase of Cu in the cathode,

$$\log_{10} (\text{Cu}_a - \text{Cu}_c) = \log_{10} (\text{Cu}_a) - \frac{2 DA p t}{2.303 m L}$$

+ The term K used in this chapter is the equilibrium constant defined by the simple mass action law and differs from that used in Chapter 2, which is that obtained from thermodynamic data.

Thus $K^{1/2}_B$ in this chapter is equivalent to $\gamma_C K^{1/2}_B$ in Chapter 2.

where/...

where Cu_a , Cu_c = wt. % Cu in anode and cathode respectively,
 D = diffusion coefficient of Cu in the melt,
 A = area of cross section of capillary,
 ρ = density of melt,
 t = time,
 m = mass of cathode,
 L = length of capillary

Fig. 20 (a) shows the variation of Cu_c with time. The mean value of Cu_a was 0.66 ± 0.07 wt. %. The variation in analysis of both anode and cathode was due to the imprecise technique then employed. The reason for the initial jump in copper concentration, which also occurred when current was passed (Fig. 21a), may be partly mechanical disturbances (i.e. splashing) and partly the changes occurring in the establishment of the concentration gradient in the capillary at the beginning of the run.

Since $A = 0.018 \text{ cm}^2$, $\rho = 5.5 \text{ g.cm}^{-3}$, $m = 70 \text{ g.}$ and $L = 0.7 \text{ cm.}$, we obtain, from a graph of $\log (Cu_a - Cu_c)$ vs t (Fig. 20 (b))

$$D_{Cu} \approx 1.2 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$$

and $t_{\frac{1}{2}} \approx 400 \text{ hr.}$

where $t_{\frac{1}{2}}$ is the time to $Cu_c = Cu_a/2$.

A similar graph for runs in which current was passed is shown in Fig. 21(a). The data are given in Table 6.

The effective diffusion coefficients, D' , may be calculated as above.

The values are as follows:

Zero current	$D'_0 = 9 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$
5 amp "	$D'_5 = 4.8 \times 10^{-3} \text{ "}$
10 amp "	$D'_{10} = 1.4 \times 10^{-2} \text{ "}$

A plot of $\log (D')$ vs current is shown in Fig. 21(b) and approximates to a straight line. The data are too scanty and imprecise for any conclusions to be drawn, but it is clear that the transfer of copper in this manner is not governed simply by Faraday's laws.

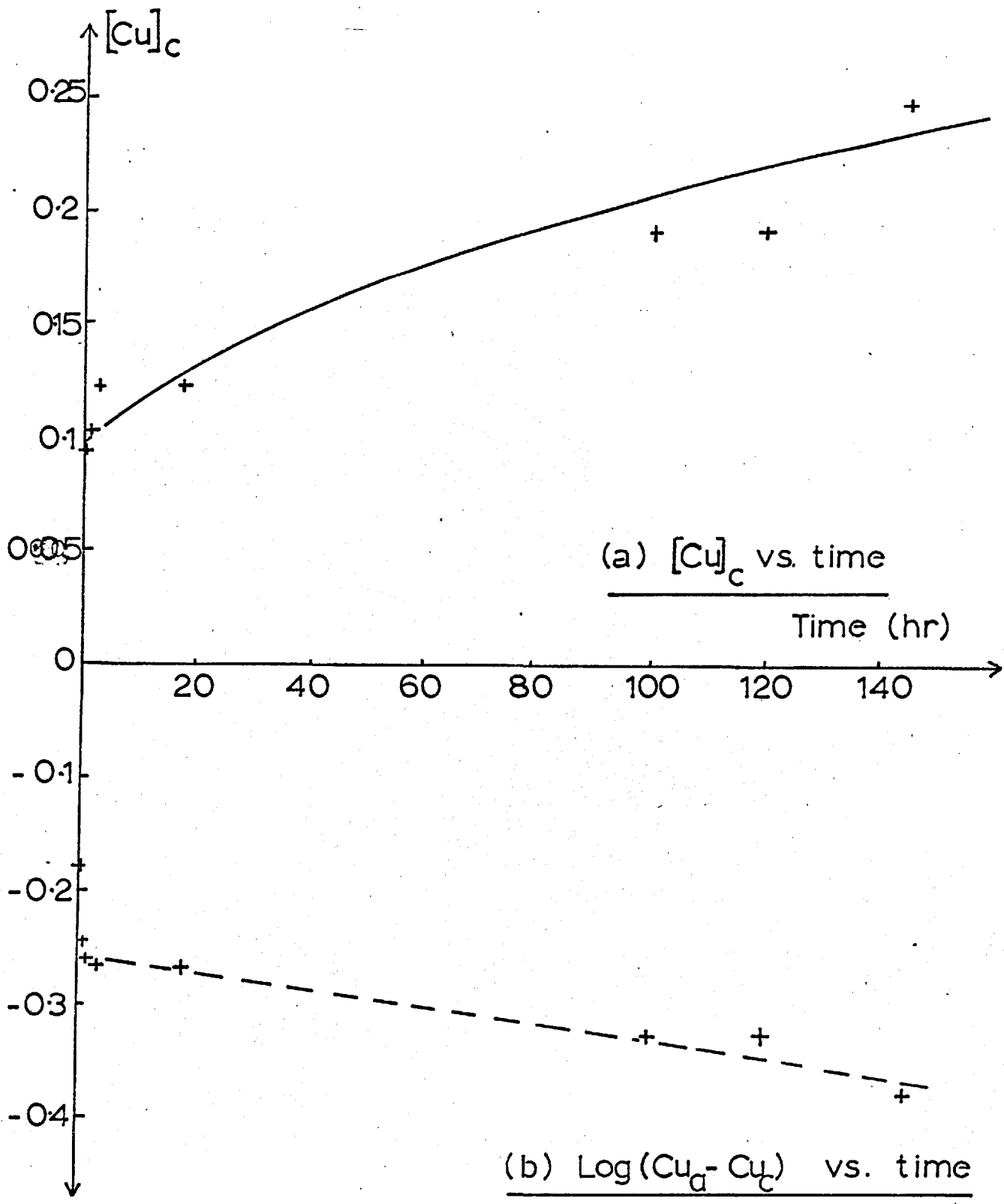


FIG. 20 DIFFUSION RUN WITH NO CURRENT

TABLE 6

EFFECT OF CURRENT ON THE RATE OF TRANSFER OF COPPER

TIME (HR)	NO CURRENT			CURRENT = 5 A/cm ²			CURRENT = 10 A/cm ²		
	Cu _c	Δ Cu	log ₁₀ (Δ Cu)	Cu _c	Δ Cu	log ₁₀ (Δ Cu)	Cu _c	Δ Cu	log ₁₀ (Δ Cu)
0	0	0.66	- 0.181	0	0.66	- 0.181	0	0.66	- 0.181
0.5	0.095	0.567	- 0.246	0.175	0.485	- 0.314	0.190	0.470	- 0.328
1.0	0.112	0.548	- 0.261	0.230	0.430	- 0.366	0.240	0.420	- 0.377
1.5				0.250	0.410	- 0.387	0.260	0.400	- 0.398
2.0				0.260	0.400	- 0.398	0.320	0.340	- 0.468
2.5	0.121	0.539	- 0.268	0.275	0.385	- 0.414	0.365	0.295	- 0.530

Cu_a taken as 0.66 wt. %: Cu_c given in wt. % Δ Cu = (Cu_c - Cu_a)

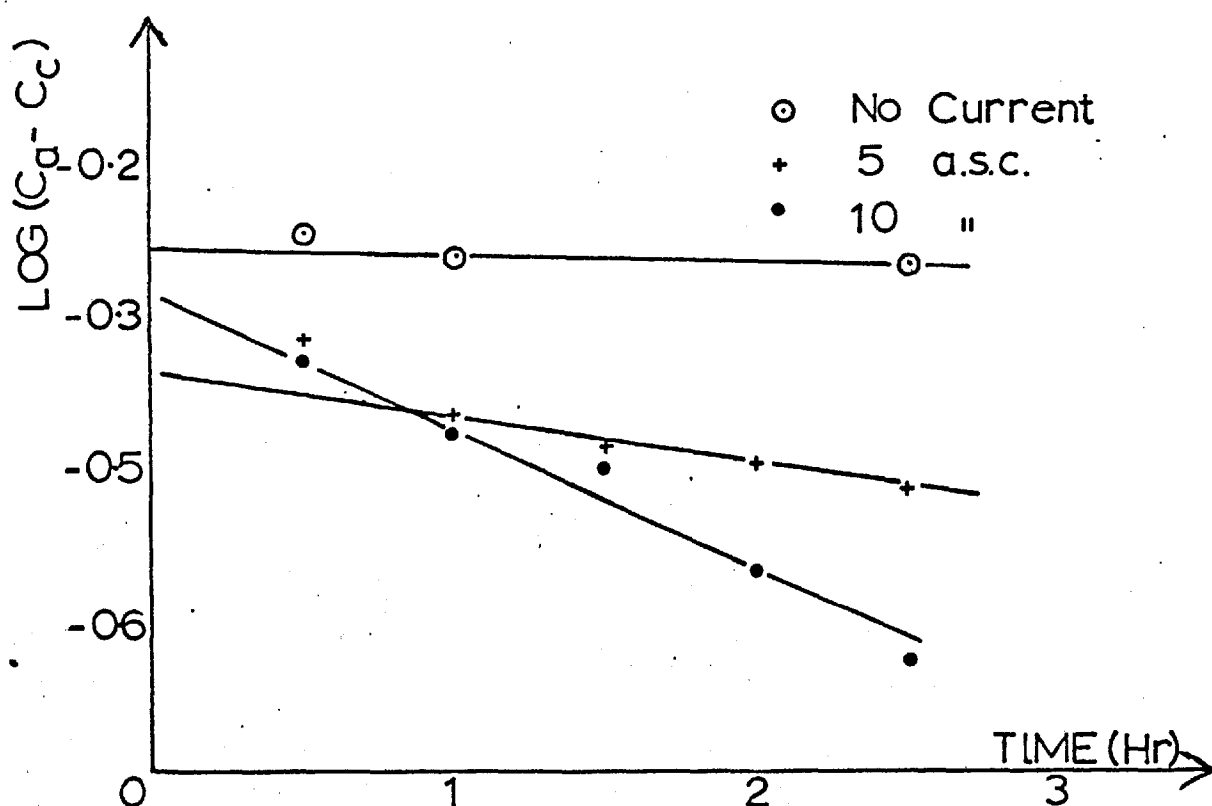


FIG.21 (a) EFFECT OF CURRENT ON TRANSFER OF COPPER

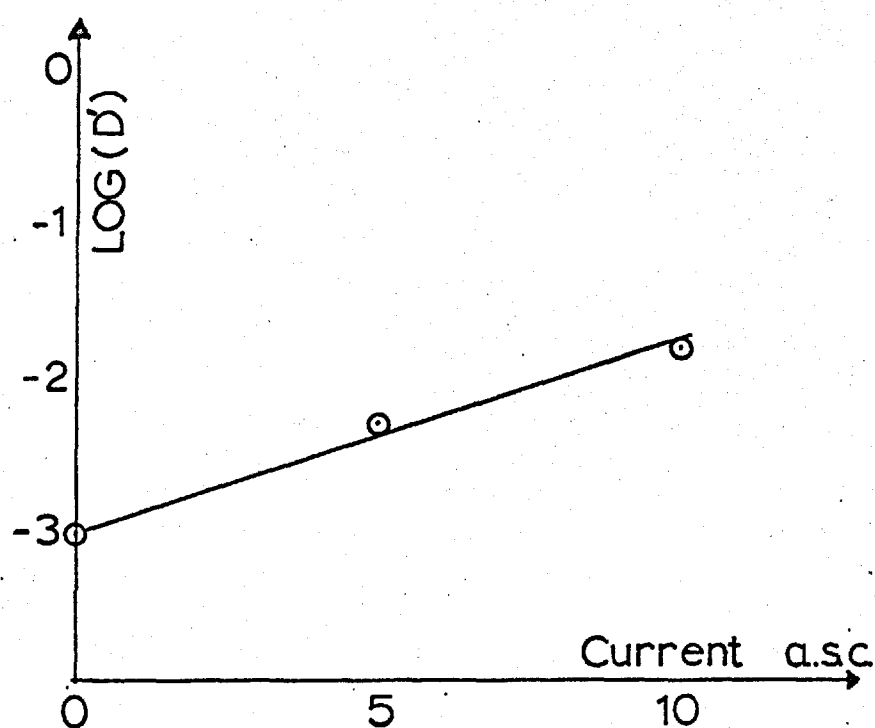


FIG.21 (b) LOG(Effective Diffusion Coeff D')
vs. CURRENT

4.2

RESULTS USING THE FINAL CELL

Two theoretical equations (derived in Chapter 2) were examined. The first showed that a limiting value of the refining ratio $[Cu]_o/[Cu]_a$ should be attained at high values of the current density parameter, i^* , according to the equation (2.30)

$$\lim_{i^* \rightarrow \infty} \frac{[Cu]_o}{[Cu]_a} = \frac{\gamma_o K^{1/Z_B}}{R^*} = \beta$$

The second equation showed the variation of the refining ratio with current density below the limiting value. This equation is

$$\frac{[Cu]_o}{[Cu]_a} = \frac{\beta}{1 + (\beta - 1) \exp(-i^*/Z_B)} \quad (2.34)$$

These two equations describe the effect of current density on the refining cell at constant temperature. The refining ratio at constant i^* should also be independent of variations in path length (and complementary variations in current density) since

$$i^* = \frac{i'' L R_{A-B}}{RTF} \quad (2.21)$$

In addition, the refining ratio should be independent of time. The effect of temperature on the refining ratio should be defined by the temperature variation of the parameter β .

$$\beta = \frac{K^{1/Z_B}}{R^*}$$

Accordingly the following variables were investigated

- (1) temperature
- (2) current density
- (3) time
- (4) current path (capillary length)

Altogether/...

Altogether some 100 runs were performed on the Pb-Cu system, but many of these failed to meet the criteria that were established for accepting or rejecting results. These criteria, as evolved, were:

- (i) Experiments must obey Faraday's law; that is, the weight should approximate to that calculated from the amount of electricity passed. Weights greater than this estimate indicate either splashing of material from the anode (gives a low value of $[Cu]_c$) or inadequate washing of the cathode deposit (gives a high value of $[Cu]_c$). The former effect occurred particularly when gas bubbling was used for stirring. Weights considerably less than the Faraday weight indicated that the cathode deposit had not been fully retrieved.
- (ii) The system must be in a steady state equilibrium. It was found that experiments performed at low current densities and for short times generally gave high results for reasons discussed in a later section (4.2.3(b)). These were experiments in which the theoretical cathode weight was 10 mg or less. Later experiments were run for times sufficient for 15-20 mg to be deposited.
- (iii) The first one or two experiments with each new melt were discarded because the cathode deposits might be contaminated with trace impurities in the materials separated by electrolysis.

The calculations made to determine the results of a run are shown in Appendix B.

4.2.1 Effect of temperature on the refining ratio

The first series of experiments (runs 1-39) were performed in the current density range of 0.2 to 4 A/cm², which is of the order of magnitude of those used in commercial processes. The value of i^* varied between 15 and 700. These experiments were intended to investigate the equation

$$\lim_{i^* \rightarrow \infty} \frac{[Cu]_c}{[Cu]_a} = \frac{\gamma_o K^{1/2} B}{R} \quad (2.30)$$

The/..

The experimental value of the temperature coefficient of the refining ratio was compared with that of the refinability parameter calculated from literature data. Temperature coefficients were compared because it was not expected that the theoretical and experimental values would agree because of the approximations made.

It may be shown that for the Pb-Cu system

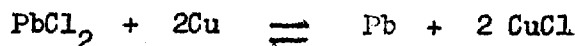
$$R^* = \frac{2 \text{ } \cancel{X} \text{ } \text{PbCl}_2}{3 \text{ } \cancel{X} \text{ } \text{CuCl}} \quad (4.1)$$

Using literature data (72) R^* can be calculated.

The temperature variation of the equilibrium constant K can be determined from thermodynamic data. The value of K at 800°K is 2.72×10^{-3} . From the equation

$$\log_{10} \left(\frac{K_1}{K_2} \right) = \frac{-\Delta H^\circ}{4.575} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4.2)$$

it is possible to calculate values of K for the reaction



at any temperature in the range covered. The value of ΔH° is 21.1 K cal (see 5.2.1).

The values of Y_{Cu} , K and R^* over the range of temperatures of interest are given in Table 7 and also the calculated values of β . A graph of the variation of β with the temperature is shown in Fig. 22. The temperature coefficient of the theoretical value of β is approximately 0.21 per cent per degree at 800°K.

A plot of the experimental values of refining ratio versus temperature for runs in the series 1 - 39 (Table 8) is shown in Fig. 23. The temperature coefficient calculated from the line of best fit is 0.52 ± 0.1 per cent per degree.

TABLE 7. VARIATION OF R^* , γ_{Cu} , $K^{\frac{1}{2}}$ AND β WITH TEMPERATURE

$^{\circ}K$	790	800	810	820	830
R^*	0.293	0.301	0.309	0.316	0.323
γ_{Cu}	16.1	15.5	15.0	14.5	14.1
$K^{\frac{1}{2}}$	0.0478	0.0521	0.0564	0.0611	0.0662
β	2.63	2.68	2.74	2.80	2.89

4.2.2 Effect of Current Density on the Refining Ratio

(a) High Current Density ($i^* > 10$)

The theoretical treatment shows that no more refining effect may be expected after the limiting current density, which corresponds to a value of i^* of about 10 (Fig. 6). Accordingly a series of runs was performed at $800^{\circ}K$ in which i^* varied between 10 and 25. These are tabulated in Table 9 and shown graphically in Fig. 24. Two runs (No: 24 and 26) at $798^{\circ}K$ are included. The errors estimated from the analysis are shown. The graph shows that the value of $[Cu]_o/[Cu]_a$ has reached a limiting value (3.65 ± 0.16) when the value of i^* exceeds 10.

(b) Low Current Density ($i^* < 10$)

The results obtained in the low current density region ($i^* < 10$) are given in Table 10 and shown graphically in Fig. 25. The errors estimated from the analysis are also shown. A well-defined curve is obtained indicating that the maximum refining effect is obtained by $i^* = 5$. The origin of the curve would be at $[Cu]_o/[Cu]_a = 1$ which represents thermodynamic equilibrium between the electrodes with no current flowing.

To obtain/...

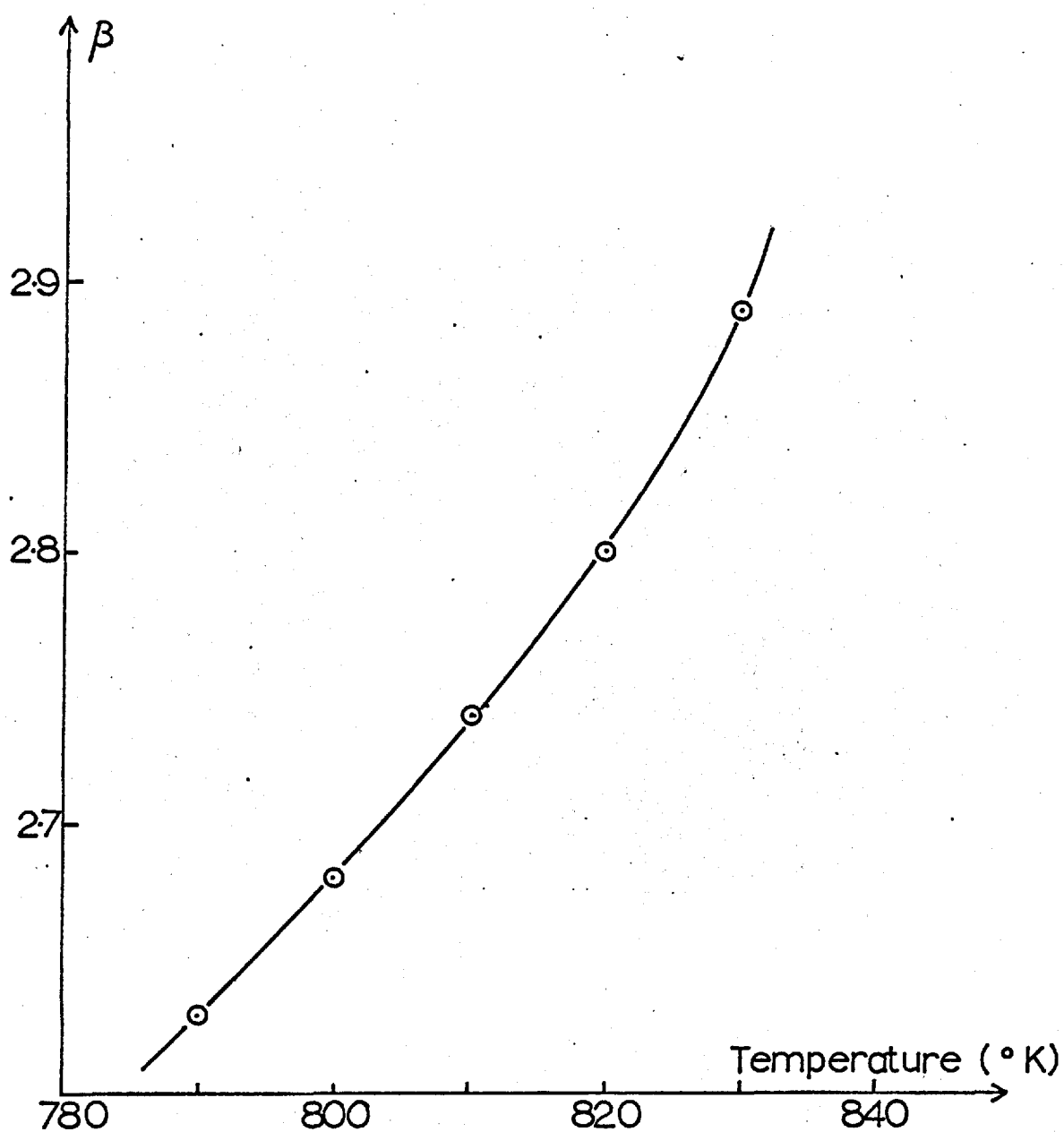


FIG. 22 VARIATION OF β WITH TEMPERATURE

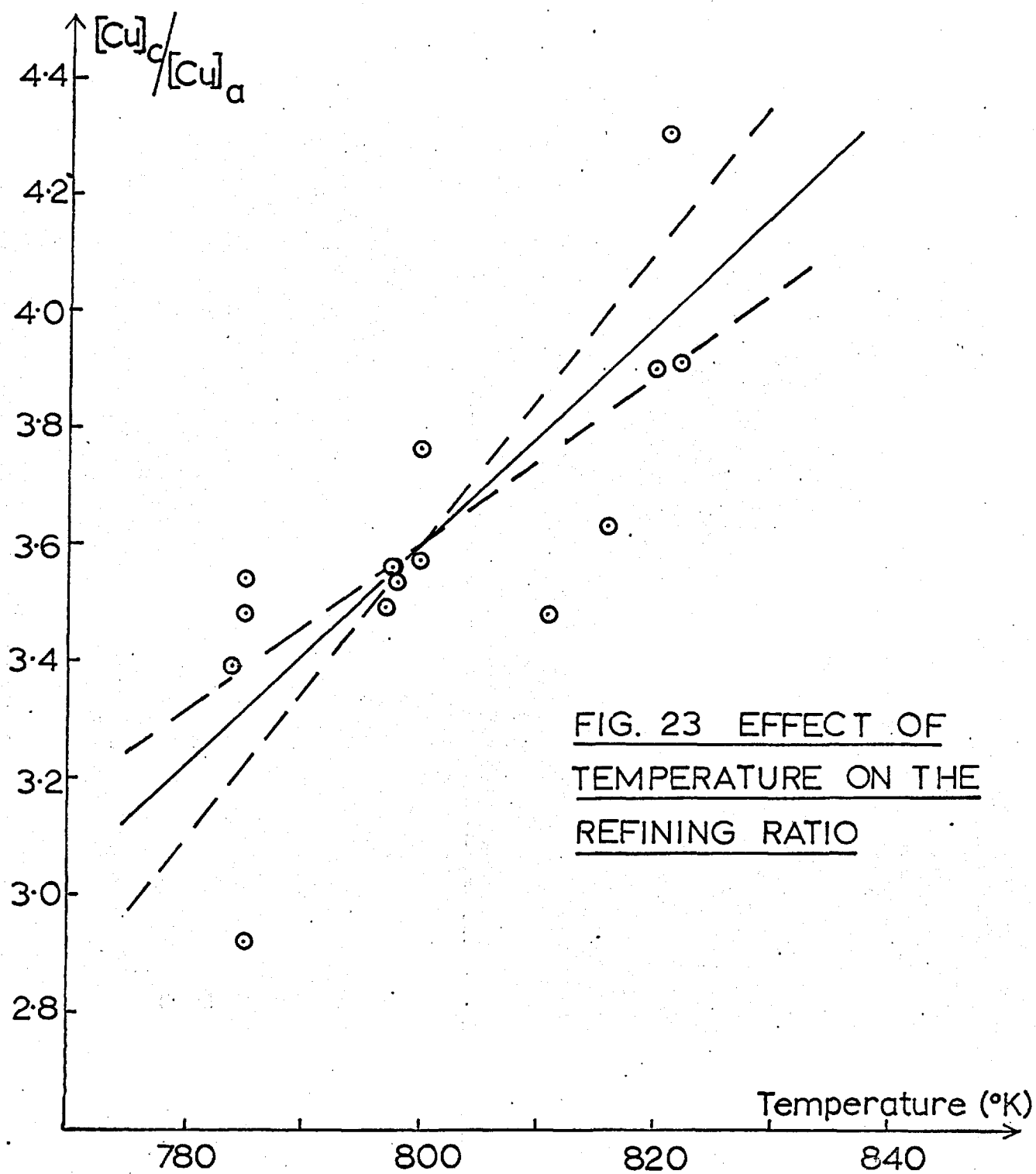
TABLE 8 RUNS 1 - 39. VARIATION OF REFINING RATIO WITH TEMPERATURE

Run No:	I mA	L CM	T °K	i*	Hr.	Cathode (mg)		C.E. %	Wt.% C.	Cu A.	$[Cu]_o / [Cu]_a$
4	17.65	3.54	816	181.6	0.5	35.34	33.68	102	2.29	0.630	3.63
5	17.65	2.69	811	142.0	1	58.10	67.36	86.5	2.09	0.600	3.48
6	17.65	2.32	821	117.6	1	68.50	67.36	102	2.65	0.616	4.30
7	17.65	0.959	820	48.8	1	68.60	67.36	102	2.34	0.600	3.90
12	35.30	2.60	822	262.5	0.5	26.58	33.68	78.9	2.41	0.617	3.91
15	26.475	2.74	797	230.8	1	101.6	101.0	100	1.92	0.550	3.49
17	26.475	3.12	785	276.7	1	102.5	101.0	102	1.60	0.453	3.54
19	35.30	1.725	784	204.8	0.5	67.59	67.36	100	1.48	0.438	3.39
20	35.30	1.295	785	153.3	0.5	66.84	67.36	99	1.56	0.447	3.48
23	70.60	2.96	785	700	0.5	137.69	134.72	102	1.39	0.476	2.92
24	4.270	1.88	798	24.6	3	45.96	48.80	94.5	1.74	0.494	3.53
26	2.714	1.545	798	14.2	4	40.11	40.30	99.5	1.85	0.520	3.56

< NEW MELT

I = Current
L = Capillary length
Hr = Time in hours
C = Cathode

Exp. = Experimental weight of cathode
Far. = Weight of cathode estimated from Faraday's law
C.E. = Cathodic current efficiency
A = Anode



4.2.2 - contd.

To obtain results at lower values of i^* , say 0.25, would have required runs of about 3 days in duration in order to attain steady state conditions and moderately-sized cathode deposits (15-20 mg.).

The value of the current density parameter, i^* , was calculated from the formula

$$i^* = \frac{i''L R_{A-B^+}}{RTF}$$

which is an approximation of the original equation

$$i^* = \frac{i''L (R_{A-B^+} Z_C + R_{B^+} C^+)}{RTF} \quad (2.21)$$

on the assumption that R_{BC} is negligible and noting that $Z_C = 1$.

The value of R_{AB} was calculated using the conductivity of the pure salt.

The value of L was determined by measurement of the resistance of the cell as described in Chapter 3. It was assumed that the conductivity of the electrolyte was that of pure $PbCl_2$ ($= 1.572 \text{ ohm}^{-1} \text{ cm}^{-1}$ at $800^\circ K$). The small amount of $CuCl$ in the melt would however lower this value and thus decrease the estimated value of L below the true values.

4.2.3 Effect of Time on the Refining Ratio

(a) Above the limiting current density

Sections 4.2.2. (a) and (b) have shown that, within the limits of the experiments, the value of the refining ratio is constant above $i^* \approx 5$. The length of these experiments varied between 1 and 5.17 hours. The refining ratio obtained is plotted against the time of electrolysis for runs where $i^* > 5$ in Fig. 26. The line of best fit can be seen to be very close to parallel to the time axis, indicating that a steady state equilibrium was attained in runs where i^* exceeded 5. Consequently it may be concluded that within the limits of experimental accuracy the refining cell was independent of time above the limiting current density.

The theoretical approach (cf. 2.2.5) shows that when the current density is above the limiting current density there should be no/....

TABLE 9

EFFECT OF CURRENT DENSITY ON THE REFINING RATIO FOR $i^* > 10$

Run No:	Current mA	Capillary Length (cm)	i^*	Time (hr)	Cathode Weight (mg)		Current Eff. %	Wt. % Cu		$\frac{[Cu]_c}{[Cu]_a}$
					Exp.	Far.		Cathode	Anode	
24 ⁺	4.270	1.88	24.6	3	45.96	48.80	94.5	1.74	0.494	3.53 ± 0.14
26 ⁺	2.714	1.545	14.2	4	40.11	40.30	99.5	1.85	0.520	3.56 ± 0.18
59	2.00	1.65	10.6	1.75	12.64	12.76	1.99	1.99	0.529	3.76 ± 0.16
69	3.00	1.63	15.08	1.75	20.01	20.04	100	2.22	0.622	3.57 ± 0.17
74	2.35	1.59	11.7	1.75	15.21	15.75	96.5	1.83	0.533	3.44 ± 0.30
76	3.53	1.75	19.4	1	11.38	13.48	84.5	1.81	0.477	3.79 ± 0.36
94	3.50	1.43	16.2	1.50	19.52	20.45	95.5	2.09	0.532	3.92 ± 0.40

+ 798°K

Exp. = experimental

Far. = estimate according to Faraday's law

TABLE 10. EFFECT OF CURRENT DENSITY ON THE REFINING RATIO FOR $i^* < 10$

<u>Run No:</u>	<u>Current mA</u>	<u>Capillary Length (cm)</u>	i^*	<u>Time (hr)</u>	<u>Cathode Weight (mg)</u>		<u>Current Effic: %</u>	<u>Wt. % Cu</u>		$\left[\text{Cu} \right]_c / \left[\text{Cu} \right]_a$
					<u>Exp.</u>	<u>Far.</u>		<u>Cathode</u>	<u>Anode</u>	
71	0.675	1.014	2.14	4.5	11.29	11.60	97.2	1.71	0.529	3.24 ± 0.08
83	0.25	1.88	1.49	18	18.72	19.09	98.1	1.58	0.531	2.97 ± 0.10
85	0.245	1.36	1.075	18	15.35	18.69	82.2	1.385	0.530	2.62 ± 0.13
86	1.20	1.375	5.46	4	17.93	18.32	97.9	1.858	0.516	3.60 ± 0.18
87	1.20	1.25	4.98	4	17.23	18.32	94.1	1.89	0.542	3.49 ± 0.17
91	0.51	1.55	2.65	9	17.90	17.50	102	1.59	0.507	3.01 ± 0.25
95	0.97	1.67	5.25	5.17	15.68	19.14	82	1.95	0.525	3.72 ± 0.18
99	0.875	1.31	3.72	4	13.69	13.36	102	1.90	0.532	3.57 ± 0.18
100	0.202	1.14	0.747	25.25	19.31	19.50	98.5	1.365	0.533	2.56 ± 0.15

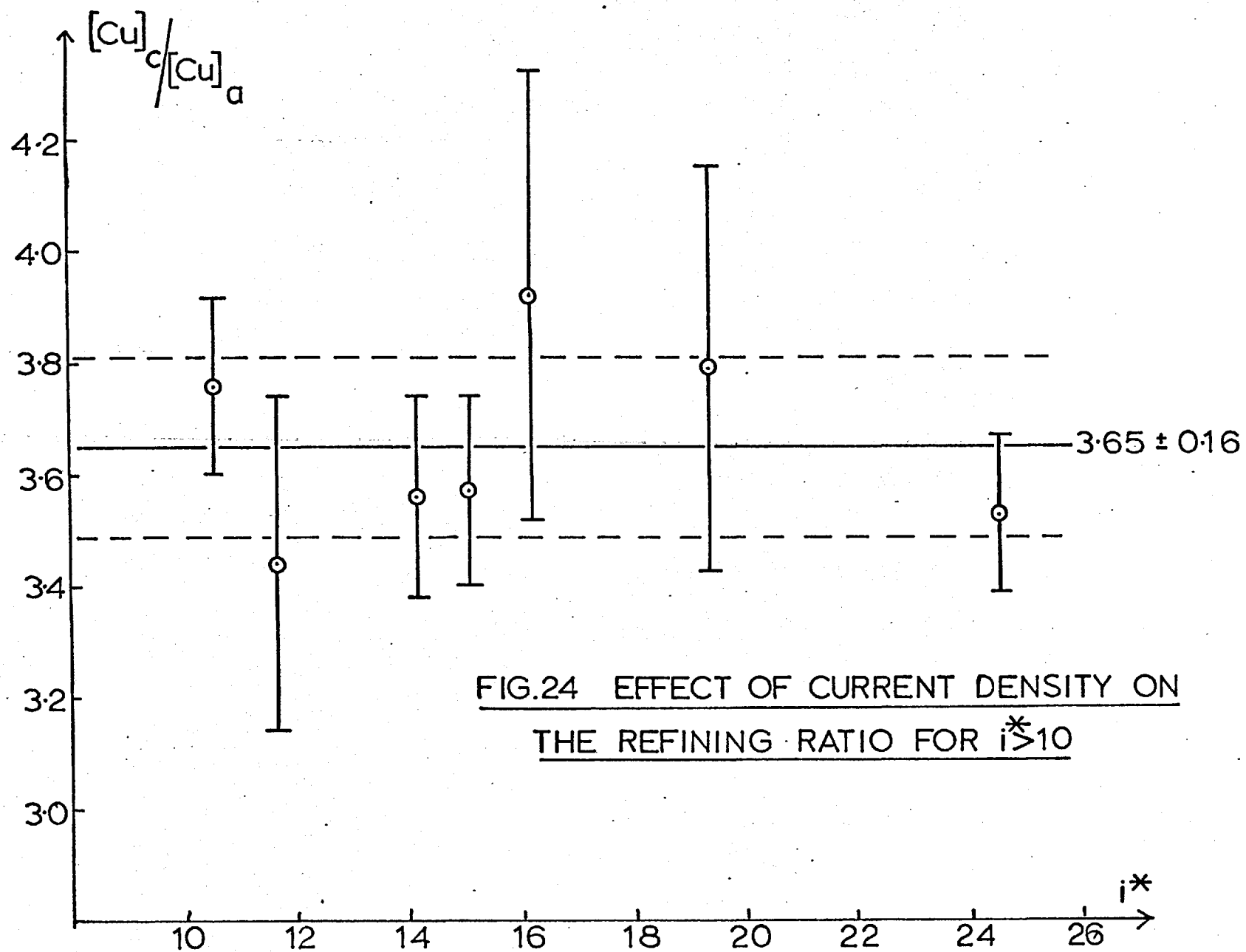


FIG.24 EFFECT OF CURRENT DENSITY ON
THE REFINING RATIO FOR $i^* \geq 10$

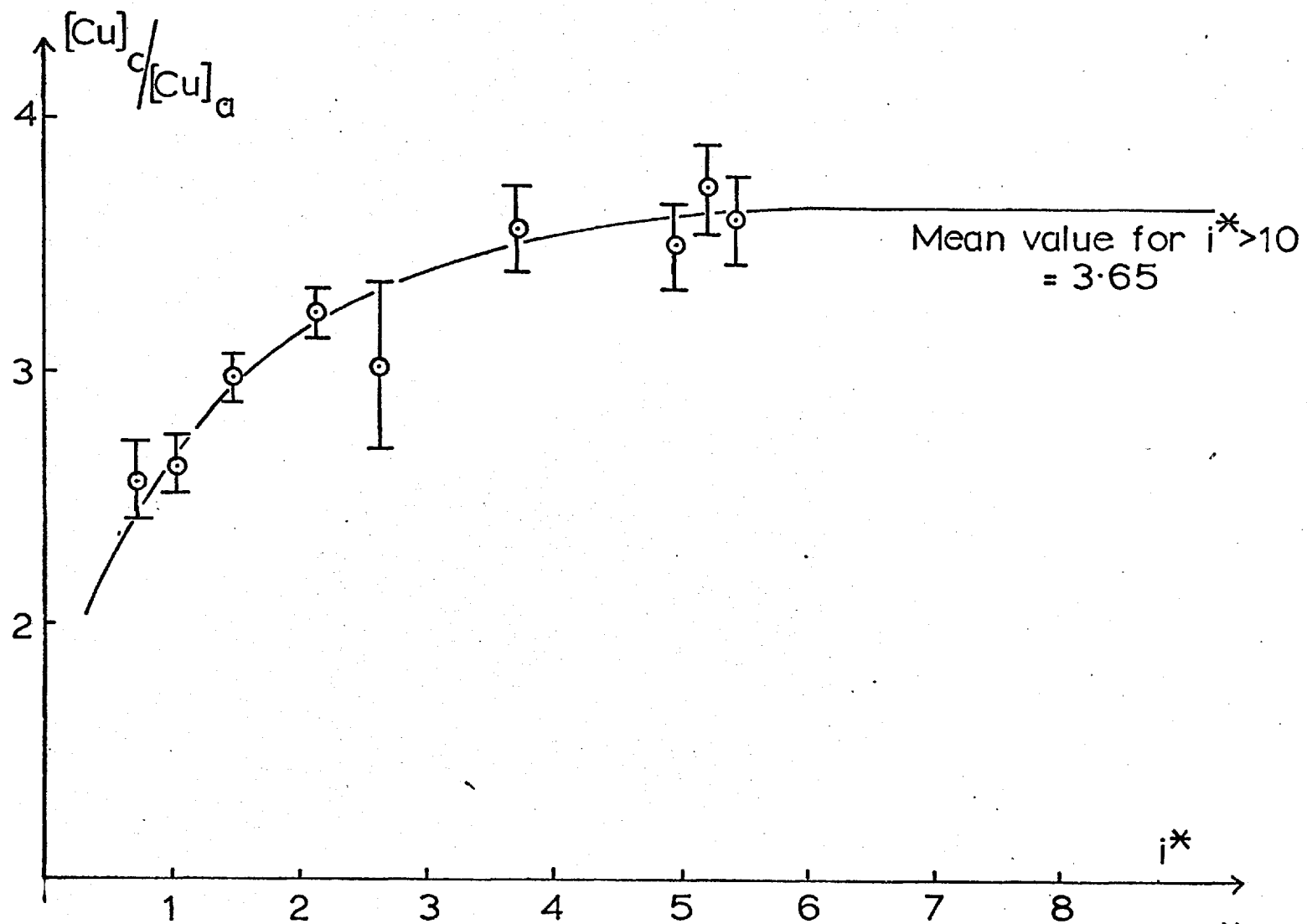


FIG.25 EFFECT OF CURRENT ON THE REFINING RATIO ($i^* < 10$)

be no concentration gradient across the cell. This is expressed by the equation

$$\lim_{i^* \rightarrow \infty} (R^* [X_{AC}]_x) \rightarrow [X_{AC}]_I \quad (2.27)$$

If no concentration gradient exists across the cell then no time is required for the steady state to be reached and the refining ratio should be independent of time above the limiting value of i^* . The experimental investigation of the hypothesis that there is no concentration across the cell is described in Section 4.2.6.

(b) Below the limiting current density.

As i^* decreases to values below the limiting value a concentration gradient begins to be set up across the cell. The gradient is set up by diffusion of copper ions away from the cathode. It should be emphasised here that the friction coefficient description of the process covers both diffusion of ions and migration of ions under an applied potential. These are in opposite directions in the case under discussion and below the limiting current density some back diffusion occurs. The diffusion coefficient of copper at zero current was found to be approximately $10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ (section 4.1.2) and the time for copper to diffuse along a 1.5 cm. capillary is therefore about 4 hours. It may be seen therefore that a period of several hours was necessary for the establishment of the concentration gradient when low currents were used. A combination of short times of experiment and low current would lead to erroneous results. These results would lead to high values of the refining ratio because of the excess copper in the cathode. A number of such experiments were performed (Table 11). When the refining ratio is plotted against Faraday's law predicted weight (which is proportional to time $\times$ current) as in Fig. 27 it can be seen that low ($i \times t$) runs must be rejected. The implications of this time effect on the observed effect of current is discussed in a later chapter (Section 5.2.2. (3)).

4.2.4 Effect of Path Length on the Refining Ratio

(a) Above the limiting current density. Fig. 28

shows a plot of the refining ratio against capillary length for runs where $i^* > 5$. The line of best fit shows a slight tendency for the refining ratio to decrease as the capillary length increases. The tendency is for

a 3%/.....

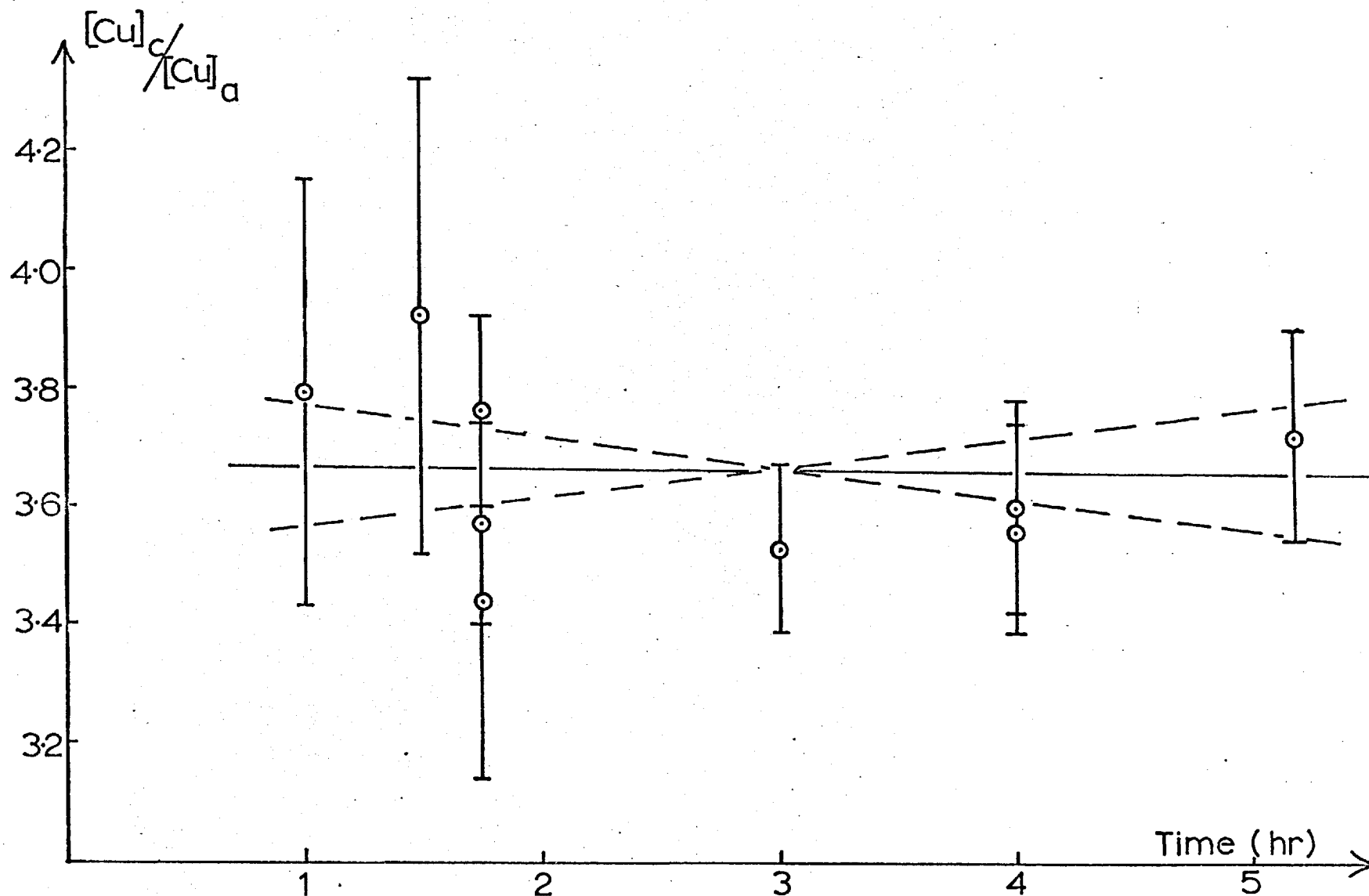


FIG. 26 EFFECT OF TIME ON THE REFINING RATIO ($i^* > 5$)

TABLE 11. EFFECT OF TIME ON THE REFINING RATIO FOR $i^* < 5$

<u>Run No:</u>	<u>i, mA</u>	<u>t, hr</u>	<u>Wt. % Cu</u>		$\frac{[Cu]_c}{[Cu]_a}$
			<u>Cathode</u>	<u>Anode</u>	
70	1.60	1.75	2.47	0.540	4.57
72	0.95	2	2.82	0.539	5.24
79	0.77	1.75	2.32	0.530	4.38
81	1.02	1.75	2.55	0.527	4.84
82	0.25	5	2.40	0.551	4.35

a 3% decrease as the path length doubles. The mean value of the results of runs above the limiting i^* is 3.65 ± 0.16 . The error is thus $\pm 5\%$ and it may be seen that the tendency for refining ratio to vary with capillary length lies well within these limits. Within the limits of accuracy of the experiments therefore, there is no significant dependency of refining ratio on path length.

(b) Below the limiting current density

Below the limiting value of i^* it is only possible to discover the effect of path length on refining ratio by comparing runs performed at the same current. Unfortunately only one pair of runs was carried out under these conditions. The two were Runs Nos: 83 and 85 and the relevant details are given below:

<u>Run No:</u>	<u>Current mA</u>	<u>Capillary Length Cm</u>	<u>i^*</u>	<u>Time Hr.</u>	$\frac{[Cu]_c}{[Cu]_a}$
83	0.25	1.88	1.49	18	2.97
85	0.25	1.36	1.075	18	2.62

Since the temperature was $800^\circ K$ in both cases it can be seen that the conditions were identical in the two runs except for the different capillary length. The different values of refining ratio/

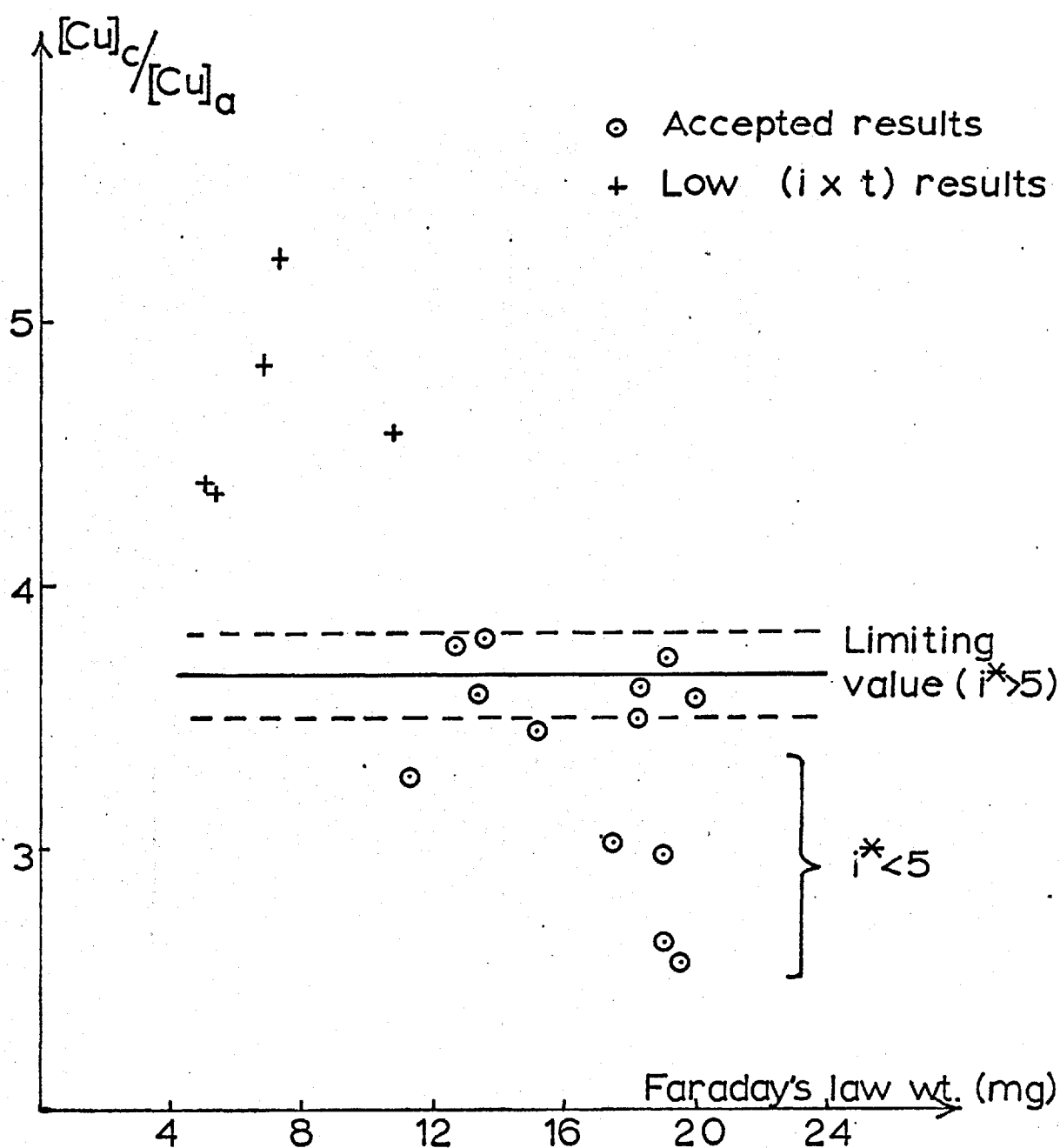


FIG. 27 EFFECT OF TIME ON REFINING RATIO

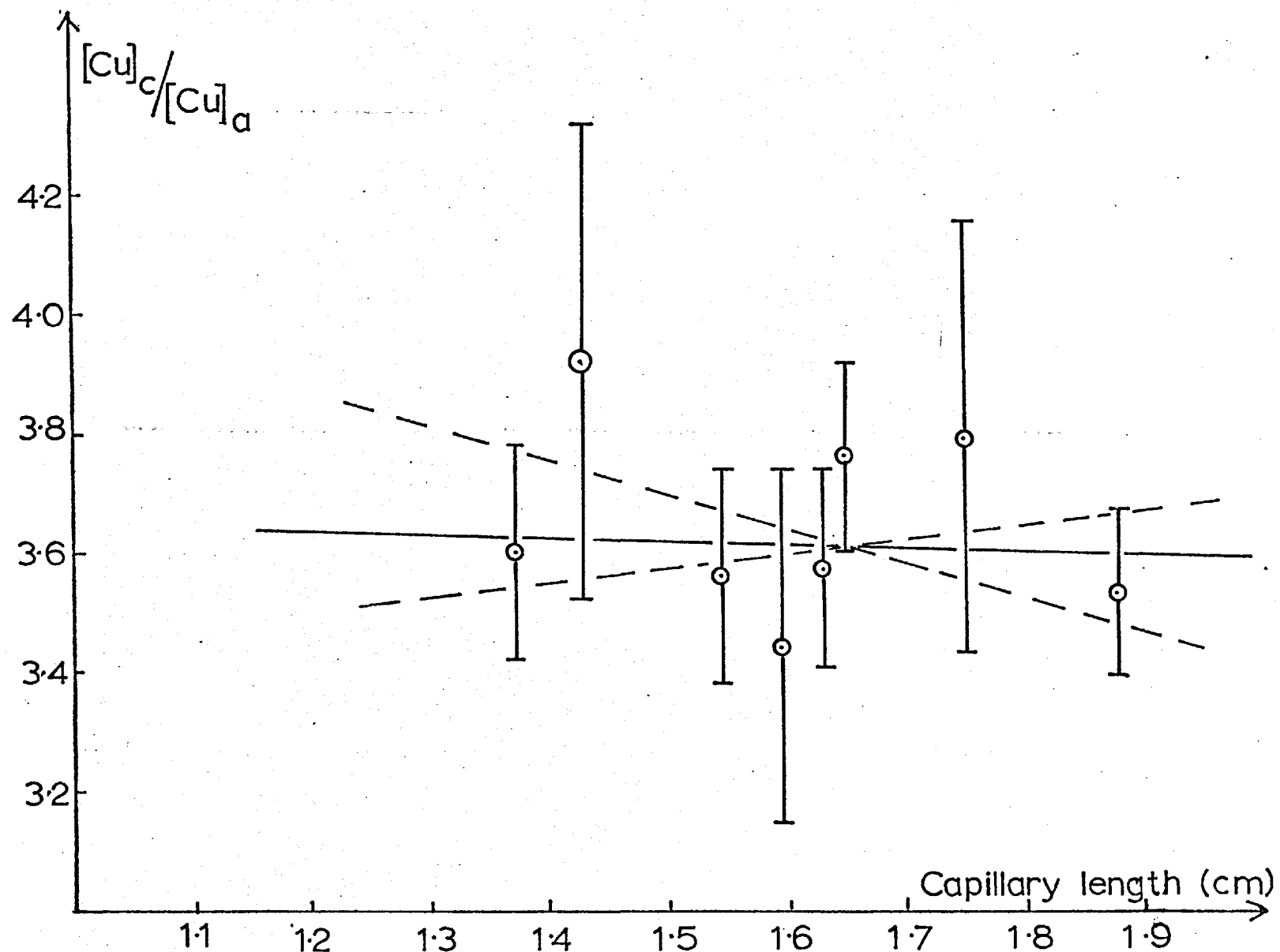


FIG. 28 EFFECT OF CAPILLARY LENGTH ON REFINING RATIO

ratio are due to the effect of the change in path length on i^* , and agree with the predicted decrease.

4.2.5 Value of the Equilibrium Constant K

As described in an earlier section (3.6.2) samples of the anode and electrolyte materials could be obtained by means of a simple sampling device. Anode samples were taken in all runs so that the refining ratio could be calculated, but electrolyte samples were not consistently taken for analysis until a later stage in the programme.

Table 12 lists the runs for the three melts in which analyses of copper concentration in anode and electrolyte were performed. The values of K and $K^{\frac{1}{2}}$ have been computed from the mean values of $[Cu]_a$ and $[Cu]_I$. In setting up the melts the conditions were kept constant as described in Section 3.6.2. The mean value of $K^{\frac{1}{2}}$ is 2.50 ± 0.23 (9%) and all three agree within the limits of accuracy of their determination.

4.2.6 Concentration Gradient Across the Cell

In Section 2.2.5 equation (2.40) was derived to describe the variation in concentration of the salts across the cell.

Fig. 7 shows the variation of $[X]_{AC}$ with distance from the anode in the case where $\beta = 5$ over a range of values of i^* . At values of i^* below the limiting value a positive concentration gradient exists.

At infinite (limiting) current densities it was found that

$$\lim_{i^* \rightarrow \infty} (R^* [X]_{AC}) \rightarrow [X]_{AC} \quad (2.27)$$

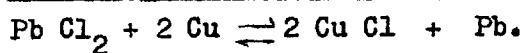
This equation implies that at limiting current densities there is no concentration gradient across the cell.

In order to test these theoretical conclusions the salt in the cathode capillary (referred to hereafter as the catholyte) was analysed in a number of experiments (Table 13). Care was taken to ensure that the liquid used to wash the cathode metal deposit was included for analysis.

The difference between the concentration of copper salt in the bulk of the melt and that in the catholyte would be small

and the/...

TABLE 12. THE EQUILIBRIUM CONSTANT K AT 800°K FOR THE REACTION



Run No:	Cu _a	[Cu] _I	K	K ^{1/2}	Error in K ²
46	0.539	0.920			
47	0.515	0.991			
48	0.545	1.080			
49	0.516				
50	0.515				
51	0.517				
53	0.529	0.850			
54	0.529	0.877			
55	0.529	1.050			
Mean	0.526	0.961	6.09	2.47	± 0.2
77	0.542	0.946			
78	0.570				
79	0.530	1.030			
81	0.527				
82	0.551	0.945			
83		0.972			
84	0.530				
85		1.220			
86	0.516				
87	0.542	0.809			
Mean	0.539	0.995	6.25	2.50	± 0.3
88		0.914			
89	0.514				
90	0.533	1.020			
91	0.507	1.010			
92	0.513	0.984			
93	0.552	0.930			
94	0.532	0.927			
95	0.525	0.959			
99	0.532	0.891			
100	0.533	1.150			
Mean	0.525	0.987	6.44	2.54	± 0.15

[Cu]_a = Cu

concentration
in the anode in
wt. %.

[Cu]_I = Cu

concentration
in the electro-
lyte in wt. %

and the difference would vary according to the value of i^* . For example, integration of (2.40) shows that in the case where $Z_B = 2$, $\beta = 4$ and $i^* = 2$, the catholyte concentration would be about 40% greater than $[X_{AC}]_I$. As i^* increases this difference decreases and vice versa.

It is clear from Table 13 that insufficient data are available, in view of the scatter of the values obtained, for conclusions to be drawn on the basis of such small margins as those predicted.

In general there was little difference between the concentration of copper salt in the catholyte and that in the bulk of the melt.

4.3 RUNS WITH SODIUM CHLORIDE ADDED TO THE MELT.

FIRST SERIES

Two series of experiments were performed with sodium chloride added to the melt in order to investigate the effect postulated in Section 2.3. The theoretical derivation, which ignored the effect of true concentration polarisation, arrived at the following equation as the description of the effect of an "inert" diluting salt on the refinability parameter.

$$\lim_{i^* \rightarrow \infty} \frac{[X_C]_c}{[X_C]_a} = \left(\frac{\gamma_C K^{1/Z_B}}{R^*} \right) \left(\frac{X_F^{Z_C/Z_B}}{Q + X_F(1-Q)} \right) = \beta' \quad (2.50)$$

Similarly the effect of current is described by

$$\frac{[X_C]_c}{[X_C]_a} = \frac{\beta'}{1 + (\beta' - 1) \exp. (-i^*/Z_B)}$$

which is equation 2.34 modified by the substitution of β' for β .

Sodium chloride was chosen as the diluting salt because it appears from phase diagram (73) and electrical conductivity (74) measurements that NaCl does not form complexes with either of the two other components.

In the two series of runs the temperature was maintained at 800°K for all experiments and at current densities not higher than $i^*/\dots$

TABLE 13 COPPER SALT CONCENTRATION OF THE CATHOLYTE

Run No:	i*	Copper Concentration in Wt. %		
		Electrolyte	Catholyte i* > 5	Catholyte i* < 5
77	13.2	0.956		
79	4.39	1.030		
82	1.075	0.945		
83	1.49	0.972		1.110
84	1.066			0.948
85	1.075	1.220		0.932
86	5.46		0.827	
87	4.98	0.809	0.860	
Mean		0.995 ± 0.15	0.844 ± 0.02	0.997 ± 0.08
88	13.6	0.914		
89	7.4		0.954	
90	< 5	1.020		
91	2.65	1.010		1.140
92	9.90	0.984	0.889	
93	1.24	0.930		
94	16.2	0.927	0.991	
95	5.25	0.959		
99	3.72	0.891		0.879
100	0.747	1.150		
Mean		0.987 ± 0.07	0.945 ± 0.04	1.010 ± 0.17

than $i^* = 20$. The capillary path was measured as described in the Experimental chapter, Section 3.3.3, and the values of electrolyte conductivity were recorded as an extra check on the constancy of the electrolyte composition.

4.3.1 Effect of Current Density on the Refining Ratio

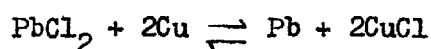
The results obtained for the variation of refining ratio with current density are tabulated in Table 15 and displayed graphically in Fig. 29. The same criteria for accepting or rejecting results were used as those described in 4.2. The cathode current efficiencies generally fell within the range 90-98%. The limiting value of the refining ratio is 2.89 ± 0.11 , and this value is reached at $i^* \approx 5$. At $i^* < 5$ the refining ratio rapidly decreases towards a value of 1, which represents thermodynamic equilibrium between the electrodes with no current flowing.

4.3.2 Composition of the Melt and Value of the Equilibrium Constant K.

The composition of the melt was obtained from a number of analyses of samples taken according to the method described in Chapter 3. The melt was analysed for lead chloride as the sulphate (Section 3.11) and copper chloride as copper (Section 3.8). The amount of sodium chloride was obtained by difference. The results of the analyses are summarised in Table 16. The mean values for the components are

PbCl ₂	76.98	±	2.06	mole %
CuCl	3.88	±	0.17	"
NaCl	19.14	±	2.10	

Using the mean values of PbCl₂ and CuCl concentration in the melt and the mean value of $[Cu]_a$ (Table 16) of 0.501 ± 0.013 wt. % for the reaction



we obtain a value of $K = 7.30 \pm 0.7$ (9%) and $K^{\frac{1}{2}} = 2.70 \pm 0.14$ (5%).

4.3.3 Composition of the Catholyte

Three samples of the catholyte were analysed for lead chloride and copper chloride. An increase in the sodium chloride content and a corresponding decrease in lead and copper chlorides can be seen (Table 17). It is apparent that concentration polarisation is beginning to have an effect even at the low current densities employed/...

TABLE 15.

EFFECT OF CURRENT DENSITY ON THE REFINING RATIO FOR MELTS CONTAINING NaCl

FIRST SERIES

<u>Run No:</u>	<u>Current mA</u>	<u>Capillary Length (cm)</u>	i^*	<u>Time (hr)</u>	<u>Cathode Weight (mg)</u>		<u>Current Efficiency %</u>	<u>Wt. % Cu</u>		$[Cu]_o / [Cu]_a$
					<u>Exp:</u>	<u>Far:</u>		<u>Cathode</u>	<u>Anode</u>	
3	2.19	1.15	9.92	3.6	27.84	29.07	95.8	1.366	0.487	2.806 ± 0.14
4	0.357	1.65	1.87	18	23.45	24.55	95.4	0.665	0.452	1.47 ± 0.15
5	1.35	1.27	5.39	3	14.99	15.47	97.0	1.487	0.484	3.08 ± 0.23
6	0.273	1.49	1.28	23	23.28	23.97	97.3	0.755		1.55 ± 0.08
7	1.12	1.25	4.39	4	16.82	17.10	98.4	1.404		2.90 ± 0.20
8	2.75	1.36	11.75	1	10.49	11.72	89.5	1.410	0.514	2.75 ± 0.20
9	0.726	1.32	2.95	6.25	16.42	17.33	94.8	1.158	0.512	2.26 ± 0.07
10	1.64	1.52	7.82	2.5	14.92	15.63	95.4	1.478	0.508	2.91 ± 0.16

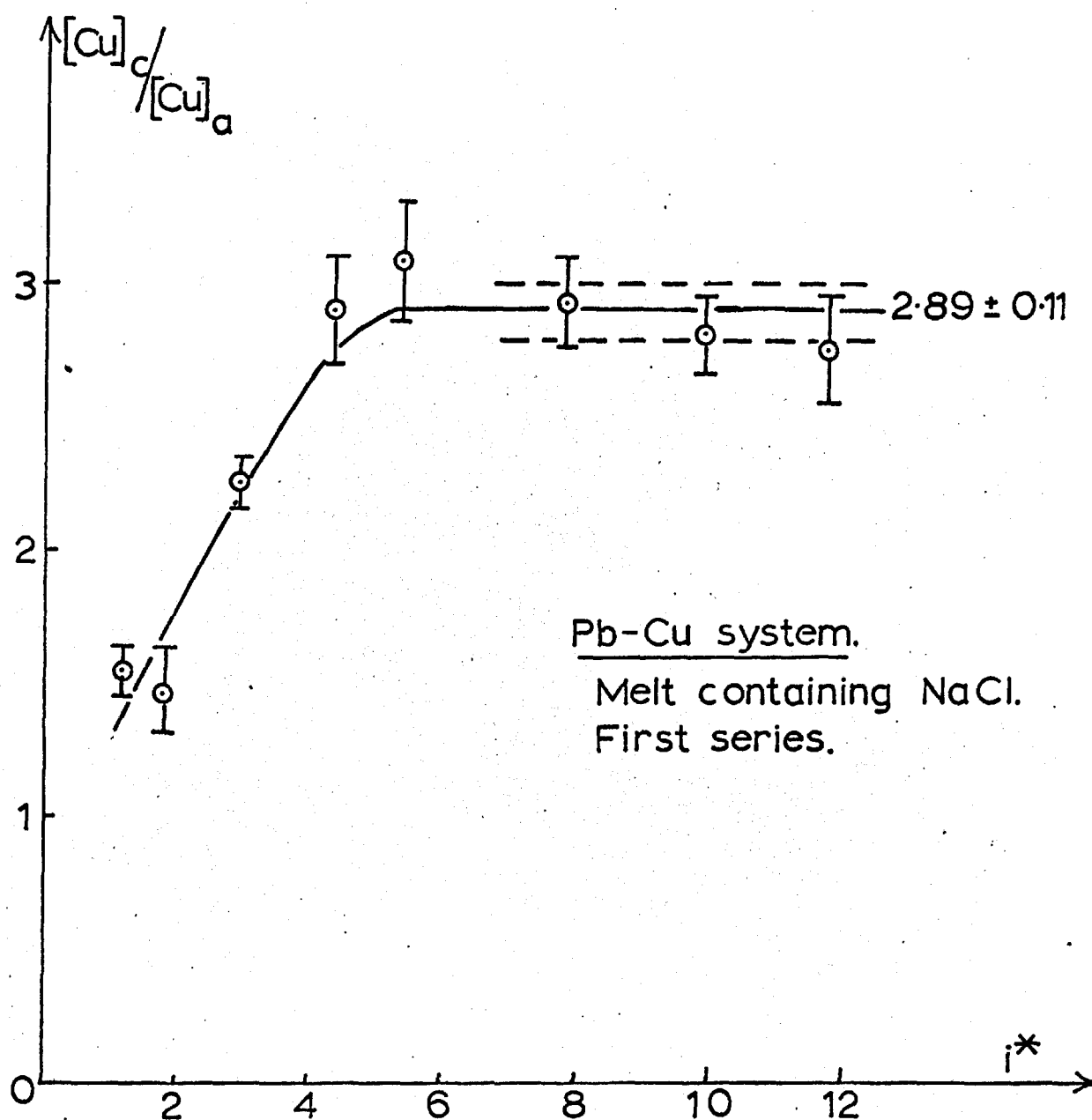


FIG. 29 EFFECT OF CURRENT ON REFINING RATIO

TABLE 16. COMPOSITION OF MELTS CONTAINING NaCl - FIRST SERIES

<u>Run No:</u>	<u>Sample Wt. (g)</u>	<u>PbCl₂ g</u>	<u>CuCl g</u>	Mole Per Cent		
				PbCl ₂	CuCl	NaCl
1	0.4634	0.4309	0.00751	74.69	3.80	21.51
3	0.4596	0.4346	0.00780	80.73	4.07	15.20
7	0.6099	0.5701	0.00940	76.10	4.10	19.80
9	0.3539	0.3287	0.00573	76.80	3.77	19.43
10	0.3608	0.3363	0.00575	76.60	3.67	19.73
Mean Composition				76.98	3.88	19.14

TABLE 17 COMPOSITION OF THE CATHOLYTE FOR MELTS CONTAINING NaCl. FIRST SERIES

<u>Run No:</u>	i#	<u>Sample Wt. (g)</u>	<u>PbCl₂ g</u>	<u>CuCl g</u>	Mole Per Cent		
					PbCl ₂	CuCl	NaCl
1	2.72	0.0954	0.0854	0.00141	65.54	3.04	31.42
6	1.28	0.1043	0.0942	0.00202	68.10	4.05	27.85
7	4.39	0.0949	0.0842	0.00169	63.9	3.59	32.51

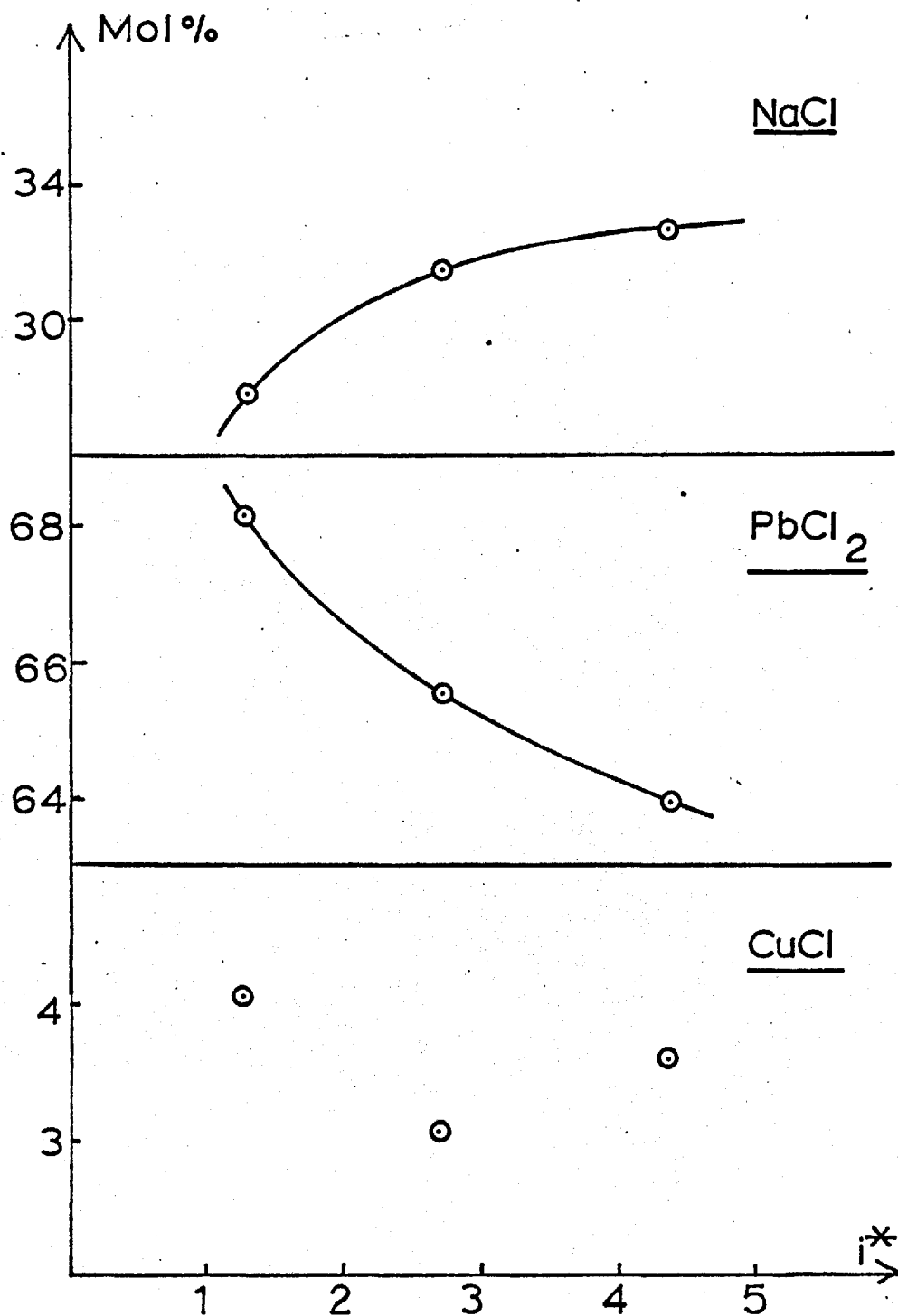


FIG. 30 VARIATION OF CATHOLYTE COMPOSITION

employed. Further, plots of the molar percentages of the three components against i^* shows the effect of increasing current density on the concentration polarisation (Fig.30). The errors in estimation of copper chloride do not permit the trend to be observed clearly. Extrapolation to values of concentration at $i^* = 0$ shows that, to a first approximation, values approach those in the bulk of the melt.

4.3.4 Conductivity of the electrolyte

The cathode capillary length was measured in KCl solutions (cf. Section 3.3.5.) and measurement of the resistance of the filled capillary in the melt enabled an estimate of the conductivity of the mixture to be made. Allowance was made for the thermal expansion of the glass. Because of the change in composition of the electrolyte in the capillary the measurement had to be made before electrolysis began. The mean value of L , used in the calculation of i^* , was taken from the values of the conductivity at the beginning and end of the run.

TABLE 18. CONDUCTIVITY OF $PbCl_2$ - $CuCl$ - $NaCl$ MIXTURES
FIRST SERIES

<u>Run</u> <u>No:</u>	Measurements in KCl			L cm.	In Melt	
	$t^{\circ}C$	χ (mho)	Cond. (G_x) μ mho		G_x mmho	χ mho
1	21.0	1.191	121.8	1.726	15.11	1.475
4	19.7	1.156	116.2	1.754	14.23	1.412
5	18.9	1.137	154.2	1.301	19.05	1.403
6	17.9	1.113	120.9	1.625	15.99	1.470
7	19.1	1.142	154.0	1.309	19.53	1.446

The mean value of the conductivity of the electrolyte at $800^{\circ}K$ was:

$$1.441 \pm 0.066 (4.5\%) \text{ ohm}^{-1} \text{ cm}^{-1}$$

It may be seen that the composition of the melt remained stable during the experimental period since a 5% variation in χ would be caused by relatively small changes in composition (or temperature).

4.4 RUNS WITH SODIUM CHLORIDE ADDED TO THE MELT

SECOND SERIES

4.4.1 Effect of Current Density on the Refining Ratio

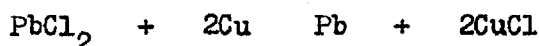
The results obtained for the variation of refining ratio with current density are tabulated in Table 19 and shown in Fig. 31. The criteria for rejection of results described in 4.2 were applied. The cathode current efficiencies fall in the range 96 - 101%. Small errors in timing account for some current efficiencies exceeding the estimated weight by small amounts. The refining ratio tends towards a limit of 2.48 ± 0.09 but the limit is not reached until $i^* \approx 10$. At lower values of i^* the refining ratio decreases towards a value of unity at $i^* = 0$.

4.4.2 Composition of the Melt and Value of the Equilibrium Constant K

The composition of the melt was obtained from a number of analyses performed as described in Section 4.3.2. The results are given in Table 20. The mean values for the components are :

PbCl ₂	60.2	±	0.4	mole %
CuCl	3.07	±	0.26	"
NaCl	36.7	±	0.2	"

Using the mean values of PbCl₂ and CuCl concentration in the electrolyte and the mean value of $[Cu]_a$ of 0.489 ± 0.022 wt. % (Table 19) we obtain a value for K of 6.20 ± 0.81 (13%) and $K^{\frac{1}{2}} = 2.49 \pm 0.16$ (6.5%) for the exchange reaction



The catholyte was not analysed for any run.

4.4.3 Conductivity of the electrolyte

The cathode capillary resistance was measured in KCl solutions and when filled with electrolyte. The conductivity of the melt could then be estimated (Table 21).

The mean value of the conductivity of the electrolyte at 800°K was

$$1.46 \pm 0.05 \text{ (3.5\%)} \text{ ohm}^{-1} \text{ cm}^{-1}$$

4B/.....

TABLE 19. EFFECT OF CURRENT DENSITY ON THE REFINING RATIO FOR MELTS CONTAINING NaCl SECOND SERIES

<u>Run No:</u>	<u>Current mA</u>	<u>Capillary Length (cm)</u>	i^*	<u>Time (hr)</u>	<u>Cathode weight (mg)</u>		<u>Current Efficiency %</u>	<u>Wt. % Cu</u>		$[Cu]_o / [Cu]_a$
					<u>Exp.</u>	<u>Far.</u>		<u>Cathode</u>	<u>Anode</u>	
2	0.323	1.12	1.14	1.5	19.05	18.50	101	0.652	0.466	1.40 ± 0.28
6	1.35	1.47	6.25	3.0	15.39	15.47	99	1.060	0.465	2.28 ± 0.09
7	2.49	1.38	10.82	1.5	13.93	14.25	97.9	1.140		2.45 ± 0.12
8	0.189	1.21	0.72	18	13.05	12.98	100.5	0.747		1.33 ± 0.07
9	2.17	1.28	8.72	2.0	6.56	16.57	100	1.155	0.514	2.25 ± 0.15
11	0.635	1.42	2.84	10.5	24.78	25.46	97.4	0.975	0.508	1.92 ± 0.14
12	4.29	1.45	19.5	1.0	16.15	16.38	98.5	1.315	0.512	2.57 ± 0.12
13	3.26	1.34	13.7	1.5	17.93	18.66	96.2	1.23		2.42 ± 0.12

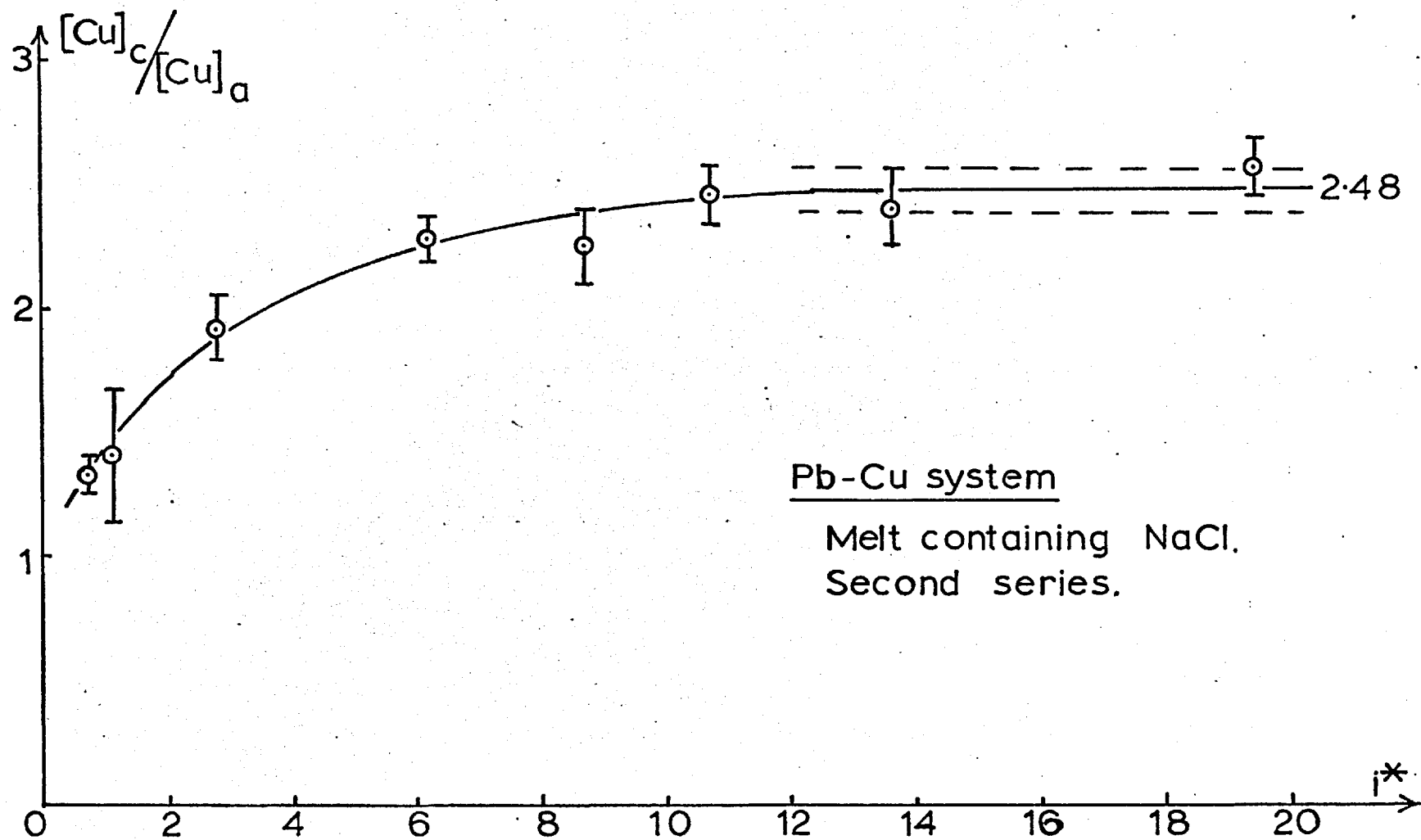


FIG. 31 EFFECT OF CURRENT ON REFINING RATIO

TABLE 20. COMPOSITION OF THE MELT. SECOND SERIES

Run No:	Sample Wt. (g)	PbCl_2 g	CuCl g	Mole Per Cent		
				PbCl_2	CuCl	NaCl
2	0.3941	0.3439	0.00611	60.3	3.01	36.7
6	0.2735	0.2392	0.00392	60.6	2.79	36.6
10	0.2596	0.2257	0.00461	59.7	3.42	36.9

Mean values PbCl_2 60.2 $\pm$ 0.4 mole %
 NaCl 36.7 $\pm$ 0.2 mole %
 CuCl 3.07 $\pm$ 0.26 mole %

TABLE 21. CONDUCTIVITY OF PbCl_2 - CuCl - NaCl MIXTURES
SECOND SERIES

Run No:	Measurements in KCl			l cm	In Melt	
	$t^\circ\text{C}$	χ (mho) $\times 10^2$	Cond. (Gx) μ mho		Gx mmho	χ (mho)
2	21.7	1.204	173.7	1.23	22.31	1.548
3	25.3	1.292	182.7	1.25	21.49	1.490
4	24.4	1.275	162.0	1.39	18.80	1.480
6	20.7	1.177	131.9	1.57	16.50	1.470
7	17.0	1.087	131.5	1.46	17.35	1.434
8	18.3	1.120	165.4	1.20	20.44	1.382
9	19.3	1.145	151.2	1.33	18.80	1.421

4B THE LEAD - SILVER SYSTEM

The lead-silver system was chosen for investigation because the predicted value of β (0.161) showed that considerable refining should occur in this system. However, such a low value of β would give rise to a low limiting value of i^* (Fig. 6) and previous experience showed that it was not possible to perform experiments at very low i^* . The purpose of the runs in the lead-silver system was therefore limited to determination of the limiting value of the refining ratio and the value of the partition coefficient K .

4.5 EFFECT OF CURRENT DENSITY ON THE REFINING RATIO AND THE VALUE OF THE EQUILIBRIUM CONSTANT K FOR Pb-Ag SYSTEM

Runs were performed at 800°K with an anode concentration of about 1 wt. % Ag. The dimensionless current density parameter i^* varied between 0.41 and 21.6. The results obtained are given in Table 22 and shown graphically in Fig. 32. One run (No: 6) was performed at a very low value of i^* and it can be seen that the refining ratio for this run is substantially higher than for other runs. Even when the errors in analysis are taken into account the value is significant, and leads to the conclusion that at low values of i^* the refining ratio tends towards a value of unity. Very large errors in analysis were prevalent throughout this series of experiments owing to the inexperience of the operator (a member of the Analytical Services Group at Imperial College). The mean value of the refining ratio, except for Run 6, was 0.071 ± 0.019 .

A value of the equilibrium constant K was obtained from the results of analysis of the electrolyte which yielded a value of 0.037 ± 0.008 wt. % for the silver content. The value of K is 3.5×10^{-3} and of $K^{\frac{1}{2}} = 5.9 \times 10^{-2} \pm 1.5 \times 10^{-2}$ (25%).

TABLE 22 EFFECT OF CURRENT DENSITY ON THE REFINING RATIO. LEAD-SILVER SYSTEM

<u>Run No:</u>	<u>Current mA</u>	<u>Capillary mA</u>	i^*	<u>Time hr.</u>	<u>Cathode Wt. (mg)</u>		<u>Current Efficiency %</u>	<u>Wt. % Ag.</u>		$[Ag]_c / [Ag]_a$
					<u>Exp.</u>	<u>Far.</u>		<u>Cathode</u>	<u>Anode</u>	
1	4.15	1.66	21.6	1.25	19.90	20.00	97	0.068	0.81	0.084
2	2.075	1.39	9.06	2.5	19.00	20.00	95	0.053	0.70	0.075
3	1.100	1.27	4.40	4	16.80	17.03	99	0.045	1.04	0.043
4	3.20	1.30	13.05	1.5	17.80	18.53	96	0.038	0.80	0.048
5	1.34	1.60	6.73	3	14.50	15.54	94	0.066	0.73	0.091
6	0.091	1.50	0.41	27	9.37	9.48	99	0.139	0.67	0.208
7	0.361	1.61	1.83	20	26.49	27.90	95	0.074		0.089
8	3.50	1.625	17.8	1.5	20.10	20.30	99	0.067	1.05	0.064

$$\text{Mean } [Ag]_a = 0.83 \pm 0.14 \quad (17\%)$$

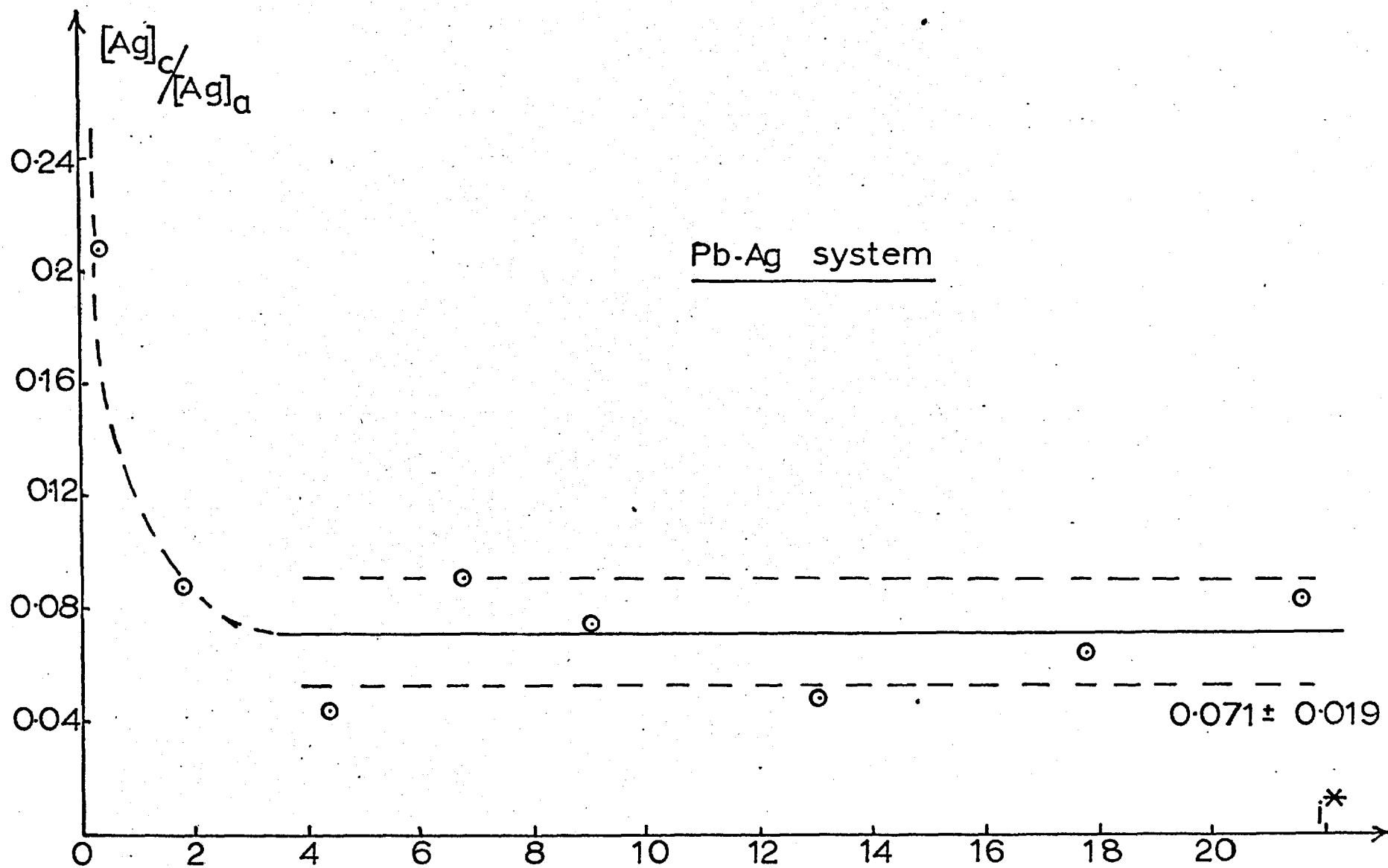


FIG. 32 EFFECT OF CURRENT ON REFINING RATIO

4C THE LEAD - CADMIUM SYSTEM

4.6 FIRST SERIES OF EXPERIMENTS

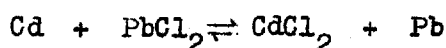
4.6.1 Effect of current density on the refining ratio

Eleven runs were performed in a lead-cadmium-chloride system in which $[Cd]_a \approx 0.127$ wt. % and the mole fraction of cadmium chloride in the melt was about 21.4 wt. %. The current density parameter i^* varied between 0.87 to 42.8, and the results are listed in Table 23 and shown in Fig. 33. The value of the refining ratio was found to be close to unity and under these conditions the effect of current density on the ratio, at low values of i^* , could not be detected because of the relatively large errors incurred when analysing very small samples by polarography in the presence of large excesses of lead. The mean value of the results was 1.13 ± 0.08 (7%).

4.6.2 Composition of the melt and value of the equilibrium constant K.

Analysis of the melt for cadmium gave a value of 9.30 ± 0.16 wt. % from four determinations. The mean value of cadmium in the anode (6 determinations) was 0.127 ± 0.008 wt. %.

Assuming that there was no excess cadmium metal in the melt the equilibrium constant for the reaction :



was calculated as

$$K = 116 \pm 8 \text{ (6\%)}$$

and so

$$K^{\frac{1}{2}} = 10.7 \pm 0.4 \text{ (3\%)}$$

4.6.3 Conductivity of the electrolyte

The conductivity of the electrolyte was measured four times by the method previously described. The results are given in Table 24. The mean value was 1.587 ± 0.016 ohm⁻¹ cm⁻¹ (1%).

4.7 SECOND SERIES OF EXPERIMENTS

4.7.1 Effect of current density on the refining ratio

A second series of runs was performed on the lead-cadmium-chloride/...

TABLE 23.

EFFECT OF CURRENT DENSITY ON REFINING RATIO. Pb-Cd SYSTEM. FIRST SERIES

Run No:	Current (mA)	Capillary Length (cm)	i^*	Time (hr.)	Cathode Wt. (mg)		Current Efflo: %	Wt. % Cd		$[Cd]_o/[Cd]_a$
					Exp.	Far.		Cathode	Anode	
1	1.30	1.63	13.3	4	19.89	20.09	98.9	0.156	0.114	1.23
3	0.121	1.15	0.87	20	9.59	9.35	102	0.149	0.124	1.20
5	3.84	1.78	42.8	1.17	17.18	17.32	99.2	0.157	0.130	1.20
6	0.175	1.70	1.88	17	11.14	11.49	96.9	0.134	0.129	1.06
7	1.30	1.95	15.9	4	19.97	20.09	99.4	0.142		1.12
8	3.00	1.55	29.2	2	22.08	22.19	99.5	0.131	0.125	1.05
10	0.500	1.65	5.18	18	35.34	34.79	101.5	0.125		0.99
11	0.502	1.37	4.32	22	42.25	42.68	99.0	0.153		1.20

TABLE 24 CONDUCTIVITY OF MELT. Pb-Cd SYSTEMFIRST SERIES

<u>Run No:</u>	<u>Measurements in KCl</u>				<u>In the Melt</u>	
	$t^{\circ}\text{C}$	χ_{KCl} $\times 10^2$	G_x μmho	L cm	G_x mmho	χ cm^{-1}
1	24.5	1.272	139.4	1.610	17.23	1.570
2	24.3	1.267	126.8	1.763	15.87	1.577
3	19.5	1.150	117.0	1.735	16.22	1.592
4	21.7	1.206	126.0	1.689	16.86	1.611

chloride system with a higher concentration of cadmium in the anode (0.258 ± 0.011 wt. %). A greater degree of accuracy was obtained with this higher concentration, but the value of the refining ratio was lowered to 0.785 ± 0.032 wt. % (Table 25 (a) and Fig. 34). The current density parameter i^* was varied between 1.95 and 34.4.

4.7.2 Composition of the melt and value of equilibrium constant K.

The mean value of cadmium in the anode was 0.258 ± 0.011 wt. %, i.e. 0.476 ± 0.020 mol. % (4%).

Samples of the electrolyte were taken and analysed for both CdCl_2 (Cd^{2+} by polarography) and PbCl_2 (as the sulphate). The results are shown in Table 27 (a). It may be seen from a comparison of the true sample weights and the sum of the weights given by analysis that very good agreement existed between the two (mean deviation was 1.5% low). The mean values were

$$\text{CdCl}_2 \quad 33.5 \pm 1.2 \text{ mole \%} \quad (3.5\%)$$

$$\text{PbCl}_2 \quad 66.5 \pm 1.2 \text{ mole \%} \quad (1.8\%)$$

The calculated value of K was 104.7 ± 6.3 (6%) and of $K^{\frac{1}{2}}$ 10.2 ± 0.3 (3%).

4.7.3 Conductivity of the Electrolyte

The conductivity of the melt was measured three times by the method previously described. The results are given in Table 26 (a). The mean value was

$$1.611 \pm 0.090 \text{ ohm}^{-1} \text{ cm}^{-1} \quad (\pm 5\%)$$

4.8 THIRD SERIES OF EXPERIMENTS

4.8.1 Effect of current density on the refining ratio

A third series of runs was performed on the lead-cadmium-chloride system having approximately the same concentrations of cadmium in the anode as in the second series of runs, but with sodium chloride added to the melt. Examination of phase diagrams and electrical conductivity data indicated that no complex ions were formed in this system (75) at the compositions used in the present experiments. The value of the refining ratio was lowered to 0.690 ± 0.049 (Table 25 (b) and Fig. 33). The mean value of $[\text{Cd}]_a$ was $0.240 \pm 0.025 \text{ wt. \%}$. ($= 0.443 \pm 0.040 \text{ mole \%}$). The current density parameter, i , was varied between 9.90 and 41.8.

4.8.2 Composition of the melt and value of equilibrium constant K.

Samples of the electrolyte were taken and analysed for both CdCl_2 and PbCl_2 as described above. The NaCl content was obtained by difference. The results for the three analyses performed are shown in Table 27 (b). The mean values were

PbCl_2	$46.7 \pm 0.9 \text{ mole \%}$	(1.8%)
CdCl_2	$23.2 \pm 0.6 \text{ mole \%}$	(2.5%)
NaCl	$30.1 \pm 1.5 \text{ mole \%}$	(4.5%)

The calculated value of K was 111.7 ± 6.4 (5.5%) and of $K^{\frac{1}{2}} = 10.5 \pm 0.3$ (3%).

4.8.3 Conductivity of the Electrolyte

The conductivity of the melt was measured four times by the method previously described (Table 26b). The mean value was

$$1.473 \pm 0.007 \text{ ohm}^{-1} \text{ cm}^{-1} \quad (1\%)$$

TABLE 25. EFFECT OF CURRENT DENSITY ON REFINING RATIO. (a) Pb-Cd SYSTEM. SECOND SERIES

Run No:	Current (mA)	Capillary Length (cm)	i*	Time (hr)	Cathode Wt. (mg)		Current Effio: %	Wt. % Cd.		$\left[\text{Cd} \right]_o / \left[\text{Cd} \right]_a$
					Exp.	Far.		Cathode	Anode	
2	1.85	1.76	19.1	3	20.94	21.15	99.0	0.215	0.264	0.814
4	0.190	1.64	1.95	16	11.18	11.61	96.5	0.181	0.242	0.748
5	1.20	1.29	9.68	3.5	15.87	16.03	99.0	0.197	0.256	0.770
6	3.90	1.40	34.4	1.25	18.28	18.61	98.2	0.219	0.271	0.809

(b) Pb-Cd SYSTEM - THIRD SERIES WITH NaCl ADDED TO MELT

1	3.40	1.96	41.8	1	10.58	11.41	92.6	0.178	0.280	0.646
2	3.40	1.27	27.2	1	11.44	11.41	100.2	0.176	0.234	0.752
4	1.65	1.40	14.5	4	24.00	25.52	94.0	0.144	0.226	0.638
5	1.20	1.32	9.90	3	12.72	13.91	91.5	0.161	0.222	0.725

TABLE 26. CONDUCTIVITY OF THE MELT

(a) Pb-Cd System. Second Series

<u>Run No:</u>	Measurements in KCl				In the Melt	
	$t^{\circ}\text{C}$	$\chi \times 10^2$	G_x (μmho)	L (cm)	G_x (mmho)	χ
3	21.5	1.196	97.9	2.160	13.99	1.707
4	19.5	1.148	120.4	1.683	17.13	1.635
6	17.4	1.094	138.6	1.393	18.88	1.490

(b) Pb-Cd System. Third Series NaCl Added to the Melt

<u>Run No:</u>	Measurements in KCl				In the Melt	
	$t^{\circ}\text{C}$	$\chi \times 10^2$	G_x (μmho)	L (cm)	G_x (mmho)	χ
1	18.6	1.127	93.5	2.125	12.96	1.480
2	16.5	1.082	147.4	1.298	20.05	1.474
3	17.8	1.112	126.5	1.552	16.66	1.462
4	19.1	1.140	133.4	1.509	17.29	1.477

TABLE 27. COMPOSITION OF THE MELT

(a) Pb - Cd System. Second Series

<u>Run</u> <u>No:</u>	<u>Sample</u> <u>Wt. (g)</u>	<u>PbCl</u> ₂ <u>Wt. (g)</u>	<u>CdCl</u> ₂ <u>Wt. (g)</u>	<u>Moles</u> <u>PbCl</u> ₂ <u>x 10⁴</u>	<u>Moles</u> <u>CaCl</u> ₂ <u>x 10⁴</u>	<u>Total</u> <u>Moles</u> <u>x 10⁴</u>	<u>Mole Per Cent</u>		<u>Sum of</u> <u>Analysis</u> <u>Wt. (g)</u>	<u>% of</u> <u>Sample Wt.</u>
							<u>PbCl</u> ₂	<u>CdCl</u> ₂		
1	0.2807	0.2068	0.0733	7.436	3.999	11.435	65.03	34.97	0.2801	99.8
2	0.2234	0.1635	0.516	5.879	2.815	8.694	67.62	32.38	0.2151	96.4
3	0.2079	0.1529	0.0528	5.498	2.881	8.379	65.62	34.38	0.2057	99.1
4	0.3325	0.2532	0.0796	9.105	4.343	13.448	67.71	32.29	0.3328	99.8

(b) Pb - Cd System. Third Series. With NaCl added to melt

<u>Run</u> <u>No:</u>	<u>Sample</u> <u>Wt. (g)</u>	<u>PbCl</u> ₂ <u>Wt. (g)</u>	<u>CdCl</u> ₂ <u>Wt. (g)</u>	<u>NaCl</u> * <u>Wt. (g)</u>	<u>Moles x 10⁴</u>		<u>NaCl</u>	<u>Total</u> <u>Moles</u>	<u>Mole %</u>		
					<u>PbCl</u> ₂	<u>CdCl</u> ₂			<u>PbCl</u> ₂	<u>CdCl</u> ₂	<u>NaCl</u>
2	0.3202	0.2191	0.0706	0.0305	7.878	3.852	5.219	16.949	46.48	22.73	30.79
3	0.3014	0.2073	0.0686	0.0255	7.454	3.742	4.363	15.559	47.91	24.05	28.04
4	0.3161	0.2143	0.0709	0.0309	7.705	3.868	5.287	16.287	45.70	29.94	31.36

* By difference

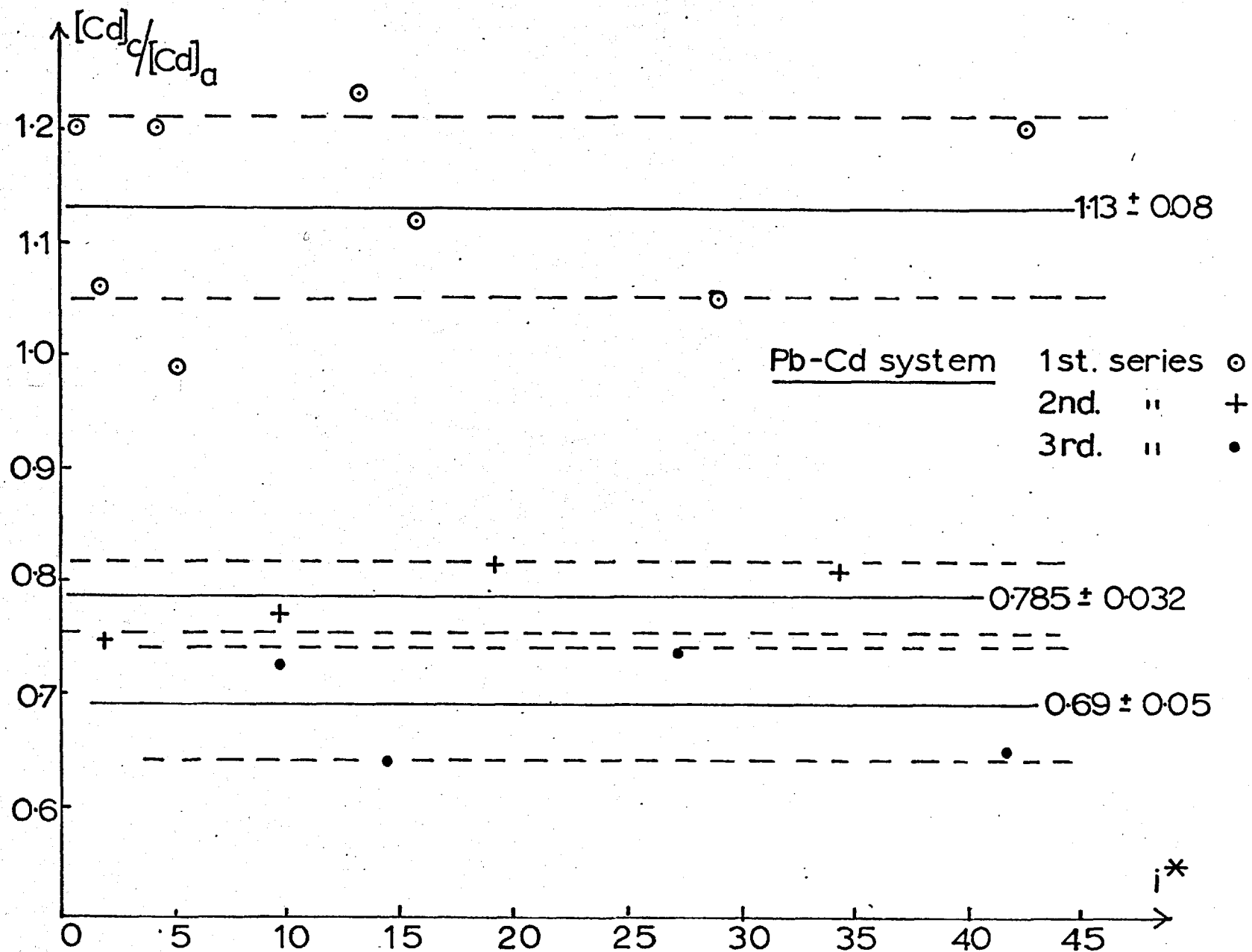


FIG.33 EFFECT OF CURRENT DENSITY ON REFINING RATIO

CHAPTER 5

DISCUSSION.

5.1 INTRODUCTION

In Chapter 2 a simplified theory of molten salt electrorefining has been presented using the friction coefficient formalism of irreversible thermodynamics and the results of experiments designed to test this theory have been described in Chapter 4. The theory predicts that behaviour of an anode impurity during electrorefining is determined by the value of a parameter β - called the 'refinability parameter.' When β is less than unity, the impurity will be concentrated in the anode; when greater than unity, the impurity will be concentrated in the cathode. An approximate value of this parameter can be determined from the free energies of formation of the main and impurity salts in the electrolyte and their electrical conductivities. Once determined, β can be used to predict the behaviour of an impurity in any refining system.

The addition of "inert" diluting salts to the electrolyte has been shown to reduce the value of β , even when the original value is less than unity. That is, addition of a diluting salt always improves refining.

Previous discussions of molten salt electrorefining (see, for example, Mullins and Leary (13)), have concentrated on the chemical aspects of the process. If the concentration of the impurity salt in the electrolyte is low, it has been assumed that very little of the metal impurity will be deposited in the cathode.

While this statement is basically accurate, the molar flux of an ionic species through an electrolyte depends, not only on its concentration, but also on the velocities of its individual ions. Should the ions of the impurity species have a very high mobility, appreciable quantities of the impurity can be deposited at the cathode even though its concentration in the electrolyte may be low. Thus both the chemical and transport aspects of the process should be considered in any theoretical treatment. This has been done in the treatment presented in Chapter 2, the refinability parameter being defined by

$$\beta = \frac{K \frac{1}{2} \gamma_c}{R^*}$$

The value of $K^{1/2}_B \gamma_C$ determines the relative concentrations of the main metal and the impurity in the melt, and that of R^* determines their relative mobilities. The value of β thus shows the relative importance of the chemical and transport effects in any one system.

In the next sections the experimental results that have been obtained in the three systems investigated here are compared with the theoretical predictions. The validity of the assumptions made in the theory is then discussed in the light of these comparisons. The three major assumptions considered are those concerning

- (1) cation mobilities in mixtures
- (2) the identity of transporting species
- and (3) the neglect of metal solubility in the salt.

5.2 THE LEAD-COPPER SYSTEM

The experimental investigation aimed to show that real electrorefining systems behave in the manner predicted by the theory. A comparison between the predicted variation of refining ratio with current density (Fig. 6) and that determined experimentally (Fig. 25) shows that this has been done. The practically determined ratio does indeed reach a limiting value, but the shape of the practical curve is not, however, exactly as predicted. The refining ratio approaches the limiting value more rapidly than the theory indicated. This may be due to one of three factors, which are discussed further in later sections (5.2.2 and 5.2.4).

At effectively infinite current densities the composition of the electrolyte does not vary across the cell so that the steady state condition is set up immediately. Thus the composition of the deposited cathode does not vary with time and the measured value of limiting refining ratio corresponds to the refinability parameter defined in the theory.

The agreement between the estimated value of the limiting refining ratio (2.68) and the experimentally determined value (3.65 ± 0.16) is fortuitous as can be seen from Appendix B. The value of $\gamma_C K^{1/2}_B$, determined from anode and electrolyte analyses (referred

(referred to as $K^{1/2}_B$ in Chapter 4), is 2.54 - as opposed to the value of 0.81 determined from the free energies of formation for lead and copper chlorides and by extrapolating activity data from 1263°K to the temperature of the experiments - 800°K (Section 2.2.4). Using the more reliable practical value, together with the estimate of R^* already made, we obtain $\beta = 8.42$. This value is greater than the experimentally determined limiting refining ratio - the difference is due to errors in the estimate of R^* and to approximations made in the theory. These will be discussed in a later section.

The results given in Chapter 4 will now be discussed in greater detail.

5.2.1 Results obtained using the preliminary cell

The preliminary experimental system approximates to a batch process and was therefore of little use in examining the predictions of the simple theory. Some information could, however, be obtained from the results of these preliminary experiments.

It was shown that the practical value of the partition coefficient (or equilibrium constant) was larger than that estimated from thermodynamic and activity coefficient data. The predicted value of $\gamma_{Cu}^{1/2}$ at 830°K was 0.93 and that obtained experimentally was 3.37.

The increase of the effective diffusion coefficient (or mass transfer coefficient) for copper produced by increasing the current across the cell (Fig. 21) confirms the prediction that copper will be concentrated in the cathode, i.e. the prediction that β is greater than unity.

The initial jump in the copper concentration of the cathode (Fig. 19) is not easy to explain. However, the subsequent steady increase can be compared with the theoretical predictions for a batch refining process if the zero-time concentration is taken as that obtained by extrapolating the steady part of the curve. The equation giving the composition of the cathode after a fraction n of the anode has been transported is

$$\frac{[X_C]_c}{n} = \frac{[X_C]_a^0}{n} (1 - (1-n)^\beta) \quad (2.55)$$

In this/....

In this case $[X_C]_a^0 = 0.66 \text{ wt. \%}$ and the value of β , obtained from the results from the final cell is about 4.

The current at 5 A/cm^2 is 0.088 A
and at current at 10 A/cm^2 is 0.176 A

$M_a^0 \approx 0.82 \text{ moles.}$ ($\approx 170 \text{ g. Pb}$)
and initial mass of cathode is 70 g.

The value of $[Cu]_c$ at zero time obtained by extrapolation is approximately $0.18 \text{ wt. \%}$ for both experiments. After three hours the value of $[Cu]_c$ had risen to 0.26 and 0.35 when the current densities were 5 and 10 A/cm^2 respectively.

Considering the 10 A/cm^2 experiment first, the values of n after 1, 2 and 3 hours are 0.77×10^{-2} , 1.54×10^{-2} and 2.31×10^{-2} respectively. Therefore the values of $[X_C]_c$ derived from (2.55) above are approximately 2.8 , 2.6 and $2.5 \text{ wt. \%}$ (these values refer to the material being deposited). The mean value of these is 2.6 . After 3 hours $2.31 \times 10^{-2} \times 170 = 3.93 \text{ g.}$ of material has been transported from anode to cathode. The concentration of copper in the cathode will therefore have been raised by

$$3.93 \times 2.6 \times \frac{1}{70} \approx 0.15 \text{ wt. \%}$$

Thus three hours electrolysis at 10 A/cm^2 raises the cathode copper concentration to about $0.33 \text{ wt. \%}$, which is close to the real value of about $0.35 \text{ wt. \%}$.

A similar treatment of the results of the 5 A/cm^2 experiment gives values of n after 1, 2 and 3 hours of 0.39×10^{-2} , 0.77×10^{-2} and 1.16×10^{-2} respectively. The values of $[X_C]_c$ are 2.0 , 2.8 and $2.6 \text{ wt. \%}$. The mean value is about $2.5 \text{ wt. \%}$. By similar calculations to those above the copper concentration in the cathode will rise by $0.07 \text{ wt. \%}$, i.e. from 0.18 to $0.25 \text{ wt. \%}$, which again shows substantial agreement with experiment.

It may be concluded therefore that the behaviour of a batch process may be predicted (Section 2.2.5) with some accuracy using the value of the refinability parameter determined in simple experiments. In addition the closeness of the two mean values of $[X_C]_c$ indicated that a limiting refining ratio had been reached.

5.2.2 Results obtained using the final cell

The effect of the five variables, temperature, time, current density, current path (capillary) length and "inert" salt concentration were investigated.

5.2.2.(a) Temperature

The first series of experiments (Runs 1 - 39) were performed at current densities ranging between 0.2 and 4 A/cm² ($i^* = 15$ to 700), which is of the order of magnitude of those used in commercial processes. The experiments were carried out in the limiting refining ratio region in order to avoid complications due to current density effects. The temperature was varied in a 50° range about 800°K (523°C) which had been set as the experimental temperature. It was not possible to extend the temperature range lower because the melting point of PbCl₂ is 498°C, and it was also thought unwise to go to higher temperatures because of the danger of distortion of the glass envelopes.

The variation of β estimated from equation (2.30) is 0.21 per cent per degree at 800°K and that found in practice is 0.52 ± 0.10 per cent per degree (Section 4.21). However, if the more reliable practical value of $(\gamma_C K^{1/z_B})$, defined as K^{1/z_B} in Chapter 4, is taken, a different variation of β is obtained. This is shown in Table 28 and Fig. 34.

TABLE 28. VARIATION OF R^* , $\gamma_C K^{1/z_B}$ AND β WITH TEMPERATURE.

Temp. °K	790	800	810	820	830
R^*	0.293	0.301	0.309	0.316	0.323
$\gamma_C K^{1/z_B} (= K^{1/2})$	2.34	2.54	2.70	2.98	3.22
β	8.04	8.42	8.87	9.41	10.0

The value of $(\gamma_C K^{1/z_B})$ was estimated from the determined values at 836°K (11.4) and 800°K (6.44). A value of 21.1 ± 1.5 kcal for ΔH° of the exchange reaction was obtained.

The variation/..

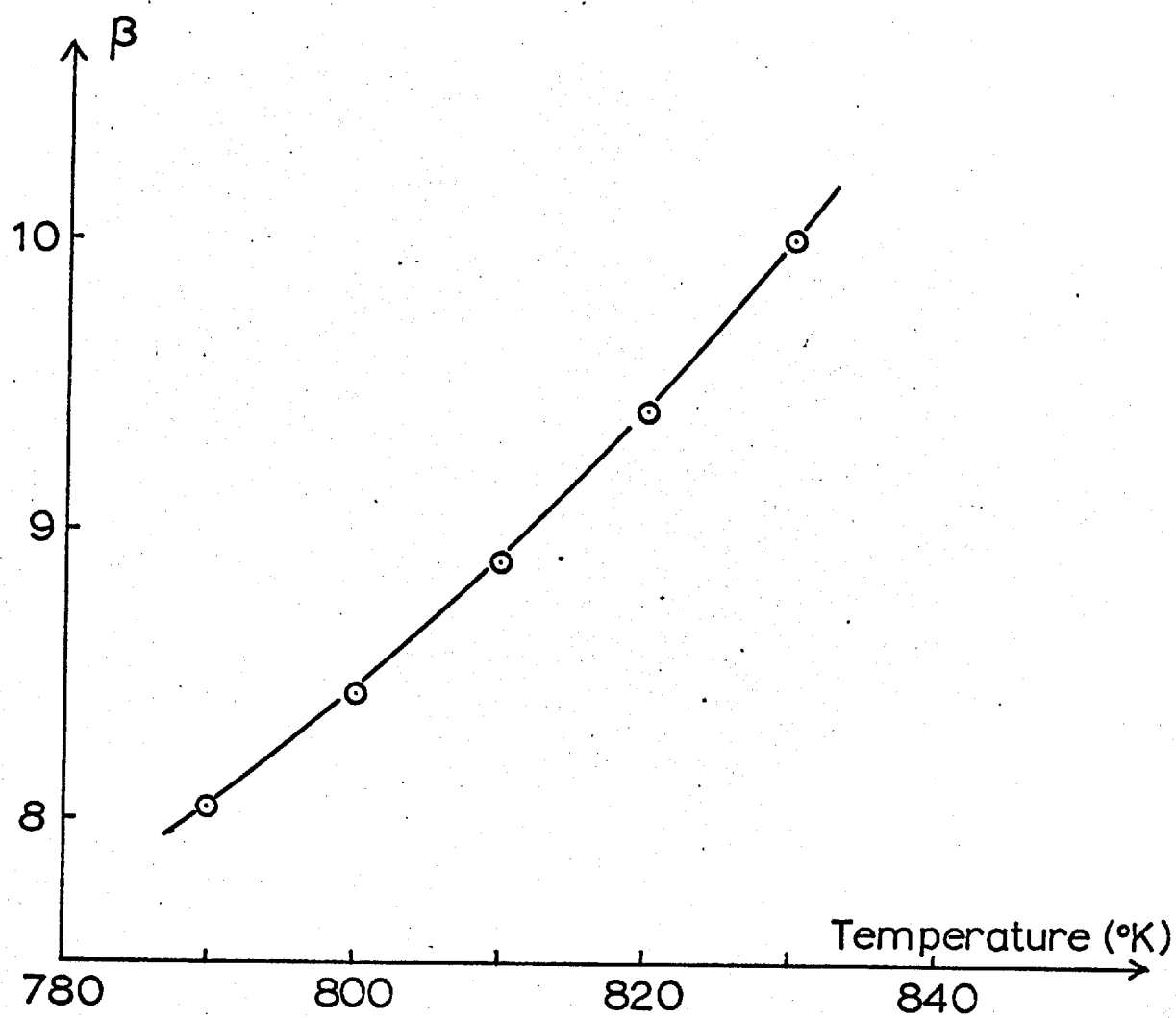


FIG.342 VARIATION OF β WITH TEMPERATURE

The variation of β obtained in this manner is 0.5 per cent per degree at 800°K, which agrees more closely with the observed value.

This conclusion agrees with the observation of previous workers (Section 1.3) who found that calculations of the partition coefficient K from the simple mass action law are generally more applicable than calculations which include activity coefficients⁽⁴²⁾.

Further, if the variation of γ_{Cu} with temperature (Table 7) is examined it is found that the temperature coefficient is - 0.35 per cent per degree. If this is deducted from the theoretical temperature variation a value of 0.56 per cent per degree is obtained. This suggests that the error lies in the calculation of the activity coefficient of copper in the anode. It should be noted that γ_{Cu} was calculated from a value at 1263°K on the assumption that Pb-Cu solutions are regular.

5.2.2.(b) Current density

The effect of current density on the refining ratio was described in Section 4.2.2 and has already been mentioned above. The theoretical treatment showed that no further refining was to be expected after the limiting current density ($i^* \approx 10$ for $\beta \approx 4$) had been reached and this was shown to be substantially true (Fig. 24) in a series of runs in which i^* was varied between 10 and 25. A limiting value of 3.65 ± 0.16 was obtained.

A series of runs performed with $i^* < 10$ indicated (Fig. 25) that this limiting value had been attained at about $i^* = 5$ and the slope of the graph up to the limiting value was steeper than predicted by the theoretical treatment. As mentioned above, this fact may be explained by one of three factors.

Firstly, at current densities below the limiting value some time is necessary in which to build up the concentration distribution in the capillary transport path. During this time the composition of the deposited metal cannot be that predicted in the theory since this assumes steady state conditions. The gradient of copper is built up in the capillary by diffusion away from the deposited metal and time is required for this process to reach the steady state (see next section).

Secondly/....

Secondly, if $R_{B^+C^+}$ is not negligible, then the estimated value of i^* will be too low. A value of $R_{B^+C^+}$ of the same order of magnitude as $R_{A^+B^+}$ would result in the values of i^* being approximately doubled, and in this case the experimental curve would fall very close to the theoretical (for $\beta = 3.65$).

Moreover, if the species transporting copper is divalent, i^* will also be doubled giving a better fit (see Section 5.2.4.).

5.2.2.(c) Time

The theoretical treatment showed that at values of i^* above the limiting value no concentration gradient exists across the electrolyte and hence that the refining ratio should be independent of time. This has been experimentally verified by plotting the refining ratio against time of electrolysis for runs in which $i^* > 5$ (Fig. 26).

Below the limiting value some time is necessary to establish a concentration gradient in the capillary. A simple calculation (Section 4.2.3 (b)) shows that this time may be of the order of several hours and it was shown (Fig. 27) that a combination of low current density and short time of electrolysis led to high values of the refining ratio. These runs were rejected for the following reason. The high results are due to the fact that the concentration gradient is built up by the diffusion of copper out of the deposited metal and into the catholyte, i.e. by diffusion of copper down the concentration gradient and against the potential gradient. The steady state was therefore not reached in experiments of short duration at low current densities.

5.2.2.(d) Path Length

The theory shows that above the limiting current density the path length should not influence the refining ratio. A graph of refining ratio for $i^* > 5$ against capillary length (Fig. 28) shows a slight tendency for the refining ratio to decrease as the capillary length increases. This tendency lies within the limits of accuracy of the mean value of the refining ratio ($\pm 5\%$) and therefore no significance can be attached to the observed trend.

In order to observe the effect of capillary length at values of i^* below the limiting value it is necessary to compare runs performed at the same current density. Runs 83 and 85 were performed under identical conditions, except for differences in the

capillary/...

capillary length. It is shown in Section 4.2.4.(b) that the expected increase of refining ratio with increased capillary length (i.e. increased i^*) occurs.

5.2.2.(e) Additions of an "inert" diluting salt

A simple theoretical treatment of the effect of inert diluting salts on refining was presented above (Section 2.3). An inert salt was defined as one whose ions do not take part in the electrode reactions. A factor modifying the refinability parameter, β , previously defined was obtained i.e.

$$\frac{X_F^{Z_C/Z_B}}{Q + X_F(1 - Q)}$$

where $(1 - X_F)$ is the mole fraction of diluting salt and Q is given by

$$(Z_D + 1)/Z_B$$

In this case $Q = 1$, and the modifying factor is $X_F^{1/2}$.

Fig. 36 is a plot of the experimentally determined limiting refining ratio against the mole fraction of NaCl added. Also plotted on the graph are values calculated using the calculated modifying factor, $X_F^{1/2}$. A considerable deviation can be seen. It can be seen that a much greater degree of agreement is achieved if the modifying factor is taken simply as X_F . This result will be discussed in a later section (5.2.4.)

5.2.3 Equilibrium Constant K

It should be noted that the equilibrium constant K for the exchange reaction did not vary significantly in the experiments performed. The three melts without NaCl gave values for $K^{1/2}$ of 2.47 ± 0.2 , 2.50 ± 0.3 and 2.54 ± 0.15 . The two melts containing NaCl gave values of 2.70 ± 0.14 and 2.49 ± 0.16 . Thus it appears that additions of NaCl do not significantly affect the value of K . This confirms the postulate made in the theoretical section that the salt solutions are ideal.

5.2.4 The Transporting Species

A better fit for the effect of additions of NaCl on the refining ratio is obtained if X_F is taken as the modifying factor.

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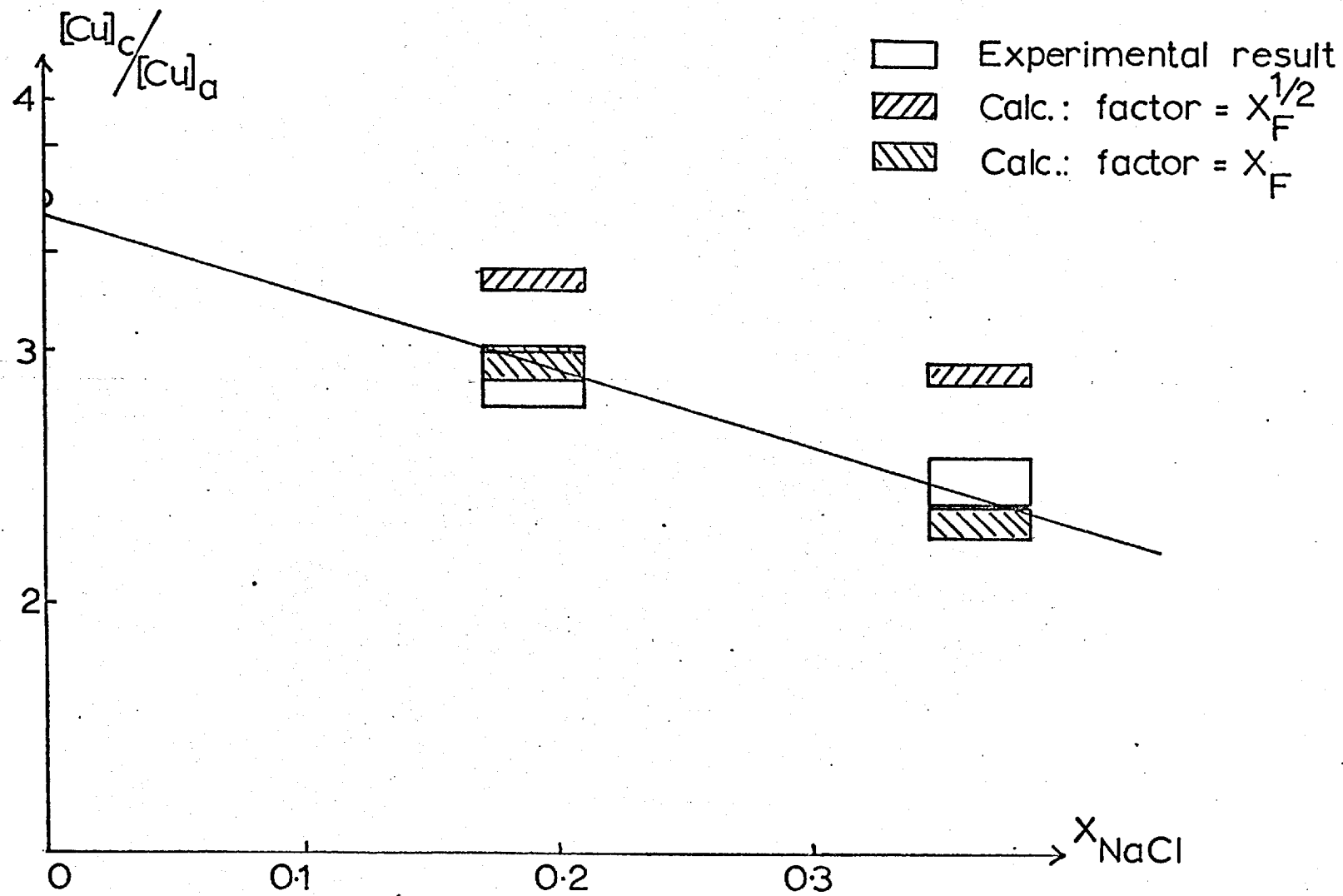


FIG. 35 EFFECT OF NaCl ADDITIONS ON THE REFINING RATIO

This suggests that the transporting entity is divalent. It could be that the ion is not Cu^+ , as assumed, but Cu_2^{2+} or even Cu^{2+} . Possibly all three ions exist and in the absence of other data it is impossible to estimate how the copper in the melt is distributed among all three ion states.

However, if it is assumed that the transporting entity is divalent the value of R_{+-} is changed from 0.53×10^{10} to 1.59×10^{10} and that of R^* from 0.301 to 0.452. The value of β using thermodynamic data therefore becomes 1.79 instead of 2.68. If the practical value of $\gamma_{\text{C}} K^{1/2}_{\text{B}}$, 2.54 is used the value of β becomes 5.62, which is nearer to the experimental limiting refining ratio than that previously calculated (8.42).

There are two possible sources of error which could account for the differences still remaining

- (1) $R_{\text{B}^+\text{C}^+}$ is not negligible: in this case R^* is nearer to unity and β is correspondingly reduced from 5.62.
- (2) $R_{\text{A}^-\text{C}^+}$ is not equal to the value derived from the pure salt conductivity: if $R_{\text{A}^-\text{C}^+}$ is in fact more closely equal to $R_{\text{A}^-\text{B}^+}$ then R^* will again be nearer unity.

These factors are discussed further below.

The model described above is one in which most of the copper in the electrolyte exists in the Cu^+ state, but most of the current is carried by a divalent ion i.e. Cu_2^{2+} or Cu^{2+} . The assumption of a divalent transporting species also means that the i^* values calculated and shown in the results should be doubled.

5.3 THE LEAD - SILVER SYSTEM

It was estimated from the theoretical treatment that refining should take place in this system, and a value of $\beta = 0.161$ was calculated. It was not possible to follow the effect of current density at low values of i^* , since the limiting refining ratio is reached rapidly when β is less than unity. One value of the refining ratio obtained at a low value of i^* (0.41) indicated, however, that the ratio tended towards unity at low current densities (Fig. ~~26~~³⁷).

A value of the equilibrium constant was calculated for comparison with that estimated from thermodynamic data and extrapolated activity coefficients (Table 6). The value of $\gamma_{\text{C}} K^{1/2}_{\text{B}}$

estimated/...

estimated is 4.4×10^{-2} , and that obtained experimentally is 5.9×10^{-2} ($\pm 25\%$). Reasonable agreement exists between the two values. It should be noted that the estimated value of γ_c at 800°K was extrapolated from a value at a very close temperature (773°K).

The value of the limiting refining ratio was found to be 0.071 ± 0.019 (25%), i.e. approximately half the estimated value. Taking account of the relative agreement found in the values of the equilibrium constant, the source of the variation must lie in the estimation of R^* . This could arise in one of two ways; (i) if $R_{\text{Ag}^+\text{Pb}^+}$ is not negligible then the value of R^* will be nearer unity than the estimated value, and β will be lower; (ii) the calculation of $R_{\text{Ag}^+\text{Cl}^-}$ from the pure salt conductivity may be incorrect. If the mobility of the Ag^+ ion is reduced, then $R_{\text{Ag}^+\text{Cl}^-}$ will be increased and R^* will again be nearer unity.

5.4 THE LEAD-CADMIUM SYSTEM.

5.4.1 Effect of Current Density and Composition on the Refining Ratio

The refinability parameter calculated for the lead-cadmium system (Table 6) of 35.9, indicated that considerable enriching of the metal deposited at the cathode should occur, i.e. anodic refining. For the concentrations of cadmium in the cathode that could reasonably be used, because of the limitations of the analytical procedure, quite large concentrations of CdCl_2 in the melt were necessary owing to the high value of K . This was a considerable departure from the theoretical treatment, but experiments were nevertheless carried out.

In order to set up the equilibrium between the anode and the electrolyte cadmium chloride was added to the melt. In industrial practice it is likely that relatively pure lead chloride, perhaps with an "inert" diluting salt, would be used. In such a case most of the cadmium would immediately go into the electrolyte by exchange. However, some cadmium would be transferred to the cathode and the theoretical value of β indicates that a much higher level would be reached in the cathode than in the anode.

It was found that the level of cadmium in the cathode remained similar to that in the anode. The mean value of the refining ratio in the first series of experiments was 1.13 ± 0.08 (7%) and at

this level/..

this level no effect of current density could be detected.

A second series of experiments was performed with a higher level of cadmium in the anode in an attempt to reduce the errors in analysis. The effect of this change of composition was to reduce the value of the refining ratio to 0.785 ± 0.032 . Again no current density effect was detected, but this may be due to the fact that only 4 runs were performed, and the lowest value of i^* was about 2.

The effect of additions of NaCl to the electrolyte was examined in a third series of experiments. About 30 mole per cent of NaCl was added and it was found that the refining ratio was reduced to 0.690 ± 0.049 . The concentration of cadmium in the anode remained the same as in the second series of experiments. This represents a decrease of $13 \pm 9\%$. The closest relationship between this decrease and the amount of salt added is found if the modifying factor is taken as $X_F^{\frac{1}{2}}$.

It should be noted that, as in the Pb - Cu system, the variations in composition in the three series of experiments did not alter the equilibrium constant. The values of $K^{\frac{1}{2}}$ were :

$$\left. \begin{array}{l} 10.7 \pm 0.4 \\ 10.2 \pm 0.3 \\ 10.5 \pm 0.3 \end{array} \right\} \text{ mean value of } K = 111 \pm 5$$

It appears therefore that the effect of altering the composition, either by changing the amount of impurity or by adding an inert salt, is to change the relative mobilities of the ions and thus R^* . This has already been noted for the lead - copper system when a diluting salt is added.

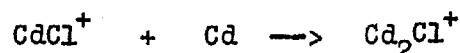
There is considerable disagreement between this figure and the value obtained using thermodynamic data, which gives a figure of 32.6 for $\gamma_C K^{\frac{1}{2}} / Z_B$. It is implied that the wrong entities have been chosen for the calculation of the constant from experimental data or that the activity coefficient should not be used.

5.4.2 The Transporting Species

Angell and Tomlinson (76) studied the mechanism of the solution of cadmium in cadmium chloride by means of measurements of self-diffusion and electrical conductance. The results were

interpreted/...

interpreted to be in accord with a model involving partial "association" to CdCl^+ ions and a solution mechanism was suggested such that



Bockris and Angell (77) had earlier suggested that the diffusion of cadmium in the system $\text{CdCl}_2 + \text{KCl}$ was best interpreted if pure CdCl_2 were assumed to contain $(\text{CdCl}_2)_n$ polymers in equilibrium with Cd^{2+} and Cl^- ions, possibly with the monomer as an intermediate. On the other hand, theoretical calculations of the conductivity of CdCl_2 (78) were consistent with a model in which CdCl^+ and Cl^- ions were in equilibrium with polymeric entities.

From their results, Angell and Tomlinson were able to calculate friction coefficients of the r_{ik} type ($= C_T R_{ik}$, where C_T = total molar concentration) for pure CdCl_2 at 601°C for two extreme models, neglecting any polymers, and the results are shown in Table 29. The ratios of the values of the equivalent conductance, calculated from the Nernst-Einstein equation, to the experimental values, are also shown.

TABLE 29 FRICTION COEFFICIENT DATA FOR PURE CdCl_2 . (76)

	Model 1 $\text{CdCl}^+ + \text{Cl}^-$	Model 2 $\text{Cd}^{2+} + 2\text{Cl}^-$
Λ , $\text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$	107.24	53.62
D_{Cd} , $\text{cm}^2 \text{sec}^{-1}$	2.68×10^{-5}	2.68×10^{-5}
D_{Cl} , $\text{cm}^2 \text{sec}^{-1}$	2.53×10^{-5}	2.53×10^{-5}
r_{+-} , $\text{watt sec}^2 \text{cm}^{-2} \text{mole}^{-1}$	1.73×10^8	5.20×10^8
r_{++} , "	3.68×10^8	-2.29×10^8
r_{--} , "	4.36×10^8	1.70×10^8
$\Lambda_{\text{calc}}/\Lambda_{\text{obs}}$	0.605	1.89

The negative value of r_{++} for the second model indicates association, according to Laity⁽⁵²⁾. The values of the friction

coefficients/..

coefficients for the first model are more reasonable and are of the same order of magnitude as those calculated for other salts⁽⁵⁴⁾. The ratio $\Lambda_{\text{calc}}/\Lambda_{\text{obs}}$ for the second model is close to 2. According to Djordevic and Hills⁽⁷⁹⁾ this should be expected if the term X_i in the phenomenological equations is regarded as the fraction of ions of the same sign rather than as a mole fraction. However, the ratio for model 1 is less than unity. This suggests that the model is an extreme case and that the association of Cd^{2+} ions each with one Cl^- ion is not complete. Polymerisation would tend to decrease the ratio still further. The extent of association cannot be calculated by assuming that the Nernst - Einstein equation is obeyed, as only three equations are available and there are four unknowns, viz: three ionic diffusivities and the dissociation constant. In an empirical description of transport processes Laity's⁽⁵⁴⁾ statement "the term association applies to any type of coupling between fluxes of oppositely charged species" is adequate, and further investigation of the nature of the complex is not required.

If the species involved in the transport of cadmium is CdCl^+ , i.e a monovalent ion, then the effect of sodium chloride additions on the refining ratio is immediately explained. The modifying factor now becomes $X_F^{\frac{1}{2}}$, in agreement with experiment, and not X_F which results from the supposition that Cd^{2+} is the species involved.

The choice of CdCl^+ as the transporting species causes a change in the value of R_{+-} , which now becomes 1.07×10^{10} , instead of 3.21×10^{10} . Consequently R^* is changed from 0.912 to 0.608. The value of the equilibrium constant calculated from the thermodynamic data does not change because the overall reaction is the same. Thus the theoretical value of β becomes 53.7 instead of 35.9 which represents an even larger difference from the practical value.

The assumption that the transporting species is monovalent also means that the calculated values of i^* should be halved.

5.4.3 The disagreement between β and the experimental limiting refining ratio

As stated above the extent of association cannot be evaluated from the data available and the equilibrium constant calculated above from the results of analysis must be used to

describe/...

describe the overall reaction. The implication is that it is incorrect to use the activity coefficient of Cd in the anode in this case, since there is a close agreement between the thermodynamic value of K (102.6) and the experimental value of (111.5). Alternately, if the CdCl_2 - PbCl_2 mixture is not ideal, which has so far been assumed, activity coefficients for PbCl_2 and CdCl_2 should be included in the expression. It has been shown (80) that for CdCl_2 - PbCl_2 mixtures CdCl_2 ($\text{PbCl}_2 : 1$).

$$RT \ln \gamma_{\text{CdCl}_2} = 600 N_{\text{Pb}}^2$$

At 800°K, and for the concentrations in the first series of experiments (4.6), we obtain a figure for the activity coefficient of CdCl_2 of 1.008. The solution is therefore approximately ideal and a correction of this type cannot be applied.

The disagreement between the experimental limiting refining ratio and the theoretical value of β remains to be explained. If it is more accurate not to include the value of γ_{Cd} in the calculation, then the value of β becomes 16.7. Thus in the first series of experiments a value of $[\text{Cd}]_0$ of about 2.12 wt. % would have been expected. The current efficiencies obtained, which lie in the range 96.9 - 102%, were calculated on the basis of a Pb - 0.12 wt. % Cd cathode. Using a Pb - 2 wt. % Cd cathode as the basis, values about 3% higher are obtained, i.e. current efficiencies of up to 105% would be obtained. While such a large error is not probable it cannot be ruled out since it could be caused by an error of 3% in the standard 1 ohm resistor used in the measurement of current.

A mechanism such as that suggested by Angell and Tomlinson (76) could be involved in the dissolution of Cd from the cathode. The excess cadmium in the melt might be confined to the melt in the capillary, which was not analysed, or, if distributed throughout the melt, would have been at too low a level to be detected by the analytical technique used.

The lower level of $[\text{Cd}]_0$ in the second series of experiments may then be explained by the greater amount of CdCl_2 in the melt, since it must be assumed that the amount of dissolution is proportional to the amount of CdCl_2 in the melt, which

is very/....

is very high in the boundary layer at the cathode (see 2.2.5). This last point explains why measurable solution does not occur at the anode.

5.5 CATION MOBILITIES IN FUSED SALT MIXTURES

Two major assumptions made in the theoretical treatment remain to be discussed. These are that :

- (i) when the impurity salt AC is in dilute solution in the salt of the main metal, the value of R_{A-C+} is the same as that calculated from pure salt conductivity data, and
- (ii) the interaction between the two cations is negligible, that is R_{B+C+} is much less than R_{A-C+} , R_{A-B+} .

These two assumptions will now be examined.

5.5.1 Mobility of the impurity cation

It is well known that conductivity isotherms in binary fused salt mixtures usually exhibit negative deviations from the "ideal" behaviour defined by connecting the equivalent conductances of the pure salts with a straight line. That is, the relative conductances of the ions are not constant throughout, and the equivalent conductance cannot be simply calculated from the conductances of the pure salts and their molar concentrations.

Early results, collated by Laity and Moynihan (81), revealed a remarkable generalisation; the mobilities of like - charged ions in binary fused salt mixtures were found to be equal (within about 15%) at all concentrations. This would imply that R_{A-C+} is equal to R_{A-B+} within 15%, and thus the value of R^* would generally be nearer unity than the value calculated from pure salt conductances.

More recent results obtained by the same workers (82) suggest that this generalisation is too sweeping. The Hittorf method was used to investigate the transport properties of KCl - LiCl melts at 640°C and these were combined with conductivity data to yield equivalent conductance isotherms for each cation. These showed monotonically decreasing behaviour with increasing concentration of K^+ (KCl has a lower conductance than LiCl), as shown

in Fig. 36/....

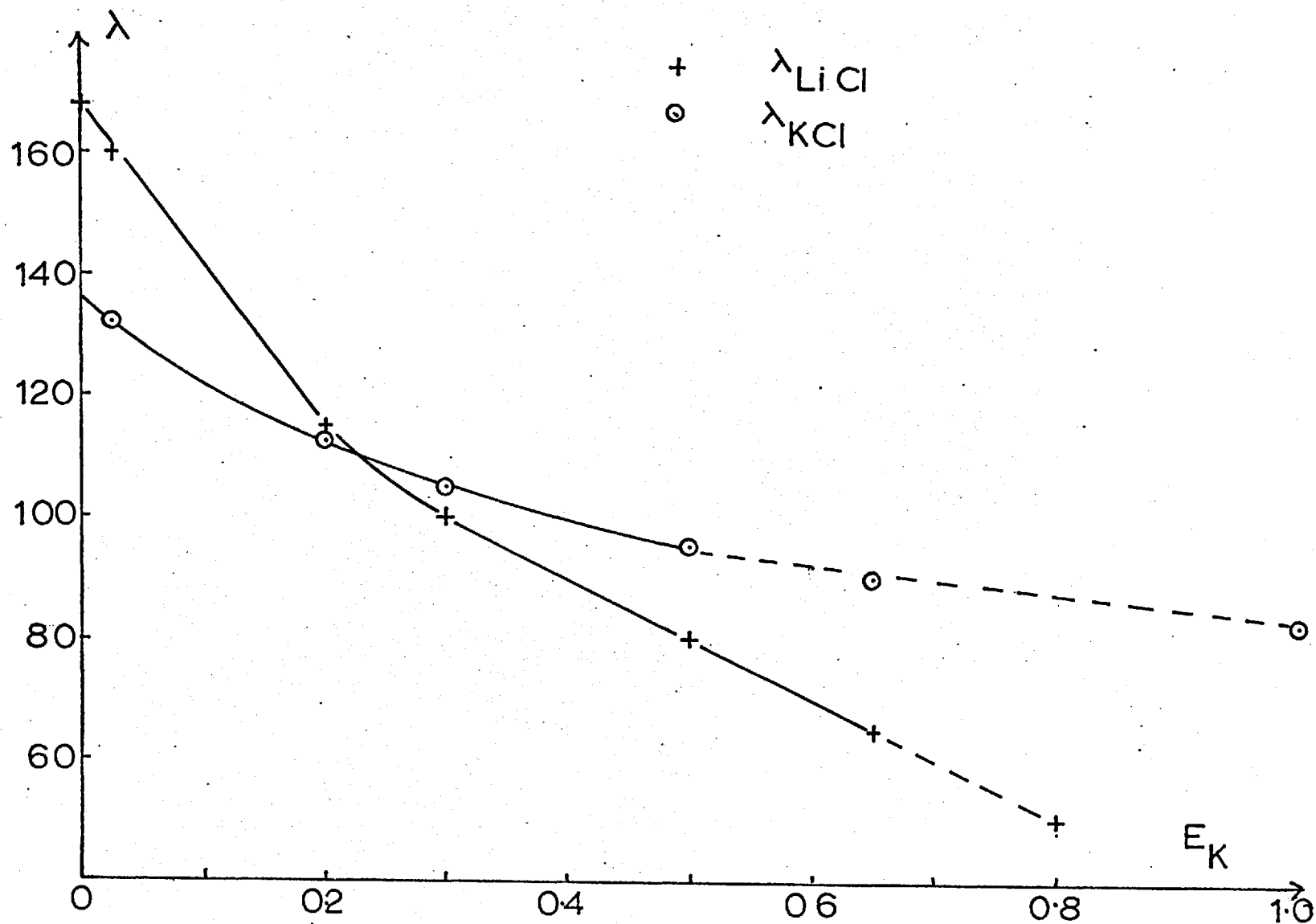


FIG. 36. RELATIVE CONDUCTANCES OF K^+ AND Li^+ IONS

in Fig. 36. The Li^+ mobility decreases much more rapidly and from extrapolation one can estimate that in pure KCl it would reach 0.2 of its value in pure LiCl. Comparison with other systems, e.g. alkali metal nitrates (83), indicates that similar behaviour may be rather general.

The recent work of Bloom and Easteal (84) approached the problem from a different angle but came to the same conclusion; that the mobilities of like-charged ions were not equal. They measured the emfs, E_t , of concentration cells with transference (i.e. with a liquid junction) and compared these with the emfs, E , of corresponding cells without transference (i.e. reversible formation cells) in order to obtain the diffusion potentials, ζ (i.e. the potential at the liquid junction), according to the relation

$$E_t = E + \zeta$$

If the mobilities of like-charged ions were equal then ζ would be zero. Experiments on lead halide-alkali halide systems generally resulted in non-zero values of ζ .

It may be seen that some danger exists in the assumption that R_{+-} for a salt in dilute solutions is the same as that in the pure salt, though it may be less for salts with similar conductances, e.g. PbCl_2 and CdCl_2 . In addition the deviations may be less in mixtures known to be ideal, e.g. $\text{PbCl}_2 - \text{AgCl}$ (80).

In the absence of transport data of the type obtained by Moynihan and Laity (82) for the systems investigated in the present work only estimates of the dilution effect can be made.

Consider the lead - copper system. If the change of R_{A-C^+} is the only cause of the difference between the theoretical β and the experimental limiting refining ratio (i.e. if $R_{B^+C^+}$ is negligible), then the true value of R^* may be calculated from the experimental refining ratio and the experimental value of $\gamma_C^K \frac{1}{Z_B}$.

Thus

$$R^* = \frac{2.54}{3.65} = 0.696$$

$$\begin{aligned} \text{and } R_{\text{CuCl}} &= 0.696 \times 3.52 \times 10^{10} \\ &= 2.54 \times 10^{10} \end{aligned}$$

The value/...

The value estimated from pure salt conductance is 1.59×10^{10} (Section 5.2.4). The specific conductance of CuCl calculated from the above figure is $2.28 \text{ ohm}^{-1} \text{ cm}^{-1}$ (pure salt, $3.52 \text{ ohm}^{-1} \text{ cm}^{-1}$). Thus a decrease of some 35% has occurred. It is not unlikely therefore that this effect may be the cause of the discrepancy between the theoretical β and the experimental refining ratio. However, the effect of $R_{B^+C^+}$ not being negligible might also account for the discrepancy, and it is not possible to separate the two effects using the results of the present investigation.

5.5.2 The Value of $R_{B^+C^+}$

It is necessary to assign a value of $R_{B^+C^+}$ in order to calculate the parameter β from literature data, but such data does not generally exist for the systems of interest.

A zero value was assigned to $R_{B^+C^+}$ based on the calculations of Laity (54) who showed that R_{++} was very much less than R_{+-} in pure molten salts. (Table 30).

TABLE 30. SOME INTERIONIC FRICTION COEFFICIENTS IN PURE
MOLTEN SALTS

Salt	Temp: °C	Λ mho cm ² equiv ⁻¹	$D_{++} \times 10^5$ cm ² sec ⁻¹	$r_{+-} \times 10^8$	$r_{++} \times 10^{-8}$
				joule. sec. cm ⁻² mole ⁻¹	
NaCl	800	135	12.3	1.38	0.1
TlCl	550	68	4.6	2.7	0.2
PbCl ₂	575	53	2.0	5.3	0.0
NaNO ₃	330	48	2.03	3.9	1.1

Equation (2.7) shows the relationship between the diffusion coefficient D_{12} in a multicomponent system (ions 1,2,3) and R_{12} , R_{13} and R_{23} . It is necessary to know R_{12} , R_{13} and D_{12} in order to be able to calculate R_{23} . In the present investigation it would therefore be necessary to know $R_{A^-B^+}$, $R_{A^-C^+}$ and $D_{A^-B^+}$

or/...

(or D_{A-C^+} or D_{B+C^+}) in order to calculate R_{B+C^+} . R_{A-B^+} is known and the last section has shown the difficulty involved in estimating R_{A-C^+} . No diffusion coefficients of the type D_{A-B^+} have been reported.

It was shown in an earlier section (5.2.2.(b)) that putting $R_{B+C^+} = R_{A-B^+}$ doubled i^* and gave a better fit between the experimental and theoretical curves showing the effect of current density on the refining ratio in the Pb - Cu system. However, if the transporting species is divalent (Section 5.2.4), i^* is also doubled giving the better fit, as shown in Fig. 37. Similar curves can be drawn for the Pb-Cu system when NaCl is added to the melt showing the greater degree of agreement between experiment and theory.

If, in addition to the transporting species being divalent and thus $Z_C = 2$, R_{B+C^+} is not negligible then the agreement would be made even better by the increase in i^* over the calculated value, though the agreement would not be complete because the curves are not parallel.

Because of the almost certain difference between R_{A-C^+} as calculated from pure salt data and the actual value in the system it is not possible to calculate R_{B+C^+} from the full equation for R^*

$$R^* = \frac{Z_B R_{A-C^+} + R_{B+C^+}}{Z_C R_{A-B^+} + R_{B+C^+}}$$

using the experimental values of β and $\gamma_C K^{1/Z_B}$. Nor can R_{B+C^+} be calculated from the differences between the theoretical and experimental curves shown in Fig. 37 because these latter are not parallel.

The inability to assign a value to R_{B+C^+} is not critical however since significant agreement has been found between the simple formula in which R_{B+C^+} is put at zero and experiment. In addition the conclusions of the last Section suggest that the differences could easily be due to variations of R_{A-C^+} and the assumption that $R_{B+C^+} = 0$ may therefore be substantially correct.

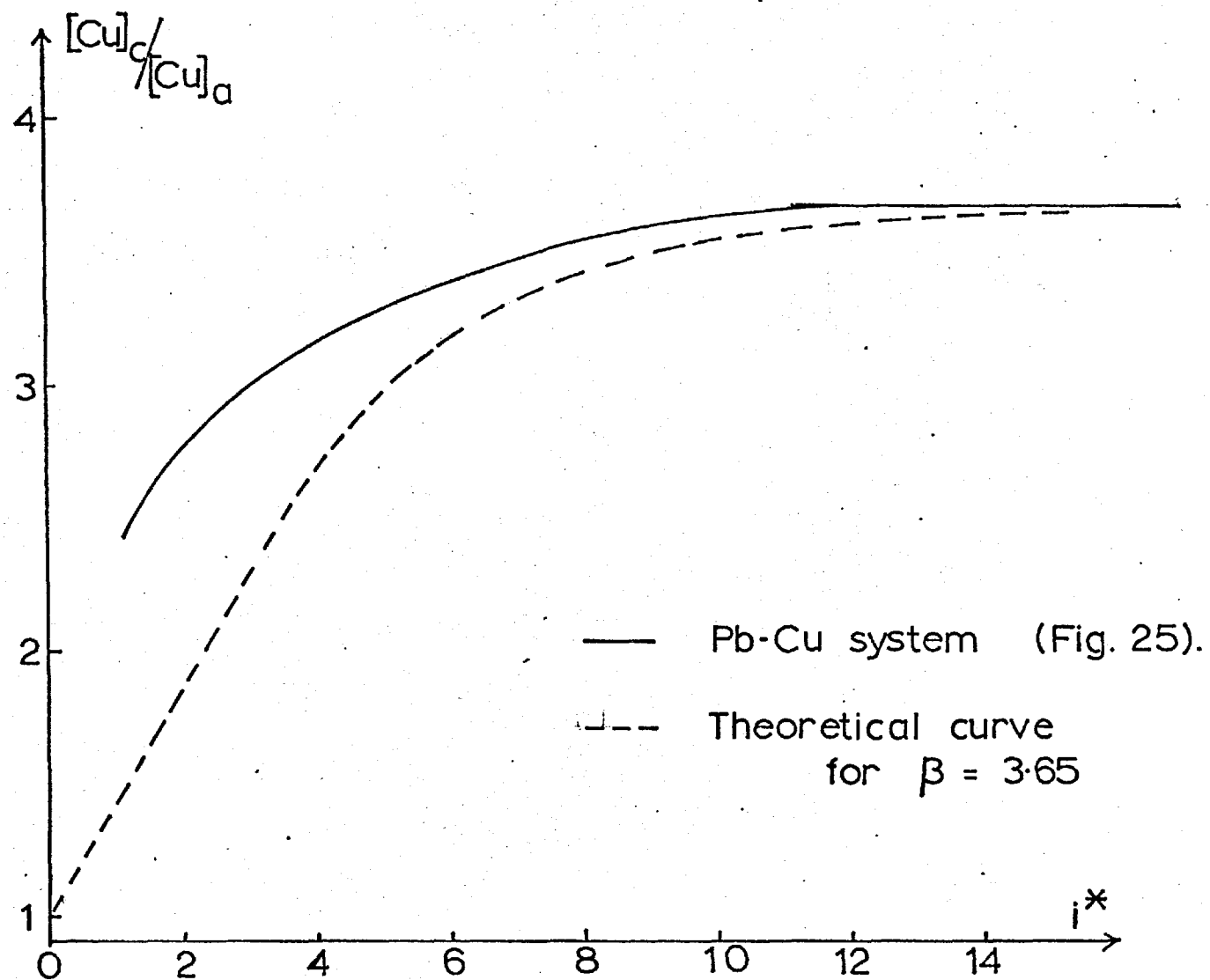


FIG. 37. Pb-Cu SYSTEM: CORRELATION BETWEEN EXPERIMENT
AND THEORY IF $Z_C = 2$

5.6 CONCLUSIONS

- (1) A refinability parameter obtained from a theoretical treatment of the refining process has been shown to predict the transfer of copper and silver impurities in lead.
- (2) The amount of cadmium transferred has been found to be less than the predicted value and it is suggested that this is due to solution of the metal into the melt from the cathode deposit.
- (3) It has been shown that the refinability parameter obtained experimentally using a simple cell can be used to predict the behaviour of impurities in a more complex process, namely, a batch refining process.
- (4) A modifying factor for the value of the refinability parameter when "inert" salts are added has been shown to apply in the lead-copper and lead-cadmium systems.
- (5) The present investigation has indicated that the transporting species for copper is divalent and that for cadmium is univalent.
- (6) The errors involved in the approximations made in the theoretical treatment, particularly in the estimation of R_{A-C^+} and the assignation of a value of R_{B-C^+} , have been discussed and it is concluded that the theory developed can make a useful contribution to the understanding of molten salt electrorefining. In particular, it shows that there is a limit to the refining that can be expected in any one system. This limit is determined by the refinability parameter β , which can be simply estimated. The parameter can be used to make semi-quantitative estimates of the refining effect that can be achieved in any proposed cell. The usefulness of this parameter is greatly increased since its value can be easily measured practically for any one system - using the experimental apparatus described here.
- (7) Several lines of investigation, both theoretical and experimental, suggest themselves. Firstly, it would be of use to extend the analysis of the behaviour of impurities to include continuous as well as batch refining processes. It is likely that under these boundary conditions the problem would have to be solved numerically. Secondly, the use of large concentrations of "inert" diluting salts, most likely in industrial practice, could well be

studied/...

studied experimentally. Finally the theoretical treatment should be extended to cover the general case in which more than one impurity is present.

APPENDIX A. SYMBOLS

A	Common univalent anion
B	Metal to be purified
C	Impurity metal
D_i	Diffusion coefficient of ions of species i
F	The Faraday
χ	Specific conductance of the electrolyte
K	Equilibrium constant
i''	Current density
L	Length of diffusion - migration path
n''	Molar flux density
R	Gas constant
R	Modified friction coefficient
T	Absolute temperature
V	Velocity of ions
X	Mole fraction of the individual species
X_F	$(1 - X_{NaCl})$
x	Co-ordinate denoting position along the diffusion - migration path
Z	Valency
γ	Activity coefficient
μ	Chemical potential
μ	Electrochemical potential

SUFFIXES

A ⁻	} Pertaining to chemical Species	(Common anion
B ⁺		(Main cation
C ⁺		(Impurity cation
D ⁺		(Cation of added salt
B		(Main metal
C		(Impurity metal
D		(Metal of added salt

Suffixes - Contd.

a	} Pertaining to position	{	in anode
c			in cathode
I			in electrolyte at anode
II			in electrolyte at cathode

Dimensionless symbols

i^*	Current density	=	$\frac{i'' L (Z_C R_{A-B^+} + R_{B^+C^+})}{RT}$
n_B^*	Dimensionless flux density of B	=	$\frac{(Z_C R_{A-B^+} + R_{B^+C^+}) \dot{n}_{B^+} L}{RT}$
n_C^*	Dimensionless flux density of C	=	$\frac{(Z_B R_{A-B^+} + R_{B^+C^+}) \dot{n}_{C^+} L}{RT}$
R^*	Friction coefficient ratio	=	$\frac{Z_B R_{A-C^+} + R_{B^+C^+}}{Z_C R_{A-B^+} + R_{B^+C^+}}$
β	Refinability parameter	=	$\frac{1/Z_B}{K \gamma_C R^*}$
Q	Modifying factor	=	$\frac{Z_D R_{A-C^+} + R_{D^+C^+}}{Z_B R_{A-C^+} + R_{B^+C^+}}$

APPENDIX B.

CALCULATION OF TYPICAL EXPERIMENTAL RESULTS

RUN 87: Practical measurements

Temperature of furnace	800°K
Time of run	4 hr.
Specific conductivity of electrolyte	1.57 mho. cm ⁻¹ (=)()
Anode/cathode conductance	2.210 x 10 ⁻² mho (=G _x)
Current	1.20 mA
Diameter of capillary	1.5 mm
Weight of cathode deposit	17.23 mg
Concentration of copper in anode	0.542 ± 0.016 wt. %
" " " " cathode	1.89 ± 0.08 wt. %
" " " " electrolyte	1.02 ± 0.06 wt. %

Calculated quantities

(1) Length of capillary

$$L = \frac{\cancel{K} A}{G_x} = \frac{1.57 \times 1.5^2 \times \pi \times 0.25 \times 10^{-2}}{2.10 \times 10^{-2}} = 1.28 \text{ cm.}$$

(2) Current density

$$i'' = \frac{1.2 \times 10^{-3}}{\pi \times 1.5^2 \times 0.25 \times 10^{-2}} = 0.070 \text{ A. cm}^{-2}$$

(3) Dimensionless current density

$$i^* = \frac{i'' L (Z_C R_{AB} + R_{BC})}{RTF} \approx \frac{i'' L R_{AB}}{RTF}$$

$$\text{At } 800^\circ\text{K } R_{\text{PbCl}_2} = 3.52 \times 10^{10} \text{ J. sec. cm. mole}^{-2}$$

Therefore

$$i^* = \frac{0.07 \times 1.28 \times 3.52 \times 10^{10}}{8.31 \times 800 \times 96500} \approx 4.98$$

(4) /....

(4) Cathodic current efficiency

Electric charge required to deposit 1 g of Pb/2% Cu alloy
 $= 9.43 \times 10^2$ Coulombs.

Total electric charge passed through cell = 17.3 Coulombs.

Therefore "Faraday's Law mass" of cathode = 18.3 mg

Therefore cathodic current efficiency = $\frac{17.23}{18.3} \times 100 = 94\%$

(5) Refining ratio = $1.89 / 0.54 = 3.48$

(6) Practical value of " β "

$$\text{Since } [X_{AB}] \approx 1 \approx \gamma_B [X_B]_a$$

$$K^{1/z_B} \gamma_C = \frac{[X_{AC}]_I}{[X_C]_a}$$

But

$$[X_{AC}]_I = \frac{0.0102}{63.5} \bigg/ \frac{1}{278} = 0.0447$$

and

$$[X_C]_a = \frac{0.00542}{63.5} \bigg/ \frac{1}{207} = 0.0176$$

Therefore

$$K^{1/z_B} \gamma_C = \frac{0.0447}{0.0176} = 2.54$$

But $R^* = 0.301$

(Section 2.2.4)

Therefore

$$\beta = \frac{2.54}{0.301} = 8.42$$

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PbCl ₂	-	CuCl,	Fig. 1252
PbCl ₂	-	NaCl,	Fig. 1310
CuCl	-	NaCl,	Fig. 1245

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